Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Talanta 64 (2004) 1196–1202
Talanta
www.elsevier.com/locate/talanta

Spectrophotometric determination of bromate by sequential injection analysis☆

J.F. van Staden*, L.V. Mulaudzi, R.I. Stefan

Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

Received 16 February 2004; received in revised form 26 April 2004; accepted 26 April 2004
Available online 6 July 2004

Abstract

A simple and rapid on-line spectrophotometric method for the determination of bromate is proposed. The method is based on the reaction of bromate and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-bromo-PADAP) with SCN^-**,** a red complex is formed and monitored at 550 nm. The linear range found is between 0.18 and 3.00 mg l^{-1} with a detection limit of 0.15 mg l^{-1}. The sampling rate was calculated to be 45 samples per hour. The proposed method has a precision of less than 0.8%.

Keywords: Disinfection; Chlorination; Trifluoperazine

1. Introduction

Trace elements play an important role in the functioning of life on our planet. Some elements can be highly toxic to various life forms while others are considered to be essential, but at higher doses they become toxic. Many of these effects depend strongly on the particular form in which the element is available in the system.

Chlorination of drinking water for the purpose of disinfection may result in the production of trihalomethanes that are health hazard agents [1,2]. Ozonation has therefore emerged as one of the best alternatives for water treatment in comparison with chlorination [2]. The oxyhalide disinfection by-product bromate is most commonly associated with ozonation of drinking water containing bromide [3] especially in sources of drinking water containing significant amounts of bromide ions. Bromate has been classified in Group 2B by the International Agency of Research Cancer (IARC) as a primary causative agent of cancer. The World Health Organisation (WHO) recommended the provisional guide-line value of 25 Φg L^{-1} which is associated with an excess lifetime cancer risk of 7×10^{-5}; because of the limitations in the available analytical and treatment methods for drinking water [4].

The bread making quality of freshly milled flour tends to deteriorate only after 2 months. The use of flour improvers increases the shelf life of flour considerably. Potassium bromate may be added to the flour at the mill or to the dough at the bakery or both provided that the total bromate content in these foods is tightly controlled. Bromate is relied upon as one of the most used flour improvers [5,6].

Because of the potential negative health effects of bromate, control of the level of bromate in foods for human consumption and drinking water is extremely important and there is an urgent need for a fast, robust, simple monitoring system to detect bromate wastes in effluent streams effectively. Analytical methods for bromate are almost entirely based on its oxidising properties. Bromate belongs to a group of oxidising anions capable of being reduced by SO_2 and can be consequently determined as bromide. Farrell et al. [7] designed a spectrophotometric method for the determination of bromate ions using phenothiazines. They used three of the dyes, 10 H-phenothiazine, chlorpromazine, and trifluoperazine. The method is based on the reduction of

---

☆ Presented at the 12th International Conference on Flow Injection Analysis, including related techniques (ICFIA'2001), held in Merida, Venezuela, 7–13 December 2003.

* Corresponding author. Tel.: +27-084-480-7263.

E-mail address: koosvanstade@telkomsa.net (J.F. van Staden).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.04.031

aqueous bromate ion by phenothiazine in acidic conditions. Determination of bromate in flour was carried out by a gas-chromatographic and inductively coupled plasma mass spectroscopy method with the ICP–MS method giving an R.S.D. value of 12% [8]. The determination of bromate was further emphasised by Weinberg when he applied a preconcentration technique for bromate analysis in ozonated waters [9]. Bromate was determined by decolourisation spectrophotometry by Jiang [10]. Measurement of bromate in bottled water by high performance liquid chromatography with a postcolumn flow reactor detection has been carried out [11]. Magnuson coupled GC–MS with negative chemical ionization for the determination of bromate [12]. Potentiometric detection of bromate after separation from other monovalent anions was performed where the determination can be carried out in the presence of other anions [13]. Elwaer et al. [14] described a flow injection system for the separation and determination of bromate in drinking waters prior to quantitation by ICP mass spectrometry. An interlaboratory trial to determine the analytical state-of-the-art of bromate determination in drinking water has also been reported [15]. However, with the advancement of technology, methods for the determination of bromate and other anions became complicated and tedious and rely on very expensive instrumentation [15]. Although it has been claimed that IC [3] and ICP–MS [14] can measure bromate at the $\sim$g l^{-1} level these types of instruments are very expensive and not suitable for remote on-site field monitoring of bromate in effluent streams at the outlet of industrial sites where bromates form part of the industrial processes in plants without fulltime attention by an operator. An urgent need arises for the on-site monitoring of bromate levels with the necessary management and immediate control especially in effluent streams of these outlets to prevent any accidental or maybe deliberate spilling/contamination of bromate into natural water systems like rivers that are sources for water networks.

Ketai et al. [16] described a FIA method for the direct determination of bromate based on the reaction of bromate, thiocyanate and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-bromo-PADAP) in acidic medium.

Sequential injection analysis (SIA) developed in 1990 [17] is increasingly recognised as an important analytical tool as it broadens the scope of flow analysis. It was developed as part of the drive to develop methods of automated analysis suitable for robust process analysis with the additional advantage of the low and economical consumption of reagents. SIA is based on the sequential aspiration of minimal quantities of reagents and samples and consecutively stacking them into well-defined zones within a holding coil (HC). Zone penetration and dispersion are finitely controlled as these stacks passes through the holding coil to the reaction coil wherein they undergo a chemical reaction before being forwarded to the detector. The aim of this paper is to use the SIA concept to supply a simple, robust, cost effective remote on-site monitoring system for the determination of bromate in effluent streams at the outlet of certain industrial sites in order to control bromate content in these effluent streams with immediate corrective feedback and action. The procedure relies on the color produced when bromate and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-bromo-PADAP) react with SCN$^-$ in acidic medium.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared from analytical grade chemicals unless specified otherwise. All solutions used were prepared by using de-ionised water from a Modulab system (Continental Water System, San Antonio, TX). All solutions were degassed with a vacuum pump system before measurement.

2.1.1. Bromate stock solution

A 1000 mg l^{-1} standard bromate stock solution was prepared by dissolving 1.3057 g $KBrO_3$ (Merck, Germany) in de-ionised water and diluting quantitatively to 1 l with de-ionised water. Appropriate dilutions were prepared from the standard solutions.

2.1.2. 5-Bromo-PADAP-solution

A 0.01 mol l^{-1} ethanolic solution of 5-bromo-PADAP was prepared by dissolving 0.0349 g 2-(5-bromo-2-pyridylazo)5-diethylaminophenol (5-bromo-PADAP, Aldrich) quantitatively in 100 ml ethanol.

2.1.3. SCN$^-$solution

A 0.01 mol l^{-1} SCN$^-$ solution was prepared by dissolving 0.9718 g of KSCN (Merck, Germany) and diluting quantitatively to 1000 ml with de-ionised water.

2.1.4. Sulphuric acid solution

A 0.2 mol l^{-1} sulphuric acid solution was prepared by dissolving 10.8 ml of 98% H_2SO_4 (Merck, Germany) and diluting quantitatively to 1 l with de-ionised water. This solution was used as carrier.

2.2. Instrumentation

The sequential injection analysis system (Fig. 1) was assembled from the following components: a Gilson peristaltic pump set at 13 rpm (flow rate 4.0 ml min^{-1}); a 10 port electrically actuated selection valve (model ECSD 10P; Valco Instruments, Houston, TX); and a Unicam (Cambridge, UK) 5625 UV–vis spectrophotometer equipped with a 10 mm Hellma (Malheim, Germany) flow through cell (volume 80 Φl) for absorbance measurements. The wavelength was set at 550 nm. Data acquisition and device control were achieved using a PC30-B interface board (Eagle Electric, Cape Town, South Africa) and an assembled distribution board (Mintek, Randburg, South Africa). The FlowTEK software package for computer aided flow-analysis (GlobalFIA) was used throughout for device control and data acquisition. The manifolds were constructed from Tygon tubing that was customised by cutting them into relevant sizes and wound around perspex rods of different lengths. The length and size of the holding coil was 3.0 m and 1.02 mm internal diameter. The reaction coil was 0.5 m in length and 0.76 mm in internal diameter. All the data given are the mean of 10 replicates of peak heights. The wavelength of maximum absorbance was identified by scanning the product of bromate and 5-bromo PADAP with SCN^- over the range 300–800 nm with a Spectronic Genesys 5 spectrophotometer (Milton Roy company).

2.3. SIA procedure

Fig. 1 shows a complete schematic diagram of the proposed SI system with the device sequence outlined in Table 1. A sample/standard from valve position 1 followed by the 5 bromo PADAP reagent from position 2 and the SCN^- from position 3 were aspirated sequentially through the selection valve into the holding coil. By flow reversal the stack of well-defined zones were propelled by the peristaltic pump from the holding coil to the reaction coil. The zones penetrate each other as they pass through the reaction coil to the detector. The absorbance of the product formed is measured at 550 nm using an UV–vis spectrophotometer.

Table 1
Device sequence for one cycle of the sequential injection system

Time (s)	Pump	Valve	Description
0	Off	Sample	Pump stops, select sample stream (valve position 1)
2	Reverse		Draw up sample solution
4	Off		Pump stops
5		Advance	Select 5-Br-PADAP at valve position 2
6	Reverse		Draws up 5-Br-PADAP
9	Off		Pump stops
10		Advance	Select SCN^- solution at valve position 3
11	Reverse		Draws up SCN^- solution
13	Off		Pump stops
14		Advance	Selects valve position 4
15	Forward		Pumps solutions to the detector
39	Off		Pump stops
40		Advance	Valve goes back to position 1

3. Results and discussion

3.1. Optimization

Key parameters that influence the performance of the proposed method were studied in order to establish the optimum working configurations. All the data given (relative peak height) and % R.S.D. in the optimisation steps for

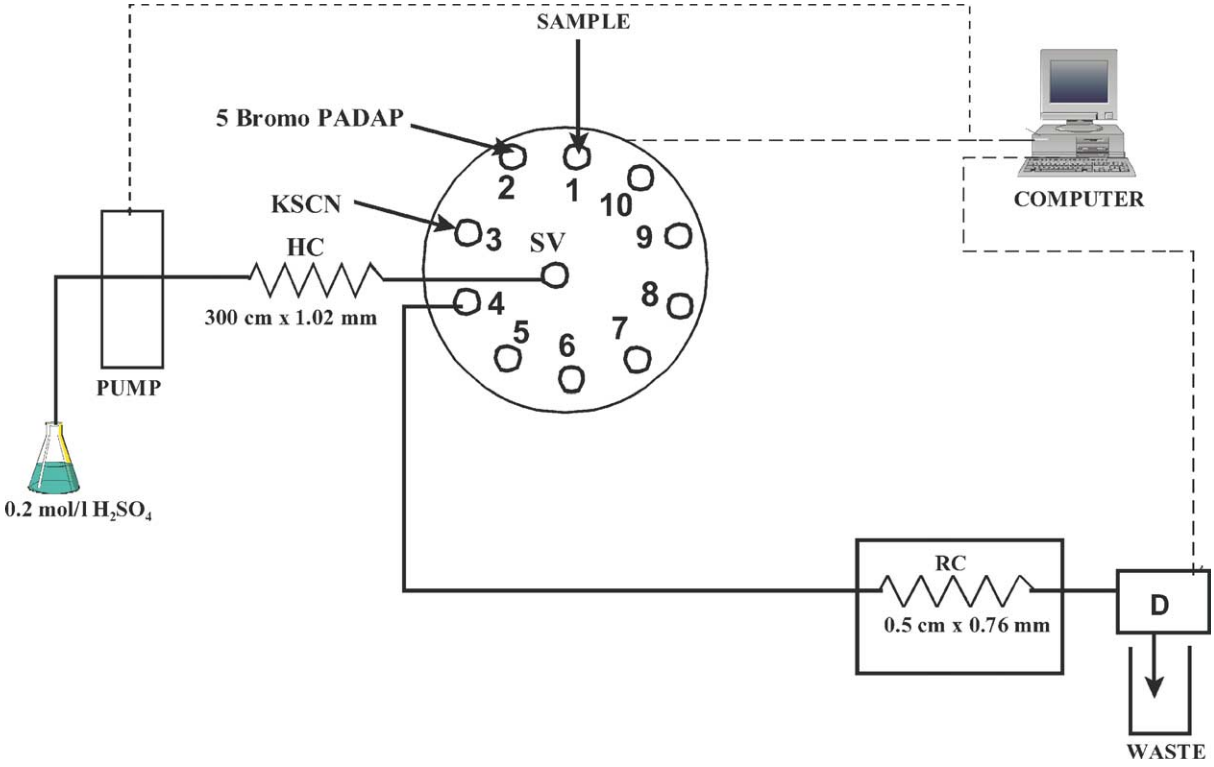

Fig. 1. SIA system for the determination of bromate. HC: holding coil, RC: reaction coil, SV: selection valve and D: detector.

both physical and chemical parameters are the mean values from 10 successive determinations. All the optimisation steps were carried out with a chosen bromate concentration of 0.5 mg l^{-1}. Zone penetration and degree of dispersion are critical for the performance of SIA systems.

3.1.1. Physical parameters

The physical parameters of the SIA system control the extend of the reaction and the degree of dispersion that the product of the reaction between the analyte and the color reagent undergoes before it reaches the detector, this is critical because the response is directly proportional to the concentration of the product plug passing through the flow cell. The physical parameters are responsible for the optimisation of the mixing of the zones and deliver an appreciable amount of the detectable species. Since the proposed system relies on the measurement of the peak height, anything that affects both the shape and the size of the peak will have a pronounced effect on the performance of the system.

3.1.1.1. Wavelength determination. In order to obtain results with minimal interferences, it was necessary to identify a wavelength that is optimum for bromate determination for the proposed method. This wavelength must be specific for the quantitative and specific monitoring of the bromate-5-bromo-PADAP–thiocyanate complex. The wavelength of maximum absorbance was identified by scanning the product of bromate and 5-bromo PADAP with SCN^- over the range 300–800 nm with a Spectronic Genesy 5 spectrophotometer. A wavelength of 550 nm gave the best results.

3.1.1.2. Flow rate. The reaction between the bromate species and the 5-bromo-PADAP ion is fast and color development after the addition of SCN^- occurs as soon as the two species come into contact. The flow rate should be optimized so that the contact period is sufficient and prevents the diffusion of the complex. The flow rate was studied between 3.6 and 4.8 ml min^{-1} (Fig. 2). The response increases with an increase in flow rate up to 4.0 ml min^{-1} whereafter it tends to flatten off. The flow rate that was chosen for yielding the best results was 4.0 ml min^{-1} (best precision).

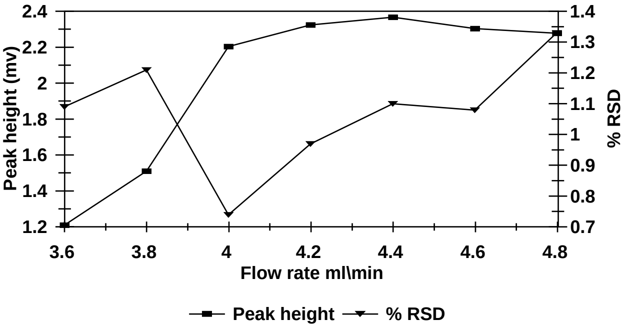

Fig. 2. Influence of the flow rate on response and precision.

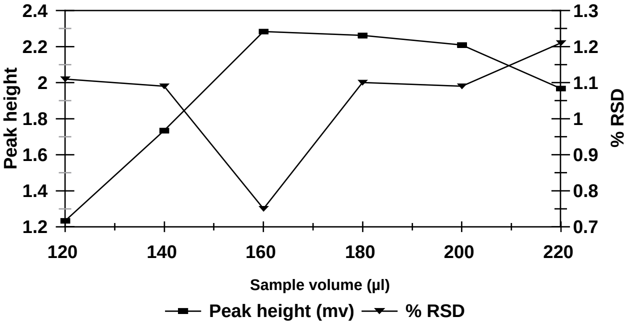

Fig. 3. Influence of sample volume on response and precision.

3.1.1.3. Effect of sample volume. The sample volume was optimised by varying the sample volume between 120 and 220 µl and the results obtained are displayed in Fig. 3. The effect of the sample volume on the linear range was also investigated at the same time. There is an increment in the peak height for the successive sample volume increments until a maximum at 160 µl is reached whereafter it started dipping. The sample volume that was finally used for this analysis was 160 µl due to maximum sensitivity and best precision.

3.1.1.4. Effect of 5-bromo-PADAP volume. The 5-bromo-PADAP (color reagent) volume was optimised by keeping the sample volume constant and varying the color reagent volume between 120 and 220 Φl. There is an increase in response from 120 to 180 µl followed by a decrease with an increase in precision from 120 to 180 µl. A volume of 180 Φl was chosen since it gave the best response and precision (Fig. 4).

3.1.1.5. Effect of SCN^- volume. The volume of the SCN^- reagent was evaluated between 120 and 220 µl. A SCN^- volume of 160 Φl gave the best response and precision and was selected (Fig. 5) for further work.

3.1.1.6. Effect of holding coil and reaction coil dimensions. The dimensions of the holding coil seemed to have a limited effect once holding coil can accommodate the stacks of volumes for different reagents without deformation in the carrier stream. A holding coil with a length of 300 cm and inner diameter of 1.02 mm gave sufficient results. The reac-

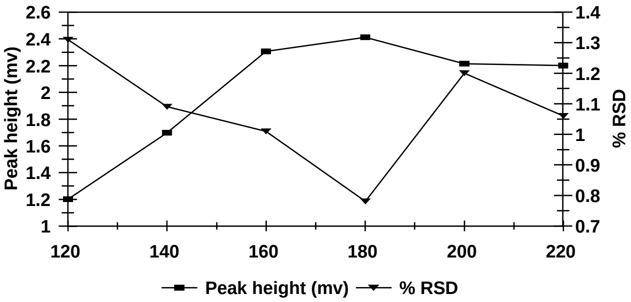

Fig. 4. Influence of 5-bromo-PADAP volume on sensitivity and precision.

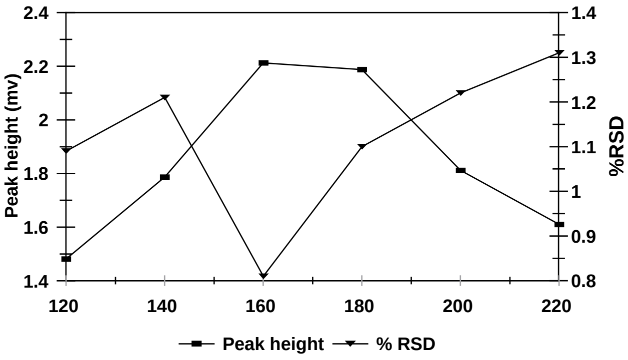

Fig. 5. Influence of SCN^- volume on response and precision.

tion coil dimensions are very influential as it determines the dispersion degree and the extent of the reaction. The zones are propelled via the reaction coil towards the detector and the reaction coil length and i.d. As the reaction is very fast, a reaction coil of 0.5 m and 0.76 mm gave a sufficient dispersion degree to obtain the required response and precision.

3.1.2. *Chemical parameters*

The proposed SIA system for the determination of bromate is based on the reaction product formed between bromate, 5-bromo-PADAP and SCN^- in acidic medium at a wavelength of 550 nm and the concentration of each of these chemicals determines the detection limit and the linear range that the system can be used for quantitative analysis.

3.1.2.1. Influence of sulphuric acid concentration on response and sensitivity. Preliminary studies showed that sulphuric acid gave the best results of the different strong acids evaluated and it was then decided to proceed with the evaluation of different sulphuric acid concentrations. Evaluation was done between 0.05 and 0.30 mol l^{-1}. The response increased rapidly up to 0.20 mol l^{-1} that also gave the best precision and this was used further on.

3.1.2.2. Influence of 5-bromo-PADAP and KSCN concentrations. A concentration of 0.01 mol l^{-1} 5-bromo-PADAP was used in subsequent experiments due to the best precision (% R.S.D. = 0.75%) and response obtained after evaluation of the reagent concentration between 0.0025 and 0.02 mol l^{-1}. The response increased rapidly up to 0.01 mol l^{-1} with a corresponding increase in precision where after both deteriorates. A concentration of 0.01 mol l^{-1} of KSCN was chosen after studying the influence of varying the concentration from 0.005 to 0.025 mol l^{-1} on response and precision.

4. Analytical figures of merit

Table 2
Optimum conditions for the proposed SIA system.

Flow rate carrier: 4.0 ml min^{-1}
Sample volume: 160 μl
Holding coil: length 300 cm and 1.02 mm (i.d.)
Reaction coil: length 40 cm and 0.89 mm (i.d.)
Sulphuric acid: 0.2 mol l^{-1}
5-Bromo-PADAP: 0.01 mol l^{-1} and 180 μl
SCN^-: 0.01 mol l^{-1} and 160 μl
Wavelength: 550 nm

The proposed sequential injection system was evaluated under the optimum conditions (Table 2) with regard to response linearity, accuracy, precision, sample carryover, interference and sampling frequency.

4.1. *Linearity, accuracy, precision, detection limit and sample frequency*

The linearity of the proposed SIA system for the determination of bromate was evaluated under the optimum conditions (Table 2). The regression calibration equation obtained under optimum conditions was:

$$Y = 1.2145X + 1.5696; \quad r = 0.9989 \text{ and } n = 10$$

where Y is the peak height (mv) and X the bromate concentration as mg l^{-1}.

The calibration curve was linear over the range 0.18–3.00 mg l^{-1}.

The detection limit gives an indication of the lowest concentration of bromate that can be distinguished from the backgrounds signal with 99% certainty. The detection limit was calculated as follows:

$$\mathrm{DL} = \frac{(3\delta + k)(k - b)}{m}$$

where k is the relative peak height of the background, δ the standard deviation of the background, b the intercept of the calibration graph and m the slope of the graph.

The calculated detection limit was 0.15 mg l^{-1} of bromate.

The accuracy of the proposed system was evaluated by comparing the results obtained for real samples (obtained from process waste effluents of an industrial factory before recycling for bromate removal before dispensing from outlets in water systems) with the proposed SIA method with those from the standard titration method. The results from the proposed SIA system compare very well with those from the standard method (Table 3). The % R.S.D. was found to be <0.8 ($n = 10$). The proposed system gave a sampling frequency of 45 determinations per hour with a sample carryover of <1%. The accuracy of the proposed SIA system was further confirmed by recovery studies after spiking the real samples with 0.20 mg l^{-1} of bromate. A very good recovery was obtained (Table 4).

4.2. *Interferences*

A number of foreign ions may be present in the process waste effluents of the industrial factory and the influence

Table 3
Comparison of results from the proposed SIA method with those from the standard titration method [17]

Real sample code	Bromate concentration (mg l^{-1})	
	Proposed SIA system[a]	Standard titration method
96780393	0.25 ± 0.01	0.24 ± 0.02
96781653	0.28 ± 0.01	0.28 ± 0.02
96781713	0.33 ± 0.01	0.32 ± 0.02
96781830	0.38 ± 0.01	0.39 ± 0.02
1231	0.36 ± 0.01	0.35 ± 0.02
1232	0.18 ± 0.01	0.20 ± 0.09
1233	0.20 ± 0.01	0.21 ± 0.02
1234	0.29 ± 0.01	0.28 ± 0.02
1235	0.38 ± 0.01	0.37 ± 0.02
1236	0.52 ± 0.01	0.53 ± 0.02

[a] $n = 10$.

Table 4
Recovery studies after spiking real samples with 0.20 mg l^{-1} of bromate

Real sample code	Bromate concentration (mg l^{-1})			
	Original	Expected	Recovered	% Recovery
96780393	0.25	0.45	0.43	95.5
96781653	0.28	0.48	0.48	100
96781713	0.33	0.53	0.52	98.1
96781830	0.38	0.58	0.59	102
1231	0.36	0.56	0.57	102
1232	0.18	0.38	0.37	97.4
1233	0.2	0.4	0.39	97.5
1234	0.29	0.49	0.48	98
1235	0.38	0.58	0.58	100
1236	0.52	0.72	0.73	101

of these possible interferences were tested on the proposed SIA system for the determination of bromate. The maximum tolerated concentration of the interfering ions on the determination of 0.30 mg l^{-1} bromate is given in Table 5. The normal salts show minimal interference. IO_3^-, ClO_3^- and $Cr_2O_7^{2-}$ interfere severely, but these ions are not present in the industrial plant studied and should therefore not be a factor. The present results are very near to those obtained by Ketai et al. [16] and confirmed the tolerated concentration ranges obtained by them.

Table 5
Influence of the interference of some foreign ions on the determination of 0.30 mg l^{-1} of bromate

Ions added	Tolerated concentration (mg l^{-1})[a]
Na^+, K^+, Cl^-, Zn^{2+}, NO_3^-	5500
$HCOO^-$	3000
Cu^{2+}, Ni^{2+}, Co^{2+}	350
$C_2O_4^-$	225
Fe^{3+}	4.5
IO_3^-, ClO_3^-, $Cr_2O_7^{2-}$	0.6

[a] Maximum concentration that gave a deviation of 5% in the peak height.

4.3. *Method validation*

In order to validate the proposed SIA system, the Student's *t*-test was performed on the results of 10 real samples (Table 3). The comparison was done between the proposed SIA method and the standard method [17] to see whether the two methods give the same results at the 95% confidence level. The *t*-test with multiple samples (paired differences) was applied to examine whether the two methods for bromate determination differ significantly at the 95% confidence level [18]. The mean of the tabulated differences was $1/2 = -0.03$ and the sample standard deviation was $S_D = 4.427 \times 10^{-7}$. For the Null hypothesis [18] we can conclude that the two methods agree only when the population mean difference is, H_0: $\Phi_1 = \Phi_2$. The alternative hypothesis, H_1 $\Phi_1 = \Phi_2$, implies the two-tailed test. There are 10 determinations $(N - 1)$, therefore $v = 9$. At the 95% confidence level $t_{\text{tabulated}}$ is 2.262.

Finally $t_{\text{calculated}}$ was computed as:

$$t_{\text{calculated}} = \frac{\text{Di}}{S_D} X \sqrt{n} = -21.43$$

That is less than the tabulated value. At the 95% significance level we accept the Null hypothesis and reject the alternative as the two methods give the same results. We can conclude that the proposed SIA method and the standard method give more or less the same result at the 95% confidence level.

5. Conclusion

The robust, simple and rapid inexpensive proposed SIA system fulfill a very important role in remote on-site field monitoring of bromate in effluent streams at the outlet of industrial sites where bromates form part of the industrial processes in plants without fulltime attention by an operator and where the necessary management and immediate control is needed to prevent environmental pollution. The system is suitable to operate at a sampling frequency of 45 samples per hour in a linear range between 0.18 and 3.00 mg l^{-1} with a precision of less than 0.8%. The results on real samples obtained with the proposed system compares very well with those from a standard titration method and was validated with the Student's *t*-test. The proposed SIA system is also very cost effective in terms of reagent consumption. Unfortunately the method is not suitable or determining bromate in drinking waters that has arisen from ozonation, e.g. 1–100 g l^{-1} [19].

References

[1] R.J. Bull, F.C. Kopfler, Health Effects of Disinfectants and Disinfection By-Products, AWWARF and AWWA, Denver, CO, 1991.
[2] M.S. Siddiqui, G.L. Amy, B.D. Murphy, Water Res. 31 (1997) 3098–3106.

[3] H.S. Weinberg, H. Yamada, R.J. Joyce, J. Chromatogr. A 804 (1998) 137–142.
[4] WHO, Guidelines for Drinking-Water Quality, second ed., vol. 1, Recommendations, World Health Organisation, Geneva, 1993.
[5] B.G. Osborne, Analyst 112 (1987) 137–139.
[6] M.J. Dennis, A. Burrell, K. Mathieson, P. Willetts, R.C. Massey, Food Addit. Contamin. 11 (1994) 633–639.
[7] S. Farrell, J.F. Joa, G.E. Pacey, Anal. Chim. Acta 313 (1995) 121–129.
[8] A. Seubert, G. Schminke, M. Nowak, W. Ahrer, W. Buchberger, J. Chromatogr. A 884 (2000) 191–199.
[9] H. Weinberg, J. Chromatogr. A 671 (1994) 141–149.
[10] H. Jiang, Fenxi Shiyanshi 20 (2001) 89–90.
[11] C.R. Warner, D.H. Daniels, F.L. Joe, G.W. Diachenko, Food Addit. Contam. 13 (1996) 633–638.
[12] M.L. Magnuson, Anal. Chim. Acta 377 (1998) 53–60.
[13] I. Isildak, Chromatographia 49 (1999) 338–342.
[14] A.R. Elwaer, C.W. McLeod, K.C. Thompson, Anal. Chem. 72 (2000) 5725–5730.
[15] K.C. Thompson, J.L. Guinamant, V. Ingrand, A.R. Elwaer, C.W. Mcleod, F. Schmitz, G. de-Swaef, P. Quevauviller, J. Environ. Monit. 2 (2000) 416–419.
[16] W. Ketai, L. Huitao, H. Jian, C. Xingguo, H. Zhide, Food Chem. 70 (2000) 509–514.
[17] J. Ruzicka, G.D. Marshall, Anal. Chim. Acta 237 (1990) 329–334.
[18] W.J. Williams, Hand book of Anion Determination, Butterworth, London, 1997.
[19] G.D. Christian, Anal. Chem., fifth ed., Wiley, 1994, pp. 34–43.