

6-20-2015

A Simple and Safe Spectrophotometric Method for Iodide Determination

Hermin Sulistyarti

Department of Chemistry, Faculty of Science, Universitas Brawijaya, Malang 65145, Indonesia LCAMIA (Low Cost and Automated Method and Instrumentation Analysis) Research Group, Universitas Brawijaya, Malang 65145, Indonesia, hermin@ub.ac.id

Atikah

Department of Chemistry, Faculty of Science, Universitas Brawijaya, Malang 65145, Indonesia LCAMIA (Low Cost and Automated Method and Instrumentation Analysis) Research Group, Universitas Brawijaya, Malang 65145, Indonesia

Qonitah Fardiyah

Department of Chemistry, Faculty of Science, Universitas Brawijaya, Malang 65145, Indonesia LCAMIA (Low Cost and Automated Method and Instrumentation Analysis) Research Group, Universitas Brawijaya, Malang 65145, Indonesia

Sita Febriyanti

Department of Chemistry, Faculty of Science, Universitas Brawijaya, Malang 65145, Indonesia

Asdauna

Department of Chemistry, Faculty of Science, Universitas Brawijaya, Malang 65145, Indonesia

Follow this and additional works at: <https://scholarhub.ui.ac.id/science>

Recommended Citation

Sulistyarti, Hermin; Atikah; Fardiyah, Qonitah; Febriyanti, Sita; and Asdauna (2015) "A Simple and Safe Spectrophotometric Method for Iodide Determination," *Makara Journal of Science*: Vol. 19 : Iss. 2 , Article 1.

DOI: 10.7454/mss.v19i2.4736

Available at: <https://scholarhub.ui.ac.id/science/vol19/iss2/1>

This Article is brought to you for free and open access by the Universitas Indonesia at UI Scholars Hub. It has been accepted for inclusion in Makara Journal of Science by an authorized editor of UI Scholars Hub.

A Simple and Safe Spectrophotometric Method for Iodide Determination

Cover Page Footnote

The authors are grateful to The University of Brawijaya Malang for facilitating research and financial support through "Institution Competitive Research Grant 2012" scheme.

A Simple and Safe Spectrophotometric Method for Iodide Determination

Hermin Sulistyarti^{1,2*}, Atikah^{1,2}, Qonitah Fardiyah^{1,2}, Sita Febriyanti¹, and Asdauna¹

1. Department of Chemistry, Faculty of Science, Universitas Brawijaya, Malang 65145, Indonesia

2. LCAMIA (Low Cost and Automated Method and Instrumentation Analysis) Research Group, Universitas Brawijaya, Malang 65145, Indonesia

*E-mail: hermin@ub.ac.id

Abstract

In order to practice green chemistry, a simple and safe spectrophotometric method for iodide determination has been successfully developed based on the formation of a blue starch-iodine complex. Iodide was oxidized to form iodine prior to the addition of a starch solution, and the blue starch-iodine complex was directly detected spectrophotometrically at a wavelength of 615 nm. The chemical parameters, such as type, reaction time, as well as concentration of oxidizing agents and solution pH were optimized with respect to sensitivity and analysis time. The method showed optimum results under iodate oxidant with a mol ratio of $\text{IO}_3^-:\text{I}^- = 1:3$, reaction time of 5 minutes, and solution pH of 5. Under these optimum conditions, the method showed linearity measurements from 5-40 mg/L iodide with a correlation (R^2) of 0.9889. This technique offers a simple, safe, accurate, and relatively fast method for iodide determination, which is prospective for monitoring iodide samples.

Abstrak

Metode Spektrofotometri Sederhana dan Aman untuk Penentuan Iodida. Penentuan iodida menggunakan metode spektrofotometri sederhana dengan bahan kimia tidak berbahaya telah berhasil dikembangkan berdasarkan pembentukan kompleks biru iodium-amilum. Iodida terlebih dahulu dioksidasi menjadi iodium yang dengan penambahan amilum menghasilkan kompleks biru iodium-amilum yang dapat dideteksi menggunakan spektrofotometer pada panjang gelombang 615 nm. Parameter kimia, seperti jenis, waktu reaksi, dan konsentrasi oksidator, serta pH larutan dioptimasi untuk meningkatkan sensitifitas dan efektifitas waktu analisis. Hasil optimasi metode menunjukkan bahwa hasil optimum diperoleh pada mol rasio oksidator iodat terhadap iodida 1:3, waktu reaksi 5 menit, dan pH larutan 1. Pada kondisi optimum tersebut, metode ini memberikan linieritas pengukuran iodida dari 5-40 mg/L dengan koefisien korelasi (R^2) 0,9889. Metode ini menawarkan cara yang sederhana, aman, akurat, dan relatif cepat untuk penentuan iodida yang prospektif untuk monitoring sampel iodida.

Keywords: iodate, iodide, persulfate, spectrophotometry, starch-iodine complex.

Introduction

The importance of developing a method for iodine determination is obvious. The concentration of iodide in urine can be used as an indicator for monitoring iodine deficiency disorder (IDD), which gives rise to hypothyroidism leading to mumps disease and mental retardation [1,2]. Although the effort to overcome iodine deficiency by consuming iodized salt has long been encouraged, IDD is still a problem in various regions of Indonesia, especially for those who live in mountainous area that lack sources of iodine.

Measurement of iodine in urine is very important to detect iodine deficiency before clinical symptoms arise, because the levels of iodine in urine can reflect the intake of iodine into the body [2]. Thus, monitoring iodide in urine is preferable compared to clinical diagnosis as it can prevent IDD. Analysis of iodide is also very essential for controlling iodide in table salts or potassium iodide tablet used for IDD treatment due to the eventual loss of iodine during the salts' treatment and long storage [3] as well as monitoring iodide in sea water, and in other pharmaceutical products, such as antiseptics and disinfectants.

There are many analytical methods available for detecting iodine and its various species in complex matrices. Most spectrophotometric methods for iodide determination, including the standard spectrophotometric method, are based on the reaction found by Sandell and Kolthoff [4]. However, this method uses an arsenic reagent, which is carcinogenic, and the reaction steps are complicated. Another standard method for iodide determination is based on the oxidation of iodide by persulfate to form iodine using leucocrystal violet as an indicator [4]. Nevertheless, this indicator is expensive and not available in ordinary laboratories and markets.

Koh, et al. (1988) proposed a spectrophotometric method based on the extraction of an oxidized form (iodine) into carbon tetrachloride followed by back extraction of iodide into 1,2-dichloroethane as an ion pair with methylene blue detected at 657 nm. The method gave a molar absorptivity of 3.15×10^5 L/mol.cm, and a linear calibration graph was obtained over the iodide concentration range of 7.5×10^{-8} – 3×10^{-6} mol/L. The proposed method was successfully applied to the determination of various amounts of iodide in natural water samples [5]. Determination of iodide at trace levels has also been reported based on the inhibitory effect of iodide on the Pd(II)-catalyzed reduction of Co(III)-EDTA by the hypophosphite ion in a weak acid medium. The measurements were conducted by monitoring the absorbance-time curves (the $A = f(t)$ curve) at 540 nm in order to obtain the slope (dA/dt) for each sample run. Then, the concentration of iodide was determined by plotting the slope to calibration graph of dA/dt versus the standard iodide concentration. This method gave a linear relationship ($r = -0.9878$) in the range of 2–35 ng/mL with a detection limit of 1.2 ng/mL [6]. Another kinetic spectrophotometric method was reported based on a catalytic effect of iodide on the reaction between Janus Green and bromate in an acidic media. The proposed method is suitable for the determination of iodide in food samples from 0.5–190 $\mu\text{g/L}$ [7]. The catalytic behavior of iodide in the oxidation of variamine blue, methylene blue, rhodamine B, and malachite green has also been used for developing iodide spectrophotometric determination by measuring the change of the absorbance dyes. This method offers highly sensitive and selective methods for trace amounts of iodide in pharmaceutical and edible salt samples in the range concentrations of 0.064–1.27 $\mu\text{g/mL}$, 3.20–9.54 $\mu\text{g/mL}$, 5.00–19.00 $\mu\text{g/mL}$, and 6.54–19.00 $\mu\text{g/mL}$ for the respective dyes of variamine blue, methylene blue, rhodamine B, and malachite green [8].

A flow-injection spectrophotometric method was also reported for the determination of iodide in ground and surface water. The method was based on the catalytic destruction of the color of the Fe(III)–SCN[–]–CP⁺–nBPy quarternary complex. The detection limit of the method was reported to be 0.1 ng/mL of iodide [9]. Another

report showed a sensitive spectrophotometric method for the determination of iodine species like iodide, iodine, iodate, and periodate. The method involved oxidation of iodide to ICl_2^- , which bleached the methyl red color measured at 520 nm. The measurement was based on the decrease in the color intensity of the dye, and the intensity was linear in the concentration range of 0–350 $\mu\text{g/L}$. The method resulted in a molar absorptivity of 1.73×10^5 L/mol.cm with a correlation coefficient (R^2) of 0.9997, and a relative standard deviation of 3.6% ($n=10$) [10]. The catalytic effect of the iodide catalyst on a 4,4'-methylenebis(N,N'-dimethylaniline)-chloramine-T reaction has also been used as the basic method for measuring iodide in sequential injection system with linearity of measurement over a range of 0.1–6.0 $\mu\text{g/L}$ [11].

Recently, a spectrophotometric method for iodide determination was reported based on the electrochemical oxidation of iodide to iodine at a platinum electrode followed by the extraction of ionic associates of iodine-iodide complexes with a brilliant green in CCl_4 . The slope of the calibration curve yielded a molar extinction coefficient of ϵ of $3 \cdot 10^5$ L/mol.cm. This method can be used for the quantification of iodide in the concentration range of $3 \cdot 10^{-7}$ – $3 \cdot 10^{-6}$ mol/L with a detection limit of $5 \cdot 10^{-8}$ mol/L and was successfully applied for the determination of iodide in real samples with a relative standard deviation of 1–2% [12].

Unfortunately, most of those methods involved complicated procedures and reagents which are either carcinogenic, costly, or of limited availability. Besides, to support green chemistry, the project method of analysis should be designed using less harmful chemicals and chemical processes to human health and the environment [13]. Meanwhile, iodine is characteristically determined by a safe and simple starch reagent to form an iodine-starch blue complex. This reaction is commonly used in qualitative analysis to identify the presence of iodide. Although this complex is insoluble in water, based on the previous investigation, under a very low concentration of iodine, it forms a clear blue solution. The formation of starch-iodine has been adopted in a flow system for iodate determination in iodized salt [14]. This reaction has also been applied in a flow system by employing a dichromate oxidizing agent as the donor stream and a gas diffusion cell consisting of a hydrophobic membrane to permeate iodine prior to reaction with starch acceptor stream. However, this method is designed for determining a high concentration of iodide (50–300 mg/L) or an extremely high concentration of iodide (6000–10000 mg/L) by adding dialyzer for the dilution process [15].

Therefore, the goal of this work is to create a simple and safe spectrophotometric method for iodide determination based on the formation of a blue iodine-starch complex

using colorless oxidizing agents of iodate and perchlorate. Thus, iodine-starch complex can be directly detected without the separation of iodine or the elimination of the excess of colored oxidizing agent. The method is also designed to fill the gap of the available methods for iodide determination between a trace level and a high level of iodide.

Materials and Methods

Materials. De-ionized water was used for the preparation of solutions. Stock solutions of iodide, iodate, and persulfate were prepared by dissolving the appropriate amount of KI (Merck), KIO₃ (Merck), K₂S₂O₈ (Merck), and H₂SO₄ (Merck) respectively in deionized water. A starch solution of 1% was prepared by dissolving 1 g of starch (Sigma) in hot water and added with preservative. All chemicals and solvents used were of analytical reagent grade. Working solutions were prepared by appropriate dilutions of the stock solution.

Instrumentation. A Shimadzu 1601 UV-Vis spectrophotometer and a Bosch Spectronic 20 visible spectrophotometer were used for scanning and absorbance measurements.

Optimization of maximum wavelength. Maximum wavelength was carried out by mixing an iodine solution with a starch solution. Then, the obtained blue solution was scanned using the UV-Vis spectrophotometer from 400-800 nm.

Optimization of the reaction time of oxidizing agents. The optimization was carried out in such a way that only one parameter changed at a time while the other parameters were maintained constant. The experiments were optimized to obtain an effective oxidizing agent and the optimum time for oxidizing iodide to iodine. Two colorless oxidizing agents potential to oxidize iodide to iodine were chosen and optimized with respect to time of oxidation. This investigation was conducted by reacting iodide with each of oxidizing agents, followed by the addition of starch solution to form a blue iodine-starch for detection. When iodate was used as the oxidizing agent, the solution was acidified with sulfuric acid (pH= 1). Absorbance of the formed blue solution was measured under different times, from 1 to 30 minutes for iodate and from 1-120 minutes for persulfate.

Optimization of iodate concentration. The concentration of iodate as an oxidizing agent was optimized to ensure the complete oxidation of iodide to iodine, forming a blue iodine-starch complex. This experiment was conducted by varying the concentration of iodate from 1.10^{-3} M to 9.10^{-3} M.

Optimization of pH Solution. The pH of iodide solution was optimized under the optimum time of oxidation and the optimum concentration of the oxidizing agent by adding sulfuric acid solution to obtain solution in the range pH of 1–3.

Optimization of Iodide Concentration (Linearity of Measurement). In order to determine the linearity of measurement of iodide, a series concentrations of iodide were reacted with the optimum concentration of iodate, under the optimum time of oxidation, and with the optimum pH solution. Then, the blue complex of iodine-starch was detected at 615 nm.

Results and Discussion

The simple characteristic reaction to identify iodide based on the formation of an insoluble blue iodine-starch complex was used for developing quantitative method for iodide determination. This is because the blue iodine-starch complex showed a clear blue solution under a low concentration of iodine as shown in Figure 1.

Optimization of maximum wavelength. It is a basic requirement in spectrophotometry to establish the maximum wavelength of an analyte prior to analytical method development as it provides the best sensitivity. The visible absorption spectrum of the iodine-starch complex scanned from 400 to 800 nm is depicted in Figure 2. The spectrum shows that the maximum absorption band is obtained at 615 nm. Thus, the absorption band at 615 nm was chosen as the basis of measurement.



Figure 1. The Clear Blue Solution of the Iodine-Starch Complex

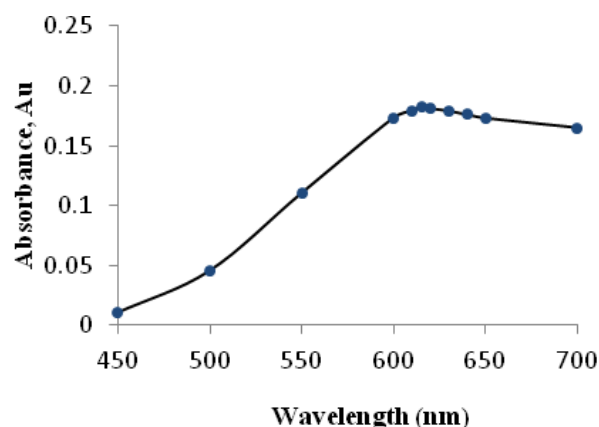


Figure 2. The Effect of Wavelength on the Absorbance of the Iodine-Starch Complex

Optimization of Reaction Time of Oxidizing Agents.

The effect of oxidant types (iodate and persulfate) and time of oxidation were studied separately, as illustrated in Figures 3 and 4. It is clear from Figure 3 that the absorbance of iodine-starch formed (absorbance) increases with increasing time up to 5 minutes. No change in absorbance was observed when the time was increased from 5–9 minutes. This indicated that, under these conditions, the complete oxidation of iodide to iodine forming a blue iodine-starch complex has occurred. At a further increase of reaction time (after 9 minutes), the absorbance decreased due to the instability of the complex, which may be caused of the iodine loss as the aqueous iodine exerts a significant vapor of iodine.

When persulfate was used as an oxidizing agent, the absorbance of iodine-starch complex was increased by increasing the time of reaction with a maximum absorbance of 0.4 AU (at 90 minutes). The absorbance remained constant at reaction times from 90–120 minutes (Figure 4). Oxidation of iodide using persulfate was kinetically slow compared to using iodate. However, the absorbance at the optimum reaction time using persulfate is slightly higher than using iodate (0.40 AU for persulfate and 0.35 AU for iodate). By considering the time of analysis, iodate was chosen for further investigation.

Optimization of Iodate Concentration. The influence of an iodate concentration was examined to optimize the formation of the blue iodine-starch complex. The effect of concentration on absorbance is illustrated in Figure 5. It can be seen that maximum absorbance is reached for an iodate concentration of 0.006 M in which the mol ratio of iodate to iodide, $\text{IO}_3^- : \text{I}^-$ equals 1:3.

However, when the concentration was increased from 0.003 to 0.009 M, the absorbance decreased, which may be due to the iodine loss. The higher concentration of

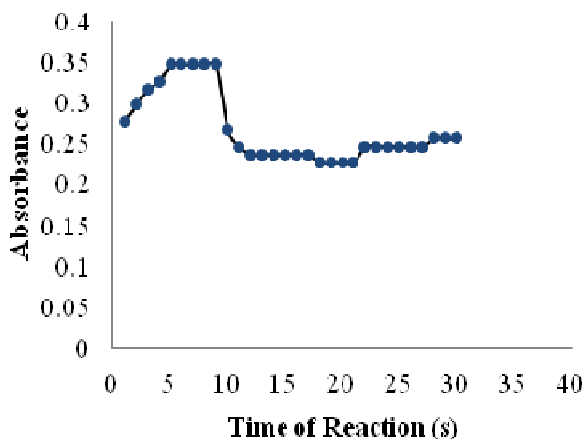


Figure 3. The Effect of Time on the Oxidation of Iodide by Iodate

iodate, the more iodide was oxidized to iodine; thus lessen the iodide presents which bound the volatile iodine to triiodide (I_3^-) complex. Therefore, the further increase of iodate concentration increased the loss of iodine forming blue starch-iodine complex. Based on these results, 0.003M iodate was considered to be the optimal concentration under the relevant experimental condition and used for the subsequent experiments.

Optimization of pH solution. Oxidation of iodide by iodate is performed under acidic conditions; therefore, the acidity of the reaction was optimized in order to achieve maximum oxidation of iodide to iodine. The solution's pH was conducted by adding sulfuric acid to obtain a solution pH of 1–3. It was found that maximum absorbance of starch-iodine was attained at a solution pH of 2 (Figure 6). No further increasing absorbance was observed for a lower pH down to a pH of 1. A solution pH of 1 was selected to ensure adequacy of acid for oxidation.

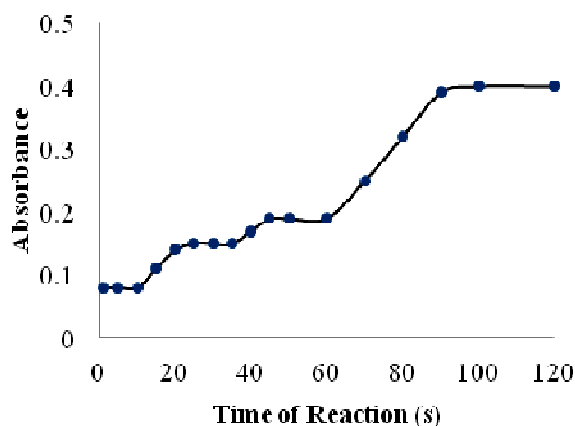


Figure 4. The Effect of Time on the Oxidation of Iodide by Persulfate

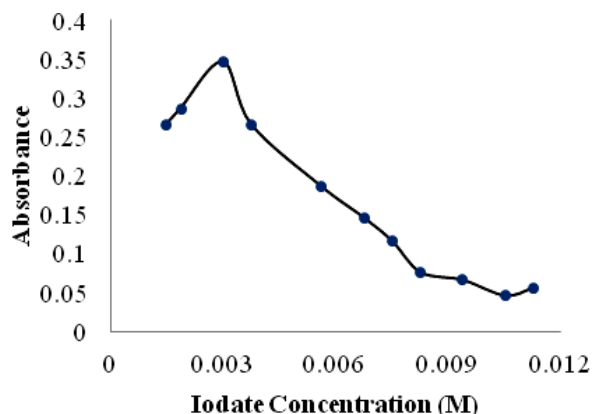


Figure 5. The Effect of Iodate on the Oxidation of Iodide to Iodine

Linearity of the measurement. Under the optimum conditions outlined above (i.e., iodate as an oxidizing agent with a concentration of 0.003 M, a reaction time of 5 minutes, and an acidic condition of H_2SO_4 [pH 1], the method was found to be linear ($y = 0.0116x + 0.2861$, $R^2 = 0.9889$) for concentrations of iodide in the sample from 5–40 mg/L (Figure 7) with an analysis time of 5 minutes. This method can fill the gap of the available spectrophotometric methods that offer measurement of iodide for trace levels [5-11] and a high level [15]. Besides its simplicity, this method employed safe, green, and low-cost reagents, while other methods involved complicated measurement [4-6] or consumed a toxic reagent [4], organic solvent [5], and organic reagents [7-12].

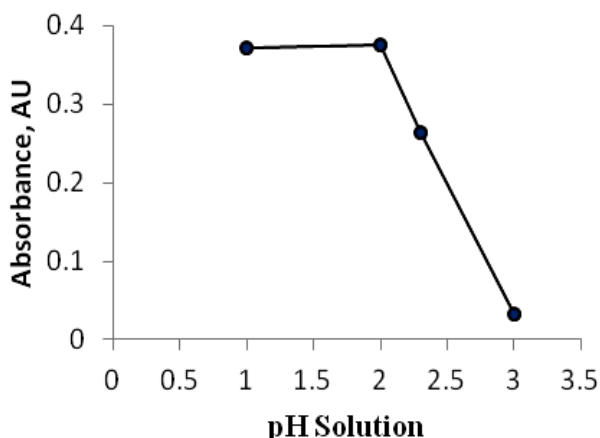


Figure 6. The Effect of pH on the Absorbance of Starch-iodine

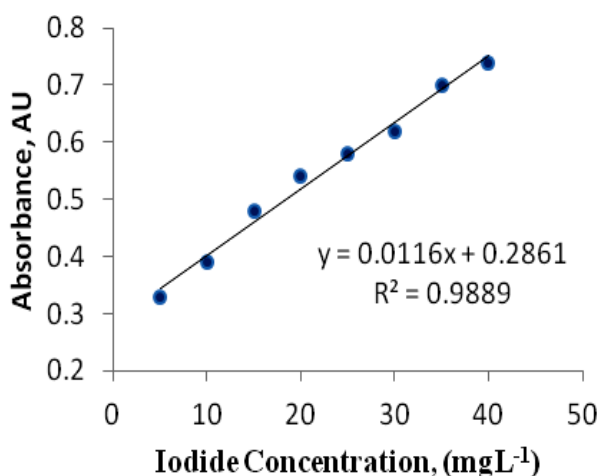


Figure 7. Calibration Curve of Iodide

Conclusions

The spectrophotometric method outlined above allows safe, simple, and sensitive determination of iodide over the range of 5–40 mgL^{-1} . This result suggests that the method mentioned above is prospective to be used for on-line iodide monitoring. However, the method is required to be validated prior to the application to real samples.

Acknowledgments

The authors are grateful to The University of Brawijaya Malang for facilitating research and financial support through “Institution Competitive Research Grant 2012” scheme.

References

- [1] Dunn, J.T., Crutchfield, H.E., Gutekunst, R., Dunn, A.D. 1993. Methods for Measuring Iodine in Urine, International Council of Iodine Deficiency Disorders. UNICEF, WHO, Netherland, pp.7-16.
- [2] Zimmermann, M.B. 2009. Iodine deficiency. *Endocr. Rev.* 30(4): 376-408.
- [3] Silva, R.S.G.N.P., de Oliveira, A.F., Neves, E.A. 1998. Spectrophotometric determination of iodate in table salt. *J. Braz. Chem. Soc.* 9(2): 101-118.
- [4] Greenberg, A.E., Clesceri, L.S., Eaton, A.D. 1992. Standard Methods for the Examination of Water and Waste Water, 18th ed. Washington D.C., pp. 4.72-4.74.
- [5] Koh, T., Ono, M. Makino, I. 1988. Spectrophotometric determination of iodide at the 10^{-6} mol/L level by solvent extraction with methylene blue. *Analyst.* 113: 945-948.
- [6] Shishehbore, M.R., Sheibani, A., Jokar, R. 2010. Kinetic spectrophotometric of trace amount of iodide in food samples. *Anal. Sci.* 26: 497-500.
- [7] Gurkan, R., Bicer, N., Ozkan, M.H., Akcay, M. 2004. Determination of trace amount of iodide by an inhibition kinetic spectrophotometric method, *Turk. J. Chem.* 28: 181-191.
- [8] El-Ries, M.A., Khaled, E., Zidane, F.I., Ibrahim, S.A., Abd-Elmonem, M.S. 2012. Catalytic spectrophotometric determination of iodide in pharmaceutical preparations and edible salt. *Drug Testing and Analysis.* 4(2): 129-135.
- [9] Kamavisdar, A., Patel, R.M. 2002. Flow injection spectrophotometric determination of iodide in environmental samples. *Microchimica Acta.* 140(2): 119-124.
- [10] George, M., Balasubramanian, N., Nagaraja, K.S. 2008. Spectrophotometric determination of iodine species in table salt and pharmaceutical preparations. *Chem. Pharm. Bull.* 56(7): 888-893.
- [11] Tesfaldet, Z.O., van Staden, J.F., Stefan, R.I. 2004. Sequential injection spectrophotometric determina-

tion of trace amount of iodide by its catalytic effect on the 4,4'-methylenebis (N,N'-dimethylaniline)-chloramine-T. *Talanta*. 64: 1213-1219.

- [12] Drozd, A.V., Tishakova, T.S. 2011. Spectrophotometric determination of trace amounts of iodide ions in form of ionic associate with brilliant green using electrochemical oxidation. *Cent. Eur. J. Chem. (CEJC)*. 9(3): 432-436.
- [13] Badami, B.V. 2008. Concept of green chemistry. *Resonance*. November: pp. 1041-1048.

[14] Choengchan, N., Uraisin, K., Choden, K., Veerasai, W., Grudpan, K., Nacapricha, D. 2002. Simple flow injection system for colorimetric determination of iodate in iodine salt. *Talanta*. 58: 1195-1201.

[15] D. Nacapricha, K. Uraisin, N. Ratanawimarnwong, K. Grudpan. 2004. Simple and selective method for determination of iodide in pharmaceutical products by flow injection analysis using the iodine-starch reaction. *Anal. Bioanal. Chem.* 378: 816-821.