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Sequential flow injection determination of iodate and periodate with spectrophotometric detection

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Abstract

A flow injection (FI) system is described for the sequential determination of periodate and iodate based on their reaction with iodide at pH 3.5. Two sample plugs were injected into the same carrier stream sequentially. One injection is for the iodate determination and the other for the sum of iodate and periodate determination. For iodate determination, molybdate solution buffered at pH of 3.5 was used for selective masking of periodate. The influences of reagent concentrations were studied by a univariable method and the influence of FI manifolds was studied using univariable and simplex method. Periodate and iodate can be determined in the range of 0.050–5.0 and 0.050–10 μg/ml, respectively. The 3σ limit of detection was 0.030 and 0.050 μg/ml for periodate and iodate, respectively. The proposed method has been applied for the sequential determinations of periodate and iodate in water samples.

Keywords: Iodate; Periodate; Sequential analysis; Flow injection; Spectrophotometry

1. Introduction

Flow injection (FI) has been increasingly used in various fields, owing to its high sample throughout, cost, effective performance and flexibility. A recent trend has been the design and optimization of measuring system for the sequential determination of multicomponents [1–6]. Periodate and iodate is important oxidants which can oxidize many organic and inorganic compounds at trace levels [7–9]. Determination of these compounds is important in organic chemistry, biology and life science. Several methods has been reported for the determination of periodate and iodate in mixtures. These include spectrophotometric [10–14], chromatography [15] and capillary electrophoresis [16,17]. Some of these methods have high limit of detection [10], suffer from many interferences [11] and/or have low dynamic range [12–14]. According to our knowledge, only a FI method have been reported for the determination of iodate and periodate in the presence of each other was reported [18], but the method needs two separate and different detectors. This paper describes a spectrophotometric FI method for the sequential determination of iodate and periodate. The method is based on the reaction of periodate and

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iodate with iodide to produce iodine ($\lambda_{max} = 352$ nm). Molybdate ions can form a stable complex with periodate and mask of periodate in the reaction, therefore, the iodate can be determined without any interference of periodate. In the absence of molybdate ions sum of periodate and iodate can be determined.

2. Experimental

2.1. Reagents and chemicals

Doubly distilled water and analytical reagent grade chemicals were used.

Stock solutions of periodate (1000 μg/ml) and iodate (1000 μg/ml) were prepared separately by dissolving 0.1120 g of sodium periodate (Merck) and 0.1229 g potassium iodate (Merck) in 100-ml volumetric flask.

A 0.100 M iodide solution was prepared by dissolving 1.6768 g potassium iodide (Merck) in water and diluting to the mark in a 100-ml volumetric flask.

A 0.0030 M molybdate solution was prepared by dissolving 0.0726 g of sodium molybdate (Merck) in a 100-ml volumetric flask.

Acetate buffer solution of pH 3.5 was prepared from acetic acid and sodium hydroxide.

2.2. Apparatus

The FI system with optimum condition is shown in Fig. 1. Two plug of sample solution was injected separately via a six port Rheodyn sample injection valve. A 12-channel peristaltic pump (Desaga) was used for delivering the carrier and solutions. A selection valve was used for selection each of stream R_1 or R_2. Silicon rubber tubes (1.0 mm i.d.) were used as flow lines. Teflon tubing (1.0 mm i.d.) was used for mixing coil. Data acquisition of FI peaks was obtained using a spectrophotometer, Shimadzu, Model 6AV, equipped with a flow cell (20 μl volume) whose output was connected to a computer and then to a recorder (Shimadzu, Model C R4AX). A thermostat water bath (Gallen Kamp, BGL) was used at given temperature of interest.

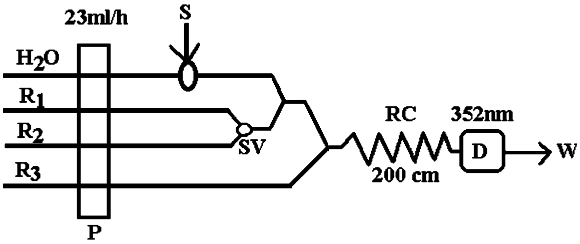

Fig. 1. FI system at optimum conditions. P, peristaltic pump; S, sample injection valve; SV, selection valve; RC, reaction coil; D, detector; W, waste; R_1, molybdate solution 0.003 M buffered at pH 3.5; R_2, buffer solution pH of 3.5 and R_3, iodide solution, 0.100 M.

2.3. Procedure

Two sample plugs (300 μl) were injected into the carrier (water) sequentially for separate spectrophotometric measurements. One was used for iodate determination and the other for the sum of periodate and iodate determination. In the first injection (iodate determination), selection valve allows R_1 stream passes and the sample plug was mixed with R_1 stream containing molybdate solution at pH 3.5 and R_3 stream containing iodide solution. After masking of periodate by molybdate ions, the absorbance of produced triiodide (I_3^-) was recorded at 352 nm (the maximum absorption wavelength of iodine). In the second injection, R_2 stream passes via selection valve and the sample plug was mixed with R_2 stream (buffer without molybdate) and then with R_3 stream (iodide solution) and the absorbance of produced iodine was recorded at 352 nm. Two peaks are observed for the two injections (Fig. 2). The first peaks corresponds to the iodate (A1) and the second peak to the sum of iodate and periodate (A_2). The peak height (absorbance) of periodate can be calculated by subtraction ($A_2 - A_1$). Adjusting the time interval of the injections can be controlled the peak separation.

3. Results and discussion

Periodate and iodate react with iodide in acidic media to produce triiodide according to the

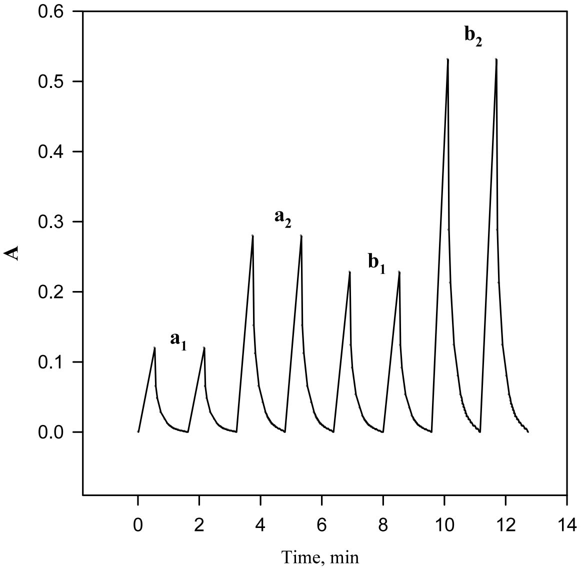

Fig. 2. Typical absorbance peaks of sequential injections of (a) 1.00 μg/ml IO_3^- and IO_4^- and (b) 2.00 μg/ml IO_3^- and IO_4^-. Subscripts 1 and 2 denote injection in the presence and absence of molybdate, respectively. Conditions, pH of 3.5; iodide, 0.100 M; molybdate, 0.003 M; reaction coil length, 200 cm; injection volume, 300 μl; pump flow rate, 23 ml/h at 30 °C.

following reactions:

$$IO_4^- + 11I^- + 8H^+ \rightleftarrows 4I_3^- + 4H_2O \qquad (1)$$

$$IO_3^- + 8^- + 6H + \rightleftarrows 3I_3^- + 3H_2O \qquad (2)$$

The reactions could be monitored spectrophotometrically by measuring the absorbance of the solution at 352 nm, which is proportional to the triiodide concentration.

It was reported that the stable heteropoly complex $[IMo_6O_{24}]^{5-}$ is formed at low concentration of Mo(VI) and periodate at pH range of 3.0–4.5 [16]. The complex formation reaction is complete and very rapid even at room temperature. On the other hand, no complex formation of iodate with Mo(VI) was occurred [16]. Because of this difference, iodate and periodate can be determined sequentially. In the absence of molybdate ions the iodine produced in the reaction (1) and (2) is proportional to the concentration of iodate and periodate with a factors of 3 and 4, respectively. When molybdate ions are present reaction (1) could not be occurred and reaction (2) occurred without any considerable change. Thus, the iodine produced is proportional to the iodate concentration only.

3.1. Study and optimization of reagents concentration

For the first, the influence of reagent concentration on the sensitivity (peak height) was studied with 1.0 μg/ml of periodate and iodate, reaction coil length of 200 cm, sample volume of 200 μl, pump flow rate of 20 ml/h for each channel and temperature of 30 °C. Optimization was carried out by univariable method.

The influence of pH was studied over the range of 2.0–4.5 (Fig. 3). The results show that with increasing pH, the peak height (absorbance) due to iodate and periodate decrease. On the other hand, at low pH values, the complex formation between periodate and Mo(VI) is not completed. At pH 3.5 the complex formation is complete and the periodate peak is disappeared. Therefore, an acetate buffer (pH of 3.5, 0.10 M) was selected for further studies.

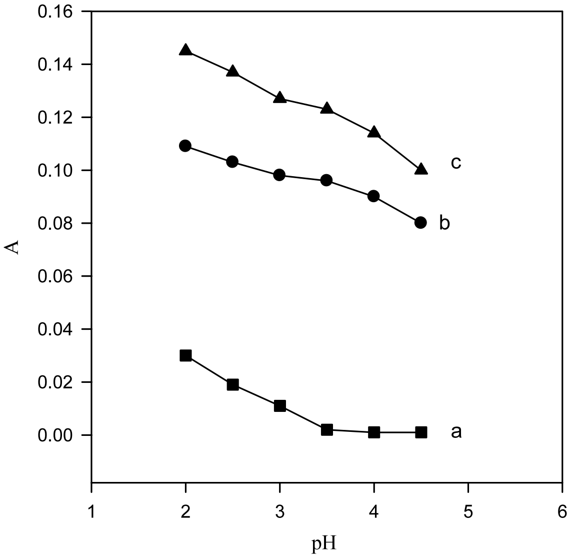

Fig. 3. Influence of pH on the peak height. (a) 1.00 μg/ml IO_4^- in the presence of Mo(VI), (b) 1.00 μg/ml IO_3^- and (c) 1.00 μg/ml IO_4^- in the absence of Mo(VI). Conditions, iodide, 0.060 M; molybdate, 0.002 M; reaction coil length, 200 cm; injection volume, 200 μl; pump flow rate, 20 ml/h at 30 °C.

The effect of iodide concentration on the sensitivity was studied in the range of 0.010–0.120 M. The results are shown in Fig. 4. The results show that with increasing iodide concentration up to 0.080 M, the peak heights increase and then level off. Thus 0.10 M iodide concentration was selected.

The influence of molybdate concentration on the peak height from iodate and periodate was studied in the range of 5.0×10^{-4}–0.004 M. Fig. 5 shows that the absorbance due to periodate decrease to zero when the concentration of Mo(VI) reaches to 0.002 M, while the absorbance due to iodate did not change. Thus, molybdate concentration of 0.0030 M was used.

The effect of temperature on the sensitivity was studied in the range of 20–45 °C. The results showed that increasing temperature above 25 °C did not cause a considerable increase in the peak heights. This means that the reactions go to the completion at room temperature. Therefore, temperature of 30 °C was used for further experiments.

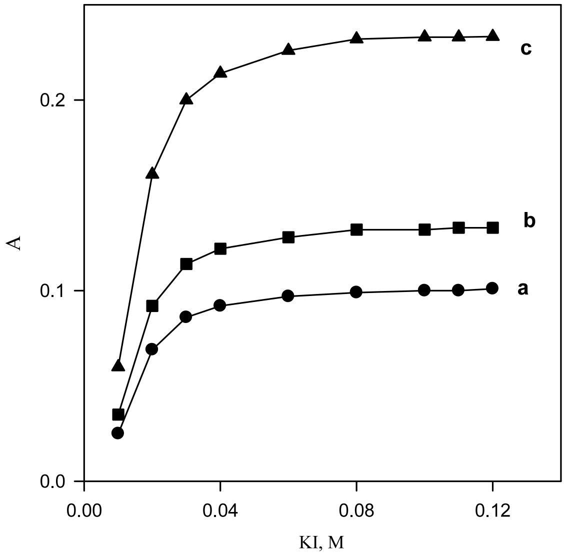

Fig. 4. Effect of iodide concentration on the peak height. (a) 1.00 μg/ml IO_3^-, (b) 1.00 μg/ml IO_4^- and (c) 1.00 μg/ml IO_4^- and IO_3^-. Conditions, pH of 3.5; molybdate, 0.002 M; reaction coil length, 200 cm; injection volume, 200 μl; pump flow rate, 20 ml/h at 30 °C.

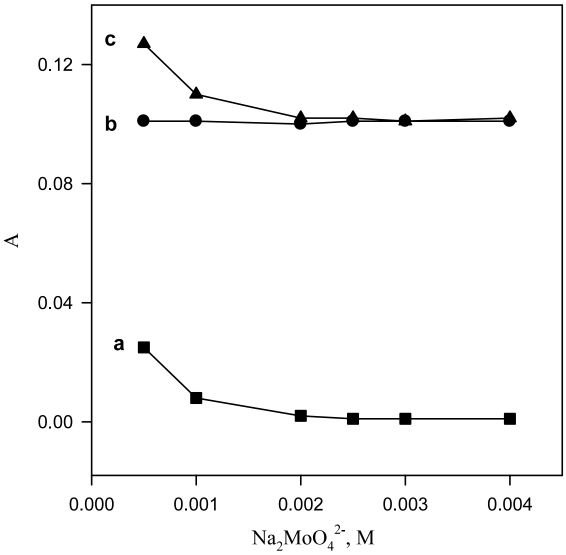

Fig. 5. Effect of molybdate concentration on the peak height. (a) 1.00 μg/ml IO_4^-, (b) 1.00 μg/ml IO_3^- and (c) 1.00 μg/ml IO_4^- and IO_3^-. pH of 3.5; iodide, 0.100 M; conditions: reaction coil length, 200 cm; injection volume, 200 μl; pump flow rate, 20 ml/h at 30 °C.

3.2. Optimization of manifold parameters

For this investigation, the optimized reagent concentrations, pH, and temperature were used with 1.00 μg/ml iodate and periodate.

The effect of reaction coil length was tested over the range of 50–250 cm. The results showed that the sensitivity increases by increasing reaction coil length up to 150 cm and above it is nearly constant. It is due to this fact that by increasing length of the reaction coil the residence time of sample increases. Thus a reaction coil length of 150 cm was selected.

The influence of pump flow rate on the sensitivity was studied over the range of 17–26 ml/h for each channel. The results showed that higher sensitivity obtained at low flow rates. On the other hand dispersion increases at low flow rate and the peak broadening were occurred. Because of this behavior, a flow rate of 21 ml/h was adopted.

The effect of sample volume on the sensitivity was investigated over the range of 200–320 μl with the optimized conditions. The results showed that that by increasing sample volume the sensitivity for both iodate and periodate increase, but peak broadening was occurred for higher volume of 250 µl. Therefore, a 250 µl sample volume was adopted.

The manifold variables also checked with a simplex method. After ten experiments, we found the following results for optimum conditions of manifold variables: flow rate of 23 ml/h; reaction coil length, 200 cm; and sample injection volume of 300 µl. Therefore, we used these optimum parameters for further study.

4. Analytical parameters

Under the optimized conditions as described in Fig. 1, mixed (1:1) standard solutions of periodate and iodate sequentially in the presence and absence of Mo(VI) was injected, respectively. The results showed that the calibration graph for periodate is linear over the range of 0.050–5.0 µg/ml, with a regression equation of $A = 0.011 + 0.144C_{IO_4^-}$ ($r = 0.9997$, $n = 8$) and that for iodate in the concentration range of 0.05–10.0 µg/ml with a regression equation of $A = 0.002 + 0.117C_{IO_3^-}$ ($r = 0.9999$, $n = 13$). It should be noted that sum of iodate and periodate not be exceed than 10.0 µg/ml. Typical flow signals are shown in Fig. 6.

The relative standard deviation (R.S.D.) for ten replicated measurements of 0.50 and 2.00 µg/ml iodate are 0.80 and 0.65%, respectively, and for ten replicate measurements of 0.50 and 2.00 µg/ml periodate are 0.92 and 0.81%, respectively.

The detection limit (3σ) 0.050 µg/ml and 0.040 µg/ml for iodate and periodate, respectively.

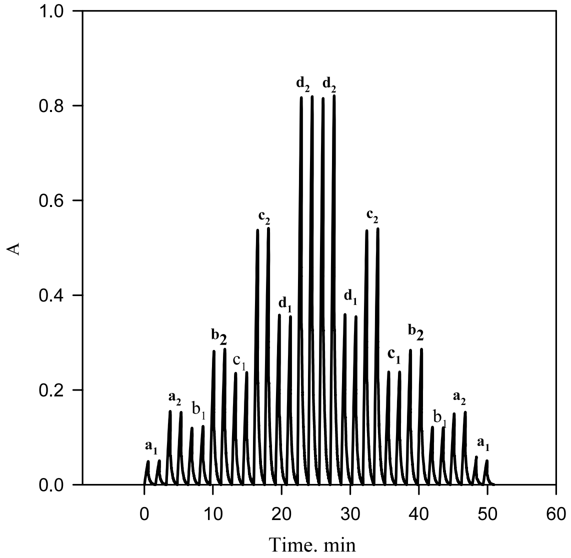

Fig. 6. Flow signals for the calibration curve obtained by sequential injection of mixture solutions (1:1) of IO_3^- and IO_4^-. (a) 0.40, (b) 1.00, (c) 2.00 and (d) 3.00 µg/ml at the optimum chemical and manifold conditions. Subscripts 1 and 2 denote injection in the presence and absence of molybdate, respectively.

5. Selectivity

In order to assess the possible analytical application of the described method, the effect of various substances presented in real samples on the sequential determination of iodate and periodate was investigated. Synthetic mixture of solution containing 1.0 µg/ml of iodate, periodate and various excess amounts of diverse ions were analyzed. The tolerance limit was defined as the concentration of added ions causing less than a ± 3% relative error. The results are given in Table 1. Many ions did not interfere in 1000-fold excess than periodate and iodate. NO_2^- caused positive error because of reaction with iodide and produce triiodide ion. Sulfide, sulfite and WO_4^{2-} caused negative interference because of react with iodate and/or periodate.

Table 1
Interference of foreign ions on the determination of 1.0 µg/ml iodate and periodate

Ion	Tolerance limit (W_{ion}/$W_{Iodate\ or\ periodate}$)
Na^+, K^+, Li^+, NH_4^+, Al^{3+}, F^-, CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$, NO_3^-, ClO_3^-, ClO_4^-	1000[a]
Sr^{2+}, Ca^{2+}, Zn^{2+}, Cl^-	800
Mn^{2+}, Pb^{2+}, Ba^{2+}, Fe^{2+}, Fe^{3+}, Citrate, BrO_3^-	100
SCN^-, Br^-	50
S^{2-}, SO_3^{2-}, NO_2^-	1

[a] Maximum limit concentration tested.

Table 2
Determination of iodate and periodate in synthetic mixtures

IO_3^- added (μg/ml)	IO_4^- added (μg/ml)	IO_3^- found (μg/ml)	IO_4^- found (μg/ml)	Recovery (%)		R.S.D. ($n=5$)	
				IO_3^-	IO_4^-	IO_3^-	IO_4^-
3.00	0.30	2.98	0.31	99	103	0.90	1.85
0.30	3.00	0.32	3.03	105	101	1.40	0.95
1.00	0.50	1.02	0.51	102	102	1.20	1.50
0.50	1.00	0.48	0.98	96	98	1.10	1.00

Table 3
Determination of iodate and periodate in water samples

Sample	IO_3^- (μg/ml)		IO_4^- (μg/ml)		Recovery (%)		R.S.D ($n=5$)	
	Added	Found	Added	Found	IO_3^-	IO_4^-	IO_3^-	IO_4^-
River water	0.50	0.51	0.50	0.48	102	96	1.05	1.70
River water	1.00	1.04	4.00	4.10	104	103	0.98	1.10
Drinking water	6.00	5.93	2.00	2.05	99	103	0.68	1.10
Drinking water	3.00	3.10	5.00	5.08	103	102	0.85	1.00

6. Analysis of synthetic and real samples

Mixed standard solutions of different concentration ratio of iodate and periodate were measured under optimized conditions. Recoveries of iodate and periodate for these solutions are given in Table 2. The results show that good recoveries of iodate and periodate in mixture can be obtained, even at different ratios. In addition, the proposed method was also applied to the determination of iodate and periodate in drinking and river waters. The results are shown in Table 3. The recoveries show that there is no serious interference in such samples.

7. Conclusion

This method described a simple, precise, sensitive and selective method for the sequential determination of the iodate and periodate in water samples at various concentration ratios with a sampling rate of 20±5 sample/h. There is no serious interference in the determination.

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