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Sequential injection spectrophotometric determination of trace amounts of iodide by its catalytic effect on the 4,4′-methylenebis(*N*,*N*-dimethylaniline)-chloramine-T reaction☆

Zeriet O. Tesfaldet, Jacobus F. van Staden*, Raluca I. Stefan

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

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Abstract

A simple and sensitive sequential injection spectrophotometric procedure is proposed for the determination of trace amounts of iodide in pharmaceutical preparations. The method is based on the catalytic effect of iodide on the (tetra base) 4,4′-methylenebis(*N*,*N*-dimethylaniline)-chloramine-T reaction in acidic solution. The method involves a sequential aspiration of 255 μl sample/standard followed by 170 μl tetra base and then 128 μl chloramine-T solutions into a carrier stream to be stacked inside a holding coil and flow reversed through a reaction coil towards a detector. The resulting colored compound is measured at 600 nm using an UV/Vis-spectrophotometer. All the parameters that affect the reaction were evaluated and the calibration curve is linear over a range of 0.1–6.0 μg l^{-1} of iodide concentration with detection limit of 0.05 μg l^{-1}. A sample throughput of 80 samples per hour and relative standard deviation of less than 2.0% was achieved. The method is successfully applied for the determination of iodide in three different samples (tablets).

Keywords: Sequential injection; Spectrophotometric determination; Reaction

1. Introduction

Iodine is essential for normal thyroid activity and is used in the treatment of iodine deficiency disorder (IDD). It is also employed as disinfectant. An excess of iodine can produce goiter and hypothyroidism as well as hyperthyroidism. It is an irritant and produces hypersensitivity reaction [1,2]. It is, therefore, essential to monitor the concentration of iodine in the diet and pharmaceutical preparations. For this reason, there is a large demand for simple, inexpensive, accurate and rapid automatic analytical methods capable of analyzing a large number of samples.

With the choice depending on sensitivity and precision required, several techniques have been employed for the determination of trace amounts of iodide and/or iodine including size exclusion chromatography [3], electrostatic ion chromatography [4], capillary electrophoresis [5] or ion chromatography [6], radiochemical neutron activation analysis (RNAA) [7], inductively coupled plasma optical emission spectrophotometry (ICP-OES) [8], inductively coupled plasma atomic emission spectrophotometry (ICP-AES) [9] inductively coupled plasma-mass spectrophotometry (ICP-MS) [10] and UV/Vis-spectrophotometry [11,12]. Iodine also has been determined by a catalytic spectrophotometric method [13]. Among these techniques mentioned earlier UV/Vis-spectrophotometry has the advantage that determinations can be made in a relatively short time, it is simple and inexpensive. Others techniques are very expensive [8–10] to be used for routine analysis.

Several flow analysis procedures have been reported for the determination of iodide in different samples including head-space flow injection for the on-line determination with chemiluminescence detection [14], reversed flow injection with spectrophotometric detection [15] and flow injection spectrophotometric determination of iodide by its catalytic effect [16–19]. Recently, Nacapricha and co-workers [20]

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* Corresponding author. Tel.: +27-084-480-7263.
E-mail address: Koosvanstade@telkomsa.net (J.F. van Staden).

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employed an iodine-starch reaction for the determination of iodide in pharmaceutical preparations using flow injection analysis. This procedure presented a very high detection limit and cannot be applied for trace iodide analysis.

As compared to the flow-based procedures mentioned above, sequential injection (SI) analysis (SIA) has an advantage due to its economical sample and reagent consumption and reduction of the volume of chemical waste generated. For this reason an SIA system with UV/Vis-spectrophotometric detection has been proposed for the determination of trace amounts of iodide in pharmaceutical preparations.

In this work, we report the implementation of SIA for the determination of trace amounts of iodide in pharmaceutical preparations. SIA involves sequential aspiration of zones of reagents and samples into the holding coil using a pump, followed by flow reversal, the well stacked zones of reagents and samples are forwarded towards the detector through the reaction coil and recorded as a peak for analytical readout by the detector. Here, the method used for the determination of trace iodide content is based on the catalytic effect of iodide on the oxidation of 4,4′-methylenebis(*N*,*N*-dimethylaniline) (tetra base) by chloramine-T in acidic solution. The resulting compound is monitored spectrophotometrically at 600 nm. All the analytical parameters that affect the system and the reaction was thoroughly studied and optimized as described below in order to achieve an optimum condition for the reaction. The optimized method is simple, sensitive, rapid and reliable and successfully applied for the determination of trace amounts of iodide in three real samples at the μg level.

2. Experimental

All reagents used were of analytical reagent grade and all solutions were prepared with de-ionized water. De-ionized water was obtained from a Modulab system (Continental Water System, San Antorio, TX, USA).

2.1. Reagents and standard solutions

Stock iodide solution was prepared by dissolving 0.1308 g of potassium iodide (Merck) with de-ionized water in a 100 ml volumetric flask. The working solutions were prepared by appropriate dilution of the stock solution with de-ionized water. Chloramine-T trihydrate solution (1.54×10^{-2} mol l^{-1}) was prepared by dissolving 0.436 g of sodium *N*-chloro-*p*-toluenesulfonamide trihydrate (Aldrich) with de-ionized water in a 100 ml volumetric flask. Working solutions were prepared by appropriate dilution of the stock solution with de-ionized water. Tetra base (1.75×10^{-2} mol l^{-1}) stock solution was prepared by dissolving 0.445 g of 4,4′-methylenebis(*N*,*N*-dimethylaniline) (Aldrich) in 10 ml of 0.20 mol l^{-1} sulfuric acid and diluted to a 100 ml volumetric flask with de-ionized water. Working solutions were prepared by appropriate dilution of the stock solution with acetate buffer pH 4. Acetate buffer was prepared from 0.1 mol l^{-1} of sodium acetate and 0.1 mol l^{-1} of acetic acid.

2.2. Sample preparation

Samples: (Table 1) Vital Multitime containing multivitamin and minerals with iron supplied by Vital Health Foods (Pty) Ltd., Kuils River, South Africa (sample 1); Kiddy Multivitamin supplied by The MY Vitamin Company (Pty) Ltd., HPA, Centurion, South Africa (sample 2); and Vita force (Kelp) supplied by Pharma Natura (Pty) Ltd., Sandton, South Africa (sample 3).

Three tablets of each sample (Vita force (Kelp), Vital Multitime and Kiddy Multivitamin, purchased from local shops) were placed individually into conical volumetric flasks and dissolved with 30 ml of hot de-ionized water, boiled gently for 5 min, cooled to room temperature, and centrifuged to separate the residue. The residue was again washed twice with de-ionized water, centrifuged and then added to the supernatant. The supernatant was transferred into a 100 ml volumetric flask and diluted to the mark with de-ionized water. This solution was further diluted for appropriate concentration before determination.

2.3. Apparatus

A single wavelength Unicam 5625 UV/Vis spectrometer (Cambridge, UK) equipped with a 10 mm Hellma-type flow through cell (Hellma GmbH and Co., Mulheim/Baden, Germany) was used in all SIA experiments. A 10 position micro-actuated selection valve (E-10-230, Valco instruments, Houston, TX, USA) and a Gilson Minipuls-3 peristaltic pump (M321, Gilson, Villiers-le-Bel, France) were also used in the SIA system. For the device control and data acquisition, a FlowTEK interface box and FlowTEK software package (obtained form MINTEK Randburg, South Africa) for computer aided flow analysis were used throughout the experiment. The manifold SIA system is given in Fig. 1.

2.4. Procedure

An illustration of the device sequence is shown in Table 2. A sample/standard, reagent (tetra base), and

Table 1
Sample content per tablet

Sample type	Content/tablet
Vital Multitime	Fe^{2+} = 18 mg; I^- = 150 μg; Mn^{2+} = 1.6 mg and vitamins
Kiddy Multivitamin	Cu^{2+} = 200 μg; Fe^{2+} = 5 mg; Zn^{2+} = 5 mg; Mn^{2+} = 2.5 mg; Mo^{6+} = 50 μg; V^{6+} = 50 μg; I^- = 30 μg and vitamins
Vita force (Kelp)	I^- = 400 μg

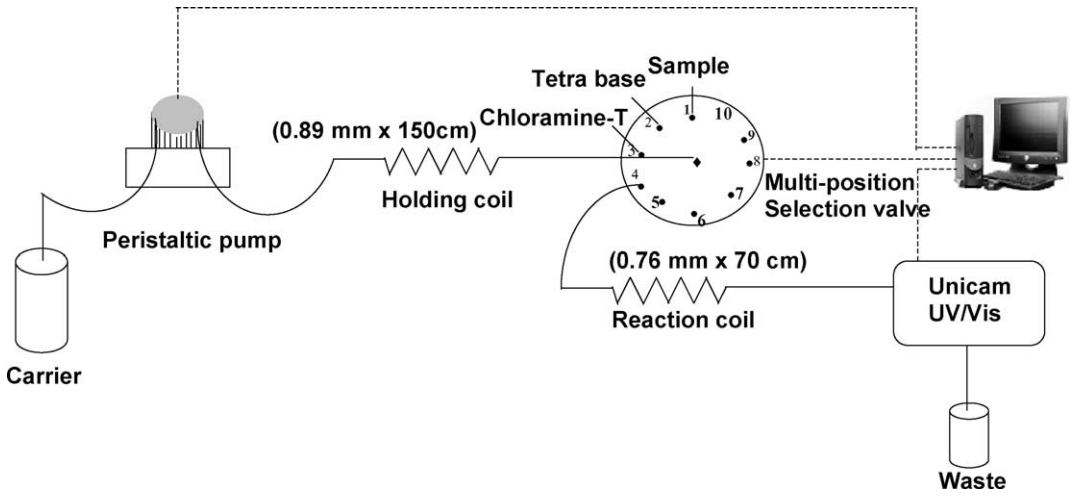

Fig. 1. Schematic representation of an SIA manifold used in the determination of trace iodide. The pH of the chloramine-T solution was adjusted to pH 4 with acetate buffer. 8.0 $\mu g\,l^{-1}$ of iodide solution was used to optimize the system.

reagent (chloramine-T) solutions 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 complex is measured at 600 nm using an UV/Vis spectrophotometer.

3. Results and discussion

In the presence of iodide, chloramine-T oxidizes 4,4′-methylenebis(*N*,*N*-dimethylaniline) (tetra base) in acidic solution to form a blue colored compound, which is further oxidized to a greenish-yellow compound. The rate of the oxidation reaction increases with an increase in the iodide concentration. This result in an increase of the peak height (absorbance), therefore this value was taken as a parameter for the determination of iodide. The temperature of the reaction coil affects the reaction rate and thus influences the maximum sensitivity and precision. The sensitivity and precision of the reaction was evaluated at three different temperatures (20, 30 and 40 °C) at a constant line length of 70 cm. It was observed that the sensitivity slightly increased with an increase in the temperature of the reaction coil. Although the best response was obtained at 40 °C, the results obtained were less reproducible. A temperature of 30 °C was selected due to sensitivity, precision and stability of the base line. It was also observed that the sensitivity and precision depends on the sequence aspiration of the solutions (standard/sample, chloramine-T and tetra base solutions) into the system. A sequence aspiration of iodide (standard/sample) followed by tetra base and then chloramine-T solutions gave the highest sensitivity and precision and were used for further work. The pH of the chloramine-T solution was adjusted with acetate buffer to a pH 4 adapted from the previous work [18] and used throughout the experiment. Furthermore, flow parameters as well as reagents concentration that affect the sensitivity and precision were optimized as described below. In all cases, the maximum relative peak height and lower relative standard deviation were taken as criteria to choose the optimum condition for the analysis.

Table 2
Device sequence used for one cycle of the SIA system for the determination of trace iodide in pharmaceutical formulations

Time (s)	Pump	Valve	Description
0		Sample	Pump off, valve select sample stream
2	Reverse		Draw up the sample solution
5	Off		Pump stop
6		Tetra base	Select tetra base solution (valve position 2)
7	Reverse		Draw up tetra base solution
8.5	Off		Pump stop
9.5		Chloramine-T	Select chloramine-T solution (valve position 3)
10.5	Reverse		Draw up chloramine-T solution
12.5	Off		Pump stop
13.5		Detector	Select the detector stream,
14.5	Forward		Pump the stack of zones to ward the
43	Off		Pump stop
45	Home		Complete one cycle, valve return back to position 1

3.1. Method optimization

3.1.1. Flow rate

The sensitivity depends on the residence time of the sample zone in the system, i.e. on the flow rate and the line length of the reaction tube. The influence of the flow rate was investigated at constant volumes of solutions and line length of the reaction tube by altering the speed of the pump and aspiration times accordingly. The results (Fig. 2) revealed that the sensitivity increases with an increase in the flow rate up to a flow rate of 5.1 ml min^{-1} and then decreased. The decrease in sensitivity at higher flow rates could be mainly due to a shortage of time for complete oxidation of the reaction to form a product zone. A flow rate of 5.1 ml min^{-1} was selected for subsequent measurement due to highest sensitivity and precision.

3.1.2. Holding coil length and diameter

In a SIA system, the line length of the holding coil should be long enough to hold the sample and reagents solutions that are sequentially pumped into it and should prevent it from entering the pump conduit. By putting this into consideration, in this experiment, three different holding coil line lengths (150, 200, and 250 cm) were studied while its diameter was kept constant. As expected, no significant difference in sensitivity was noticed with increasing line length. A line length of 150 cm for the holding coil was selected due to its sensitivity and precision (lower standard deviation, %R.S.D.). Furthermore, the effect of this coil diameter on sensitivity and precision was investigated by varying the diameter (0.89, 102 and 1.14 mm) at constant holding coil line length of 150 cm. A 0.89 mm coil diameter gave the highest sensitivity and precision and was selected as optimum.

3.1.3. Reaction coil length and diameter

Depending on the dimension and line length of the reaction coil, the formed product zone may undergo physical dispersion as the stack of zones is forwarded from the holding coil through the reaction coil towards the detector. Thus, the reaction coil between the selection valve and the detector is usually kept as short as possible to avoid excessive dilution of the formed product zone. The effect of this coil was studied between 70 and 160 cm line length with increasing steps of 30 cm and a constant inside diameter (0.89 mm i.d.). It was observed that there is a decrease in sensitivity with an increase in line length of the reaction coil confirming the rapidness of the reaction and the decrease is mainly due to physical dispersion of the formed product zone as it is transported all the way to the detector. An optimum line length of 70 cm for the reaction coil was selected due to its sensitivity and precision. The effect of this coil diameter was investigated (0.76, 0.89, 1.02 and 1.14 mm) on sensitivity and precision. There is a slight decrease in sensitivity with increasing coil diameter but no difference in precision was noticed. Therefore a coil diameter of 0.76 mm was selected.

3.1.4. Reagents concentrations

By varying the concentration between 3.5×10^{-5} and 2.1×10^{-4} mol l^{-1}, the effect of the tetra base concentration on sensitivity and precision was tested and the results are given in Fig. 3. The results show that increasing the tetra base concentration increases the sensitivity up to 1.75×10^{-4} mol l^{-1}, beyond which the slope flattened off. Thus a concentration of 1.75×10^{-4} mol l^{-1} tetra base was selected.

The effect of chloramine-T concentration was studied between 0.77×10^{-3} and 3.85×10^{-3} mol l^{-1} at the optimum constant tetra base concentration. The results are shown in Fig. 4 and it clearly indicates that the sensitivity increases

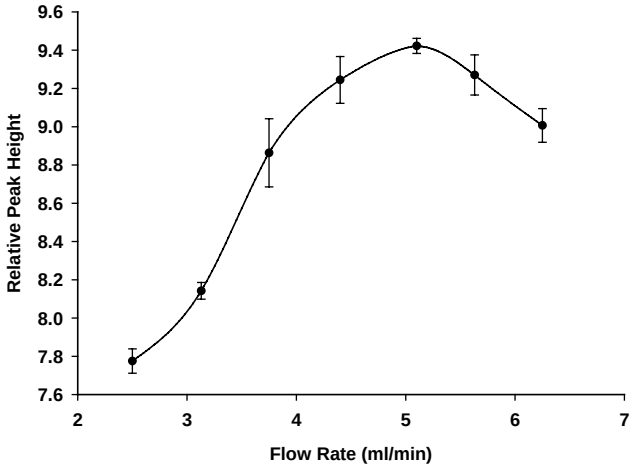

Fig. 2. Influence of flow rate on sensitivity and precision. Experimental conditions were: reaction coil: 0.89 mm × 90 cm, holding coil: 1.02 mm × 200 cm, aspiration of sample, tetra base and chloramine-T: 170, 128 and 128 μl volumes, respectively, concentration: 1.05×10^{-4} and 3.85×10^{-3} mol l^{-1} of tetra base and chloramine-T, respectively.

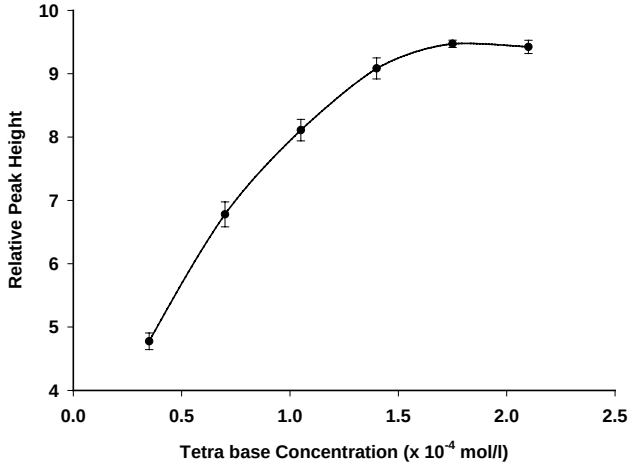

Fig. 3. Influence of tetra base concentration on sensitivity and precision. Experimental conditions were: reaction coil dimensions: 0.76 mm × 70 cm, holding coil dimensions: 0.89 mm × 150 cm, aspiration of sample, tetrabase and chloramine-T: 170, 128 and 128 μl volumes, respectively, concentration of chloramine-T: 3.08×10^{-3} mol l^{-1} and flow rate: 5.1 ml min^{-1}.

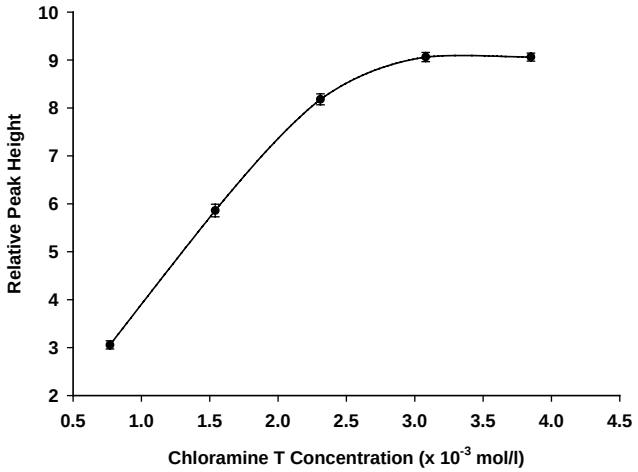

Fig. 4. Influence of chloramine-T concentration on sensitivity and precision. Experimental conditions were: reaction coil dimensions: 0.76 mm × 70 cm, holding coil dimensions: 0.89 mm × 150 cm, aspiration of sample, tetra base and chloramine-T: 170, 128 and 128 μl volumes, respectively, concentration of tetra base: 1.05×10^{-4} mol l^{-1} and flow rate: 5.1 ml min^{-1}.

with an increasing chloramine-T concentration up to 3.08 $\times 10^{-3}$ mol l^{-1}, beyond which it remained virtually constant. Therefore, a chloramine-T concentration of 3.08×10^{-3} mol l^{-1} was selected.

3.1.5. Sample and reagents volumes

The effect of sample volume was investigated between 43 and 298 μl with increasing steps of 43 μl while keeping the two reagent solutions and flow rate constant (Fig. 5A). As expected the sensitivity increases with an increasing sample volume of up to 255 μl, above which it remained virtually constant. A sample volume of 255 μl was selected for subsequent measurements.

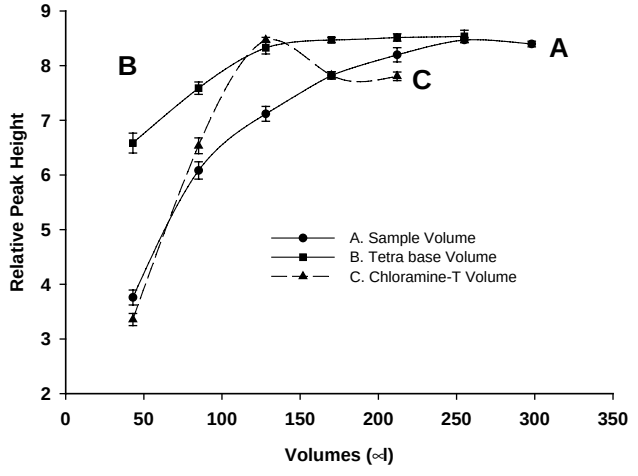

Fig. 5. Influence of sample (A), tetra base (B) and chloramine-T (C) volumes on sensitivity and precision. Experimental conditions were: reaction coil dimensions: 0.76 mm × 70 cm, holding coil dimensions: 0.89 mm × 150 cm, flow rate: 5.1 ml min^{-1}, tetra base: 1.75×10^{-4} mol l^{-1}, chloramine-T: 3.08×10^{-3} mol l^{-1} and aspiration of (A) tetra base: 128 μl and chloramine-T: 170 μl, (B) sample: 255 μl and chloramine-T: 128 μl and for (C) sample: 255 μl and tetra base: 128 μl.

The effect of tetra base volume on sensitivity and precision was evaluated between 43 and 255 μl with increasing steps of 43 μl at constant chloramine-T and sample volumes (Fig. 5B). There is an increase in sensitivity up to 128 μl, where after the slope flattened off and remained virtually constant. A volume of 170 μl was selected due to the best sensitivity and precision achieved and used for subsequent measurements.

The effect of reagent (chloramine T) volume on sensitivity and precision was studied between 43 and 212 μl with increasing steps of 43 μl at constant sample and tetra base volumes (Fig. 5C). There is a sharp increase in sensitivity up to 128 μl, above which the sensitivity decreases and became constant. A reagent volume of 128 μl was selected for further work.

3.2. Method evaluation

The proposed sequential injection system was evaluated under the optimum conditions (Table 3) with regard to response linearity, accuracy, precision, sample carryover, sampling rate and interferences.

3.2.1. Linearity, detection limit, accuracy, sample carryover, precision and sampling rate

The linearity of the current method for the determination of iodide was evaluated under the optimum conditions. The relationship obtained between the relative peak height and iodide concentration is given by the equation

$$\text{relative peak height} = 0.107[\text{iodide}] + 0.776, \quad R^2 = 0.996$$

The proposed SIA system is linear between concentration ranges of 0.1 and 6.0 μg l^{-1}.

The detection limit gives an indication of the lowest concentration of iodide that can be distinguished from the back-

Table 3
Optimum working conditions

Parameter		Value
Flow rate		5.1 ml min^{-1}
Holding coil	Diameter	0.89 mm
	Length	150 cm
	Configuration	Coiled
Reaction coil	Diameter	0.76 mm
	Length	70 cm
	Configuration	Coiled
Sample volume		255 μl
Tetra base volume		128 μl
Chloramine-T volume		170 μl
Acetate buffer solution	Concentration	0.1 mol l^{-1}
Tetra base	Concentration	1.75×10^{-4} mol l^{-1}
Chloramine-T	Concentration	3.08×10^{-3} mol l^{-1}
Acetate buffer solution	pH	4

Table 4
Comparison of the results (as results μg/tablet) obtained for the determination of trace iodide in real pharmaceutical preparations

Samples	Proposed SIA system	Manual method	Claimed values	*t*-calculated
Kiddy Multivitamin	149.01 ± 1.43	152.5	150	1.58
Vita force (Kelp)	411.85 ± 0.50	406.06	400	0.91
Vital Multitime	31.15 ± 0.78	30.5	30	0.16

All values are from averages of three determinations.

grounds 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 is the standard deviation of the background, b is the intercept of the calibration graph and m is the slope of the graph. The calculated detection limit was 0.05 $\mu g\,l^{-1}$ iodide.

In order to estimate the accuracy of the current method, three real samples (three tablets of different compositions) were analyzed for iodide content and the results are shown in Table 4. The results obtained are in good agreement with a manual method described previously [21] and labeled values by the manufacturers. This indicates that the proposed SIA system is highly selective, sensitive and valid for the analysis of trace iodide content at μg level in pharmaceutical samples and other matrices.

Sample interaction/carryover effect between consecutive samples were investigated by analyzing a sample with lower analyte concentration followed by that of higher concentration and again with the lower concentration. A sample containing 3.0 $\mu g\,l^{-1}$ iodide was used for the lower concentration and 30 $\mu g\,l^{-1}$ iodide was used for the higher analyte concentration. The carryover was then calculated as follows:

$$\text{carryover} = \frac{H_3 - H_1}{H_2} \times 100$$

where H_1 is the relative peak height of the analyte containing 3.0 $\mu g\,l^{-1}$ iodide, followed by H_2 is the relative peak height of the analyte containing 30 $\mu g\,l^{-1}$, followed by H_3 is the relative peak height of the analyte containing 3.0 $\mu g\,l^{-1}$ iodide. The calculated carryover effect was found to be 0.88%, which is negligible.

The precision of the method was evaluated by ten-repetitive determinations of the standard solutions and the %R.S.D. for the linear range from 0.10 to 6.0 $\mu g\,l^{-1}$ was found to be between 0.80 and 2.0%.

The experimental period for one complete analytical cycle was 45 s long that gave an over all sampling rate of 80 samples per hour.

3.3. Interference study

The effects of foreign ions present in appreciable concentration in the tablets (Table 1) were tested as possible interferences for the method. The study was conducted by analyzing a standard solution of iodide (5.0 $\mu g\,l^{-1}$) to which increasing amounts of interfering species was added. The results are listed in Table 5. The tolerance limit was defined as the concentration of added ions causing less than a 3% relative error of the average absorbance for ten repetitive measurements for the standard iodide solution with no interferences. Many ions did not interfere in 1000-fold excess to iodide. It was observed that the interference of iron(II) depends on temperature. The interference of iron was tested at 20, 30 and 40 °C; a 100-fold excess of Fe(II) was found to interfere at 20 °C and with increasing temperature the interference decreased and remained constant at both temperatures tested. Thus, 30 °C was selected to reduce the interference of Fe(II). Thus, it can conclude that the method is highly selective for the determination of iodide and can be used for the determination of trace amounts of iodide in various sample matrices under the optimum conditions described above (Table 3).

Table 5
Interference of foreign ions on the determination of 5.0 $\mu g\,l^{-1}$ iodide

Ions added	Tolerance ratio (W_{ion}/W_{iodide})
Zn(II), Mn(II), Cu(II), SO_4^{2-}, Cl^-, Na^+, K^+	1000[a]
Fe(II), Mo(VI), NH_4^+	300
V(VI)	50

[a] Maximum concentration ratio tested.

3.4. Statistical comparison

A statistical comparison was carried out between the proposed SIA system and a manual method [21] and the results are given in Table 4. We conducted the null hypothesis testing (*t*-test) at 95% confidence level. The calculated value for t is much less than the tabulated critical values of t (tabulated critical values at four degrees of freedom = 2.78), indicating that there is no statistically significant difference between the results obtained and the manual method. Thus, the null hypothesis cannot be rejected.

4. Conclusion

The proposed SIA system is simple, accurate, highly sensitive, selective and reliable and most of the common ions do not interfere in the determination of trace amounts of iodide. The method is successfully applied for the determination of iodide in three different compositions of real pharmaceutical samples. The system presented a high sam-

ple frequency, which makes it suitable for routine analysis. It is also highly economical in terms of sample and reagent consumption with minimum waste generation. The system is fully computerized and uses inexpensive and readily available instrumental components. The calibration curve is linear from 0.10 to 6.0 $\mu g\,l^{-1}$ with a detection limit of 0.05 $\mu g\,l^{-1}$ and process 80 samples per hour with a relative standard deviation of less than 2.0%.

References

[1] H.A. Guthrie, M.F. Picciano, Human Nutrition, Mosby-Year Book, 1995.
[2] E.N. Whitney, S.R. Rolfes, Understanding Nutrition, nineth ed., Wadsworth Group, Belmont, USA, 2002.
[3] H.-Bin. Li, F. Chen, X-Rong. Xu, J. Chromatogr. A 918 (2001) 335.
[4] W. Hu, P.-J. Yang, K. Hasebe, P.R. Haddad, K. Tanaka, J. Chromatogr. A 956 (2002) 103.
[5] K. Ito, T. Ichihara, H. Zhuo, K. Kumamoto, A.R. Timerbaev, T. Hirokawa, Anal. Chim. Acta 497 (2003) 67.
[6] H.L. Tucker, R.W. Flack, J. Chromatogr. A 804 (1998) 131.
[7] X. Hou, H. Dahlgaard, B.R.U. Jacobsen, S.P. Nielsen, A. Aarkrog, Anal. Chem. 71 (1999) 2745.
[8] K. Krengel-Rothensee, U. Richter, P. Heitland, J. Anal. At. Spectrom. 14 (1999) 699.
[9] K.A. Anderson, P. Markowski, J. Assoc. Off. Anal. Chem. 83 (2000) 225.
[10] L.F. Sanchez, J. Szpunar, J. Anal. At. Spectrom. 14 (1999) 1697.
[11] O. Agrawal, G. Sunita, V.K. Gupta, Talanta 49 (1999) 923.
[12] T. Yoshinaga, T. Shirakata, H. Dohtsh, H. Hihatsuka, M. Hasegawa, M. Kobayashi, T. Hoshi, Anal. Sci. 17 (2001) 333.
[13] A.A. Mohamed, Monatsheffe Für Chemie 132 (2001) 919.
[14] J.L. Burguera, M.R. Brunetto, Y. Contreras, M. Burguera, M. Gallignani, P. Carrero, Talanta 43 (1996) 839.
[15] Z. Xie, J. Zhao, Talanta, in press.
[16] K. Oguma, K. Kitada, R. Kuroda, Microchim. Acta 110 (1993) 71.
[17] A.R. de, A. Nogueira, F. Mockiuti, G.B. de Souza, O. Primavesi, Anal. Sci. 14 (1998) 558.
[18] B. Rezaei, Anal. Lett. 33 (2000) 2553.
[19] D. Nacapricha, K. Ratanawimarnwong, K. Grudpan, Anal. Biochem. 378 (2004) 816.
[20] W. Chantore, S. Muangkaew, J. Shiowatana, D. Nacapricha, LAV 11 (1999) 37.
[21] R.-I. Stefan, S.G. Bairu, J.F. van Staden, Anal. Lett. 36 (2003) 1493.