The Analyst
FULL PAPER

Automated *in situ* preparation of Azomethine-H and the subsequent determination of boron in fertilizer process and water effluent streams with sequential injection analysis

J. (Koos) F. van Staden* and Thomas A. van der Merwe

Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa.
E-mail: Koos.vanStaden@chem.up.ac.za; Fax: +27 12 362 5297

Received 24th May 2000, Accepted 18th August 2000
First published as an Advance Article on the web 25th October 2000

A sequential injection system for the automated *in situ* preparation of Azomethine-H and the on-line monitoring of boron in water effluents and fertilizer process streams is described. Azomethine-H, a condensation product of salicylaldehyde and H-acid (8-amino-1-naphthol-3,6-disulfonic acid) is used as the chromogenic reagent. The Azomethine-H is prepared *in situ* by mixing salicylaldehyde and H-acid in the presence of boron. A single bead string reactor is used to promote the mixing process. In solution the chromogenic reagent exists as its two constituents. When boron is added to the solution, Azomethine-H is formed and measured at 420 nm. The proposed system is fully computerised and is able to monitor boron at a rate of 30 samples per hour with a relative standard deviation of $< 1.4\%$. The calibration graph is linear up to 100 mg l^{-1}. The system has a detection limit of 0.61 mg l^{-1}.

Introduction

Boron is one of the trace elements in nature, occurring only in minute concentrations in natural systems.[1–8] Yet, it is one of the most important trace elements or micronutrients of growing plants. Sources of boron in the terrestrial environment are mainly soil minerals and parent material, fertilizers, irrigation waters, sewage sludges and effluents, and coal combustion. Fertilizers are one of the biggest industrial applications of boron.

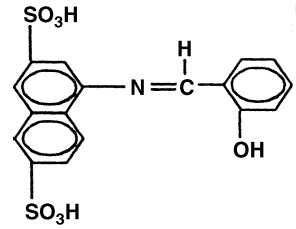
Several methods exist for the determination of boron in various sample types,[8] for example isotachophoresis,[9] ICP-AES,[10] titrimetric,[11] and automated methods such as segmented continuous flow,[12] flow injection[13–17] and stopped-flow injection analysis.[18] All these methods, except for the automated methods, are fairly time consuming and are, therefore, not ideally suited for industrial use. The automated methods have the advantage of possible automatic in-line sampling and analysis, making this a time and labour saving method of analysis. The reagent consumption in segmented continuous flow and flow injection analysis is, however, very high due to the continuous modes used for reagent streams. With the added advantages of sequential injection analysis (SIA), it is possible to design a boron analyser that is both convenient and economical.

Sequential injection analysis coupled with a spectrophotometer is a relatively simple analytical technique.[19] The simplicity of the sequential injection (SI) manifold and its low need for maintenance makes it an ideal tool in process analysis. As the reduction of reagent consumption is becoming worldwide a major issue due to the environmental impact of chemical waste, the more cost effective use of reagents is becoming the major advantage of SIA.

For the spectrophotometric determination of boron, several specific and sensitive colorimetric reagents have been developed.[8,20–23] These reagents include hydroxyanthraquinone reagents such as quinalizarin (1,2,5,8-tetrahydroxyanthraquinone)[20] and carminic acid,[21] as well as other anthraquinones and their derivatives (*e.g.* rufigallic acid[22] and curcumin[23]).

All the above mentioned methods, where concentrated sulfuric acid is used as reaction medium, damage the piston pumps used and require expensive "Acidflex" tubing in the SI manifold to withstand such acidic conditions. They also require exact acid concentrations, temperatures and heating times for optimum performance. A chromotropic acid method that was suitable for automation was developed in 1957 by James and King,[24] but difficulties were experienced as both the reagent and the borate–chromotropate components were sensitive to light.

Petrovsky[25] suggested the use of Azomethine-H as a chromogenic reagent for the determination of boron. Azomethine-H is the condensation product of salicylaldehyde and H-acid (8-amino-1-naphthol-3,6-disulfonic acid). This reagent is used in aqueous solution, and is ideally suited for use in SIA systems that utilise normal tubing. The structure of Azomethine-H is as follows:



It can be obtained from chemical suppliers and works well under a variety of physical and chemical conditions. One drawback of this chromogenic reagent is that it is unstable unless stored in a desiccator. Results obtained are, therefore, inconsistent and calibration graphs have to be adjusted when the reagent is used over long periods.[17,26] It was found that aqueous solutions of Azomethine-H hydrolyse rapidly, when stored for periods longer than one day, with a loss of sensitivity, if not refrigerated properly.

This problem may be solved by the preparation of Azomethine-H just prior to use. The immediate use of freshly prepared Azomethine H ensures better sensitivity and accuracy over long periods, without the need for recalibration as the reagent deteriorates. Basson and co-workers[26] accomplished an *in situ* preparation of Azomethine-H with the use of an Autoanalyser and the two components of Azomethine-H, salicylaldehyde and H-acid.

 DOI: 10.1039/b004166l

Azomethine-H is prepared by mixing its two components, salicylaldehyde and H-acid. Basson and co-workers[26] described the formation of a Schiff base from a carbonyl compound and a primary amine, in the presence of an acid catalyst. First, a carbinol amine (**A**) is formed, then water is eliminated to form the Schiff base (**B**):

$$RR'CO + R''NH_2 \rightleftharpoons R{-}\underset{\displaystyle R'}{\overset{\displaystyle OH}{C}}{-}NHR'' \rightleftharpoons RR'C = NR'' + H_2O \quad (1)$$

A **B**

Hammett[27] concluded that the addition of a proton to the carbonyl group gives a carbonium ion, $RR'COH^+$, which rapidly forms the base by deprotonation. This deprotonation is the rate-determining step leading to the formation of the carbinol amine (**A**). For the preparation of Azomethine-H by the SI method the same reaction principles apply. The reaction rate, however, is changed as the conditions of the deprotonation are changed.

Our laboratory was recently approached by a manufacturer of liquid fertilizers to develop a process analyser capable of monitoring the boron concentration in fertilizer process and water effluent streams. Other prerequisites of the analyser were that the system should be simple and robust, reliable with a low frequency of maintenance and that the consumption of reagents should be very low. Sequential injection analysis seemed to be an ideal technique for such an analyser and this paper reports on a sequential injection analyser that was optimised, developed and which is at present in operation.

Experimental

Reagents and solutions

Only analytical-reagent grade reagents were used unless specified otherwise. De-ionised water, supplied by a Modulab system (Continental Water Systems, San Antonio, TX, USA), was used to prepare aqueous solutions. The solutions were de-gassed, by boiling in a microwave oven, and were stored in an oxygen-free environment when not in use.

Standard boron solution. The standard boron solution was prepared by dissolving 0.5716 g of boric acid in 1 l of de-ionised water. This solution was stored in a polythene container and used to prepare working boron standards by suitable dilutions with 0.10 mol l^{-1} HCl.

Buffer solution. The buffer solution was prepared by dissolving 132 g of ammonium phosphate and 25 g of disodium EDTA in 500 ml of de-ionised water. The pH of this solution was adjusted to 7.0 by alkali addition.

Carrier. The carrier stream was prepared by adding 11.39 ml of 32% v/v HCl to de-ionised water and diluting it to 1 l.

H-acid. The H-acid (8-amino-1-naphthol-3,6-disulfonic acid; Merck, Darmstadt, Germany) solution was prepared by dissolving 2.5 g of H-acid with 250 ml of de-ionised water and adjusting the pH of this solution to 2.25 with a 16% v/v HCl solution.

Salicylaldehyde. The salicylaldehyde solution was prepared by diluting 1.0 ml of salicylaldehyde (Merck) with 250 ml of an 80% v/v ethanol solution.

Sample preparation

The samples from the liquid fertilizer were prepared by diluting 1 ml of liquid fertilizer with 20 ml of de-ionised water. The solution was filtered to remove any solid substances that formed during the dilution. For the SIA process analysers employed in the fertilizer process streams the concept of automated pre-valve dilution previously described[28] and/or principle of automated dialysis previously described[29,30] as a pre-SIA sample clean-up/dilution were used for in-line dilution of actual process samples depending on the actual nature and location of the concentrated samples in the process. The effluent water samples were used directly from the effluent streams.

Equipment

The SI manifold used is shown in Fig. 1. The manifold consisted of a Gilson Minipuls peristaltic pump (Gilson Medical Electronics, Villiers-le-Bel, France), with a pumping tube inside diameter of 1.85 mm, operating at a speed of 17 rpm. The pump was connected to a holding coil (HC), consisting of 0.76 mm inside diameter Tygon tubing wound around a Perspex tube with an outside diameter of 10 mm.

The holding coil was connected to the first reaction coil (RC 1) using PTFE tubing with an inside diameter of 0.76 mm wound around a Perspex tube with a 10 mm outside diameter. RC 1 was connected to a ten port electrically actuated selection valve (Model ECSD10P, Valco Instruments, Houston, TX, USA) using PTFE tubing with a 0.76 mm inside diameter. A single bead string reactor (SBSR) was incorporated into RC 1 to ensure proper mixing with minimal band broadening. The SBSR consisted of a PTFE tube (100 × 3 mm inside diameter) which was packed with boron-free beads with an inside diameter slightly smaller than 3.0 mm. The second reaction coil (RC 2) connected the sequential valve (SV) and the spectrophotometer *via* 0.76 mm inside diameter PTFE tubing wound around a Perspex tube with a 12.5 mm outside diameter.

A Unicam 8625 UV–visible spectrophotometer equipped with a Hellma-type flow-through cell (volume 80 μl, as supplied by the manufacturer) was used as detector and the absorbance was measured at 420 nm. Data acquisition and device control were achieved using a PC30-B interface board (Eagle Electric,

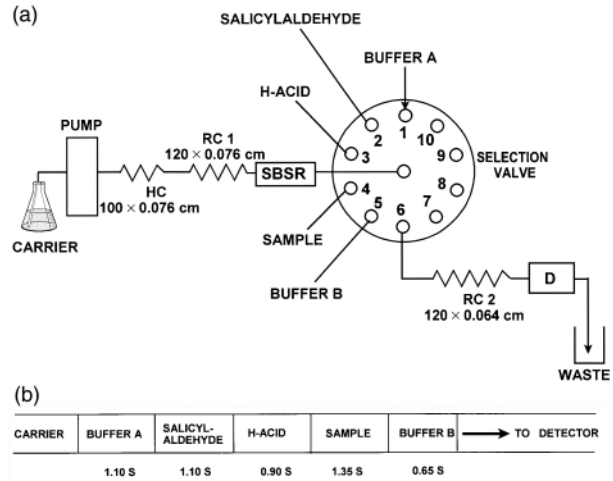


Fig. 1 Sequential injection system for the determination of boron with *in situ* preparation of Azomethine-H. Buffer A, salicylaldehyde, H-acid, sample, and another buffer B solution plug are aspirated through the sequential valve (SV) into the first reaction coil (RC 1) through the single bead string reactor (SBSR). Carrier solution, propelled by the peristaltic pump, is pumped through the holding coil (HC), flushing the reacted zone towards the detector (D) and waste, *via* the second reaction coil (RC 2). (a) Schematic flow diagram; (b) sequence of buffer A, salicylaldehyde, H-acid, sample and buffer B.

Cape Town, South Africa), as well as an assembled distribution board (MINTEK, Randburg, South Africa). The FlowTEK[31,32] software package (MINTEK) for computer-aided flow-analysis was used throughout for device control and data acquisition.

Procedure

The device sequence for the *in situ* preparation of Azomethine -H, and the subsequent determination of boron by SI, is given in Table 1. As seen from the SI system depicted in Fig. 1, one cycle of the sequence (buffer A, salicylaldehyde, H-acid, sample, buffer B and flush to the detector) involves ports 1–6 of the selection valve. Buffers A and B are the same buffer solution, of which the volumes were optimised separately in order to obtain the optimum conditions.

Method optimisation

Physical parameters

Physical parameters, optimised for the *in situ* preparation of Azomethine-H and the subsequent determination of boron, were flow rate, order of injection and mixing chamber parameters. The physical parameters were optimised by using the actual reagents used in the determination of boron.

Flow rate. The flow rate plays an important role in the dispersion of the reacting zones, and consequently the sensitivity and precision of the analytical method. Flow rates were varied between 7.6 and 14.5 ml min^{-1} by changing the pump speed, and keeping the pump tube inside diameter constant at 0.76 mm. An increase in the flow rate improved both the sensitivity and precision, up to a flow rate of 13.7 ml min^{-1}. Higher flow rates increased the sensitivity, but the precision decreased due to the development of back-pressure in the system. The best precision (1.35%) was obtained with a flow rate of 13.7 ml min^{-1}. This flow rate was used for further optimisation of the method.

Table 1 Device sequence for one full cycle of the sequential injection system used in the *in situ* preparation of Azomethine-H and determination of boron

Time/s	Pump	Valve	Description
0.00	Reverse	Buffer A	Draw up buffer A solution (Valve position 1)
1.10	Off		Pump stop
1.60		Salicylaldehyde	Valve selects salicylaldehyde solution (Valve position 2)
2.10	Reverse		Draw up salicylaldehyde solution
3.20	Off		Pump stop
3.70		H-acid	Valve selects H-acid solution (Valve position 3)
4.20	Reverse		Draw up H-acid solution
5.10	Off		Pump stop
5.60		Sample	Valve selects sample solution (Valve position 4)
6.10	Reverse		Draw up sample solution
7.45	Off		Pump stop
7.95		Buffer B	Valve selects buffer B solution (Valve position 5)
8.45	Reverse		Draw up buffer B solution
9.10	Off		Pump stop
9.60		Detector	Valve selects detector position (Valve position 6)
10.10	Forward		Pump stacked zones to detector
119.00	Off		Pump stop
120.00		Home	Return valve to starting position

Order of injection. In SI, the order of injection plays an important role in the determination of factors such as sensitivity, precision, and carry-over. With the *in situ* preparation of Azomethine-H the order of injection of five separate solutions (buffer A, salicylaldehyde, H-acid, sample, buffer B) had to be determined. The four possibilities in Table 2 were evaluated.

For the *in situ* preparation, the sample had to be aspirated after the chromogenic reagents to prevent carry over between successive runs of the method. The best precision and sensitivity were obtained with salicylaldehyde aspirated first followed by H-acid and then the sample.

Mixing devices. While optimising the sequence, it was noticed that the individual zones did not mix properly. The buffer solution used in the proposed method contained 264 g l^{-1} ammonium hydrogenphosphate, and as a result of this high salt content, its refractive index differed considerably from that of the other solutions used. Without proper mixing of the plugs containing different salt concentrations, the absorption detected by the spectrophotometer would fluctuate, leading to poor and inconsistent results.

This problem could be solved in one of three ways. Firstly, by the addition of a salt (*e.g.* NaCl) to the solutions with low salt content until the difference in refractive indices is negligible. Secondly, by measuring the absorbance of the product zone at the wavelength at which the chromotropic compound absorbs as well as at a wavelength at which none of the reacting species absorbs. The last option is by using a mixing device (*e.g.* a mixing chamber), that will be able to homogenise the refractive index of the reacting zones.

The addition of NaCl to the solutions with low salt content had a negative effect on the sensitivity of the method, excluding it as a possibility. In order to implement the second option, additional software was required to measure the absorbance at two different wavelengths and, as a result, this possibility could not be evaluated either. A mixing device, such as a mixing chamber or a single bead string reactor (SBSR), was the only viable option left to consider.

SBSRs (Fig. 2) reduce the refractive index differences by mixing the solutions of high salt content with those solutions containing less salt. Owing to a small amount of dead volume within the SBSR, an increase in dispersion is obtained. The dispersion of the system was calculated by using the following equation:

$$D^{\max} = \frac{C^{o}}{C} \qquad (2)$$

where D^{max} is the dispersion coefficient, C^{o} is the concentration of the sample before the dispersion process begins, and C is the concentration of the sample after dispersion has taken place.[33] A dispersion coefficient of 2.8 was obtained without the SBSR, and a value of 3.91 with the SBSR. The precision of the method improved substantially from 1.2 to 0.8% with only a small loss of sensitivity.

Table 2 Effect of a change in order of injection on the peak height and % RSD

Order of injection	Peak height	RSD (%)
(1) Buffer A–H-acid–sample–salicylaldehyde–buffer B	4.22	2.28
(2) Buffer A–salicylaldehyde–sample–H-acid–buffer B	4.47	2.10
(3) Buffer A–salicylaldehyde–H-acid–sample–buffer B	4.56	1.90
(4) Buffer A–H-acid–salicylaldehyde–sample–buffer B	4.44	2.43

A mixing chamber[34,35] was also evaluated as an alternative to the SBSR. Unfortunately, the loss of sensitivity with the mixing chamber was greater than that obtained with the SBSR and therefore the SBSR was chosen for the proposed system.

Chemical parameters

Salicylaldehyde. Basson *et al.*[26] suggested a salicylaldehyde : ethanol (80% v/v) ratio of 1 : 250 v/v and this ratio was also used in the proposed method with good results. One aspect of the salicylaldehyde solution evaluated was the volume aspirated (varied between 0 and 280 μl) with the following results.

According to Basson *et al.*,[26] salicylaldehyde reacts with H-acid in a 1 : 1 ratio. With the H-acid concentration kept constant, the peak height should have a linear increase up to the point where both the reagents are present at the same concentration. Theoretically, a higher salicylaldehyde concentration would not increase sensitivity since the H-acid will then be the limiting reagent. This is exactly what was found when the salicylaldehyde volume was increased, with the H-acid volume kept constant (Fig. 3). According to Fig. 3, there is an increase between 0 and 240 μl, with the sensitivity levelling off at higher salicylaldehyde volumes. The best results were obtained with a salicylaldehyde volume of 240 μl. The absorbance obtained at 0 μl salicylaldehyde is a result of the small refractive index difference between the solutions aspirated.

H-acid. For the segmented continuous flow system ("Auto-analyser" system), Basson *et al.*[26] suggested a 1% m/m H-acid solution. In order to determine the optimum concentration the H-acid concentration of the SI system was varied between 0.2 and 1.2% m/m. The results obtained are given in Table 3.

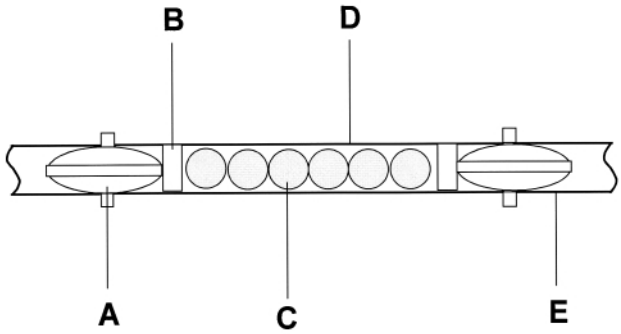


Fig. 2 Construction of the SBSR used in the determination of boron with *in situ* preparation of Azomethine-H. PTFE (Teflon) connectors (A) were used to connect the SBSR to the PTFE tubing of RC 1 (E). A polythene stopper (B) was used to keep the beads (C) in place. A PTFE tube (D) was used in the construction of the reactor.

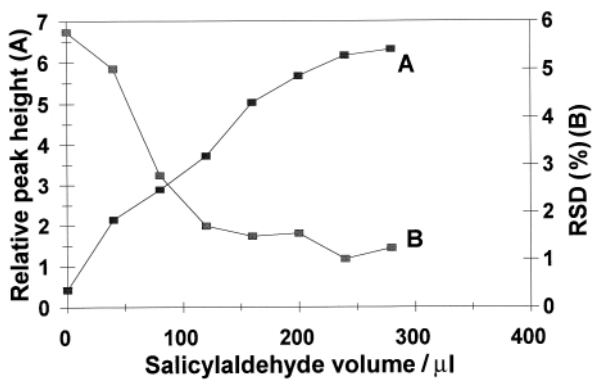


Fig. 3 Effect of salicylaldehyde volume on the relative peak height (sensitivity) and % RSD (precision).

The method reached its maximum sensitivity at a H-acid concentration of 1.2% m/m, and its best precision (0.95%) at a concentration of 1.0% m/m. The linear relationship between the salicylaldehyde concentration and peak height ended at a concentration of 1.0%, the value at which the H-acid and salicylaldehyde concentrations are more or less equal. Higher H-acid concentration had no effect on the sensitivity. With the H-acid concentration optimised, the volume of H-acid aspirated had to be optimised (Fig. 4). H-acid volumes between 0 and 407 μl were considered. H-acid volumes up to 203 μl had positive effects on both the precision and the sensitivity, while the precision decreased (% RSD increased) for volumes larger than 203 μl. Under these conditions, the smaller reagent plugs gave the best reproducibility, with salicylaldehyde being able to penetrate most of the H-acid plug.

Sample. Tucker *et al.*[36] and Ruzicka and Gubeli[37] determined that, for an optimised region of mutually interdispersed sample and reagent zones, the reagent volume zone should be at least twice that of the sample zone. The optimised chromogenic reagent zones had a total volume of 453 μl. Therefore, according to the above-mentioned studies, the sample should have a theoretical optimum volume in the region of 225 μl. The results obtained are shown in Table 4.

According to Table 4, the sensitivity did not change much with an increase in the sample volume. The % RSD, on the other

Table 3 Influence of H-acid concentration on relative peak height and % RSD

H-acid concentration (% m/m)	Relative peak height	RSD (%)
0.2	1.14	4.00
0.4	1.32	2.09
0.6	1.55	1.03
0.8	1.74	1.07
1.0	1.95	0.95
1.2	2.07	1.31

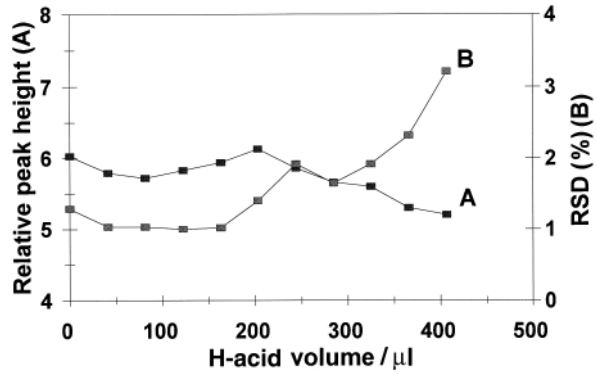


Fig. 4 Influence of H-acid volume (μl) on relative peak height (A) and % RSD (B).

Table 4 Influence of sample volume (μl) on relative peak height and % RSD

Sample volume/μl	Relative peak height	RSD (%)
0	5.09	1.88
50	4.60	1.59
100	4.19	1.86
150	4.42	2.20
200	4.51	1.75
250	4.47	0.94
300	4.31	0.69
350	4.44	2.38
400	3.95	2.64

hand, shows that the best precision values are obtained between 250 and 300 μl of sample. In this region, the sample volume is slightly more than half the reagent volume, confirming the theory of Tucker *et al.*[36] and Ruzicka and Gubeli.[37] The best % RSD was obtained with a 300 μl sample volume, which is two-thirds the volume of the reagent zone.

Buffer solution. A buffer solution consisting of 132 g of ammonium hydrogenphosphate and 25 g of disodium EDTA dissolved in 500 ml of de-ionised water[38] was used in the determination of boron. With the *in situ* preparation of Azomethine-H and the subsequent determination of boron, the procedure and order of injection of the method changed. This change necessitated the re-optimisation of the buffer volumes.

The buffer solution was originally introduced first before the sample and reagents and in the second series of runs thereafter. Poor sensitivity and precision were obtained, indicating that zone penetration under these circumstances was not sufficient. It was then decided to sandwich the sample and reagents between the buffer solution. The same buffer solution was used but in order to distinguish between the different volumes of the two zones the zone before was named buffer A and the one after buffer B. The buffer solution was introduced into the system in front of the Azomethine-H plug (buffer A) as well as after the sample plug (buffer B, see Fig. 1). A change in volume of any one of these buffer plugs influenced the sensitivity and accuracy of the method, making it necessary to optimise the two buffer volumes separately. The results of the optimisation are shown in Fig. 5.

According to Fig. 5 the two buffer zones gave the best precision at different volumes. For buffer A it is at a volume of 254 μl and for buffer B it is at 152 μl; volumes larger than this had only a limited effect on the sensitivity.

Disodium EDTA. EDTA is used as a masking agent in the determination of boron.[34] It is the most effective complexing agent for removing large amounts of interfering metals. The EDTA concentration should be high enough to remove all possible interfering elements and low enough not to affect the reaction itself. A 20 g l^{-1} disodium EDTA solution proved to be the most effective with little influence on the reaction.

Evaluation of the method

Linearity

The linearity of the SIA system was evaluated under the optimum operating conditions, determined by the optimisation of the physical and chemical parameters. The relationship of the relative peak height *versus* the boron concentration is:

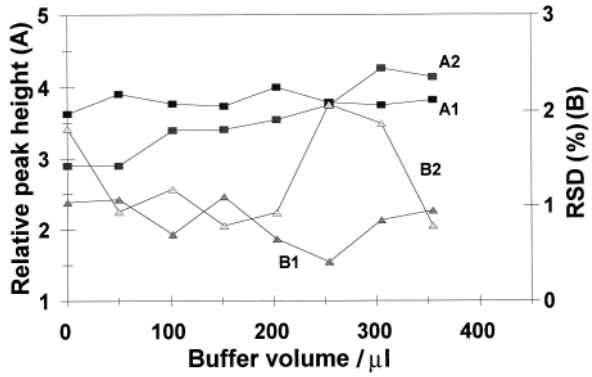


Fig. 5 Influence of a change in buffer concentration on relative peak height (A1 for buffer A and A2 for buffer B) and % RSD (B1 for buffer A and B2 for buffer B).

$$y = 0.0504x + 1.520;\ r = 0.995$$

where y = relative peak height and x = boron concentration in mg l^{-1}. The calibration graph is linear for boron concentrations between 0 and 100 mg l^{-1}.

Accuracy

To evaluate the feasibility of the proposed SIA system, samples from the fertilizer process and effluent water streams from the factory were analysed. The factory used the segmented Autoanalyser system proposed by Basson *et al.*[12,26] which satisfied their requirements. A set of samples was analysed by the proposed system, by the Autoanalyser system and also by inductively coupled argon plasma atomic emission spectrometry (ICP-AES). Two effluent water samples were also spiked by adding 10 mg l^{-1} boron and analysed by the three different methods. The results, given in Table 5, revealed a good correlation between the three methods.

Precision

The precision of the proposed SIA system was evaluated by ten repetitive analyses of a number of boron samples from the process and effluent water streams and standard boron solutions. For all the cases, the RSD was below 1.40%, the highest value being obtained for effluent water sample E and with a best case scenario of 0.40% for a boron concentration of 100 mg l^{-1}.

Detection limit

The detection limit of the proposed method was determined *via* the following equation:

$$\text{Detection limit} = \frac{(3\sigma + K)(K - c)}{m} \quad (3)$$

where σ is the relative standard deviation of the baseline (1.55), K is the average signal value of the baseline (1.515), c is the intercept (1.520) and m is the slope of the calibration graph (0.0504). By using eqn. (3) a detection limit of 0.61 mg l^{-1} was obtained.

Interferences

Basson *et al.*[12] tested the following ions for interferences: copper(II), iron(II), manganese(II), zinc(II), calcium, magnesium, aluminium, sodium, potassium, phosphate, sulfate, and nitrate. Since the proposed SIA method was developed for use in the fertilizer industry, where fertilizers contain a number of

Table 5 Comparison of the results obtained by the proposed SIA method with those of the Autoanalyser and ICP-AES

	Boron/mg l^{-1}		
Sample	SIA method	Autoanalyser	ICP-AES
Fertilizer 1	37.1	35.5	36.8
Fertilizer 2	36.6	36.2	36.5
Effluent water sample A	3.25	3.19	3.23
Effluent water sample B	7.43	7.36	7.42
Effluent water sample C	2.38	2.37	2.38
Effluent water sample D	2.68	2.66	2.65
Effluent water sample E	1.79	1.73	1.76
Spiked water sample A	12.65	12.51	12.61
Spiked water sample B	15.94	15.89	15.91

Table 6 Effect of some ions and anions on peak height of boron determination

Sample (50 mg l^{-1} B + X mg l^{-1})	Without EDTA	With EDTA (2%)
No ions added	4.86	4.74
50 Ca^{2+}	4.05	4.75
100 Ca^{2+}	3.50	4.66
1000 Ca^{2+}	3.35	4.58
50 Mg^{2+}	3.40	4.32
100 Mg^{2+}	3.63	4.60
500 Mg^{2+}	3.60	4.59
50 Zn(II)	3.94	4.10
100 Zn(II)	3.70	4.03
50 NO_3^-	3.63	4.53
100 NO_3^-	3.70	4.58
500 NO_3^-	3.69	4.49
50 SO_4^{2-}	3.82	4.45
100 SO_4^{2-}	3.49	4.41
500 SO_4^{2-}	3.45	4.39
50 K^+	3.45	4.58
100 K^+	3.58	4.72
500 K^+	3.14	4.18

different elements, the effect of some common elements present in fertilizers was studied, with the results shown in Table 6. Some of the ions had little effect on the proposed method (*e.g.* Zn^{2+} and Mg^{2+}) with added EDTA while others depressed the boron signal to a certain extent (*e.g.* high K^+ concentrations).

Sampling frequency

The proposed method employed a 120 s cycle, giving the method a sampling frequency of 30 per hour. It is possible to increase the frequency further by shortening the waiting period of 30 s, at a cost of a small amount of precision.

Conclusion

The proposed SI system with *in situ* preparation of Azomethine-H is suitable for the on-line monitoring and direct determination of boron in effluent water streams and diluted fertilizer samples in the range up to 100 mg l^{-1} with a detection limit of 0.61 mg l^{-1}. The proposed method is a simple, inexpensive and reliable method for the detection of boron at low and intermediate concentrations. This method has the added advantage of being sensitive over a wide linear range, making it ideal for use in routine analysis in industry. Ions and anions that interfere with the method can be masked by the addition of 2.0% m/m EDTA. Also, the H-acid and salicylaldehyde solutions are more stable at room temperature than the Azomethine-H in solution, which requires refrigeration when used over long periods. As a result of this stability, the sensitivities are constant over longer periods, requiring fewer reagent exchanges over the same period of time. The method is slightly faster (two samples per hour) which is an important factor in the process industry. By using the *in situ* preparation, the linear range may be slightly narrower but the detection limit is better, justifying the use of the *in situ* method.

References

1 D. C. Adriano, *Trace Elements in the Terrestrial Environment*, Springer-Verlag, New York, 1986.
2 D. J. D. Nicholas and E. R. Egan, *Trace Elements in Soil–Plant–Animal Systems*, Academic Press, New York, 1975.
3 H. G. Gauch, *Organic Plant Nutrition*, Dowden, Hutchinson and Ross, Strousburg, PA, 1972.
4 I. Bonilla, C. Cadahia and O. Carpena, *Plant Soil*, 1980, **57**, 3.
5 R. A. Wildes and T. E. Neales, *J. Exp. Bot.*, 1969, **20**, 591.
6 C. F. Crosswell and L. C. Nelson, *Soil Sci.*, 1941, **52**, 351.
7 V. Sauchelli, *Trace Elements in Nature*, Van Nostrand Reinhold, New York, 1969.
8 R. N. Sah and P. H. Brown, *Microchem. J.*, 1997, **56**, 285.
9 A. L. Dawidowicz, J. Matusewicz and J. Wysocka-Lisek, *Talanta*, 1989, **36**, 581.
10 A. J. Jeffrey and L. E. McCallum, *Commun. Soil. Sci. Plant Anal.*, 1988, **19**, 663.
11 J. R. Melton, *J. Assoc. Off. Anal. Chem.*, 1982, **65**, 234.
12 W. D. Basson, R. G. Bohmer and D. A. Stanton, *Analyst*, 1969, **94**, 1135.
13 F. J. Krug, J. Mortatti, L. C. R. Pessenda and E. A. G. Zagatto, *Anal. Chim. Acta*, 1981, **125**, 29.
14 I. Sekerka and J. F. Lechner, *Anal. Chim. Acta*, 1990, **234**, 199.
15 K. Nose and M. Zenki, *Analyst*, 1991, **116**, 711.
16 A. R. A. Nogueria, S. M. B. Brienza, E. A. G. Zagatto, J. L. F. Costa-Lima and A. N. Araujo, *Anal. Chim. Acta*, 1993, **276**, 121.
17 C. De Azevedo-Tumang, G. Caseri de Luca, R. Nunes-Fernandes, B. F. Reis and F. J. Krug, *Anal. Chim. Acta*, 1998, **374**, 53.
18 M. A. Z. Arruda and E. A. G. Zagatto, *Anal. Chim. Acta*, 1987, **199**, 137.
19 R. E. Taljaard and J. F. van Staden, *Lab. Robot. Autom.*, 1998, **10**, 325.
20 A. J. Johnson and M. J. Toogood, *Analyst*, 1954, **79**, 493.
21 R. C. Calkins and V. A. Stenger, *Anal. Chem.*, 1956, **28**, 399.
22 L. Rosenthaler, *Microchimie*, 1937, **23**, 194.
23 D. F. Boltz, *Colorimetric Determination of Non-metals*, Interscience, New York, 1958, ch. VIII, p. 345.
24 H. James and G. H. King, *Automation in Analytical Chemistry*, Technicon Symposia Media, New York, 1965, vol. I, p. 123.
25 V. Petrovsky, *Talanta*, 1963, **10**, 175.
26 W. D. Basson, P. P. Pille, and A. L. du Preez, *Analyst*, 1974, **99**, 168.
27 L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1940, p. 333.
28 J. F. van Staden, *Fresenius' Z. Anal. Chem.*, 1985, **322**, 36.
29 J. F. van Staden and A. van Rensburg, *Analyst*, 1990, **115**, 1049.
30 J. F. van Staden, *Fresenius' Z. Anal. Chem.*, 1995, **352**, 271.
31 G. D. Marshall and J. F. van Staden, *Anal. Instrum.*, 1992, **20**, 79.
32 G. D. Marshall and J. F. van Staden, *Process Control Quality*, 1992, **3**, 251.
33 J. Ruzicka and E. H. Hansen, *Flow Injection Analysis*, Wiley, New York, 2nd edn., 1988.
34 H. L. Pardue and B. Fields, *Anal. Chim. Acta*, 1981, **124**, 39.
35 H. L. Pardue and B. Fields, *Anal. Chim. Acta*, 1981, **124**, 65.
36 D. J. Tucker, B. Toivola, C. H. Pollema, J. Ruzicka and G. D. Christian, *Analyst*, 1994, **119**, 975.
37 J. Ruzicka and T. Gubeli, *Anal. Chem.*, 1991, **63**, 1680.
38 F. J. Krug, J. Mortatti, L. C. R. Pessenda and E. A. G. Zagatto, *Anal. Chim. Acta*, 1981, **125**, 29.