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Spectrophotometric determination of periodate and iodate by a differential kinetic method

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Abstract

A rapid, simple and sensitive differential kinetic method is presented for the determinations of periodate and iodate ions. The method is based on their reaction with iodide in the presence of methylene blue. The reactions can be monitored spectrophotometrically by measuring the decrease in absorbance at 665 nm. Two sets of conditions were established that in one set of conditions only periodate reacted with iodide but in the other set both the ions reacted with iodide during the first 180 s after initiation of the reaction. The data were evaluated by proportional equations. The method allowed the determination of periodate and iodate at concentrations between 0.1 and 1.0 and 0.1 and 1.3 $\mu g\ ml^{-1}$, respectively. The method was applied to the determination of periodate and iodate in tap water and spring water with satisfactory results. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Differential kinetic; Periodate; Iodate; Spectrophotometry; Iodide

1. Introduction

Differences in kinetic behavior have been used extensively for the simultaneous determination of two or more components in mixtures. Many differential kinetic methods have been proposed for the analysis of mixtures of closely related species without prior separation. Proportional-equation method is a mathematical method of wide use in differential kinetic methods for the resolution of closely related species. This method depends on changing the ratio of two rate constants by vary-

ing the reaction medium or the conditions [1].

Different methods have been reported for the determination of periodate, such as photometric titration [2], thin layer chromatography [3], chemiluminescence [4], fluorimetry [5] and spectrophotometry [6–9]. Several spectrophotometric methods have been reported for the determination of periodate and iodate [10–14]. El-Shahawi [15] used the ion-associate of periodate with amiloride hydrochloride for simultaneous spectrophotometric determination of periodate and iodate by liquid-liquid extraction. Iodate has been determined after prior oxidation to periodate with potassium peroxodisulphate.

In this paper we wish to describe a rapid, simple, precise and accurate differential kinetic

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method for spectrophotometric determination of periodate and iodate ions in mixture. The method is based on the reaction of periodate and iodate with iodide in acidic media at two different conditions. The reaction between liberated iodine and methylene blue is used as indicator reaction.

2. Experimental

2.1. Apparatus

A Shimadzu model UV-265 UV-visible recording spectrophotometer with 1-cm glass cells was used for absorbance measurements.

2.2. Reagents

All of the chemicals were of analytical grade and triply distilled water was used throughout. A 2.14×10^{-3} M methylene blue solution was prepared by dissolving 0.1750 g methylene blue (Merck) in water and diluting to the mark in a 250 ml volumetric flask. Iodide solution (1.6×10^{-2} M) was prepared by dissolving 0.5906 g sodium iodide (Merck) in water and diluting to the mark in a 250 ml volumetric flask. Standard solution (1000 mg l^{-1}) of periodate was prepared by dissolving 0.2301 g sodium periodate (Merck) in water and diluting to the mark in a 250 ml volumetric flask. Standard solution (1000 mg l^{-1}) of iodate was prepared by dissolving 0.3100 g sodium iodate (Merck) in water and diluting to the mark in a 250 ml volumetric flask.

2.3. Determination of periodate and iodate in mixture

Two kinetic runs are needed for each sample.

2.3.1. Procedure 1

An aliquot solution containing 1.0–35 µg of periodate and 1.0–13 µg of iodate was transferred in a 10 ml volumetric flask containing 1.0 ml of 1.0×10^{-4} M sulfuric acid and 1 ml of 2.19×10^{-4} M methylene blue solution. The solution was diluted to ca. 9 ml with triply distilled water and then 1.0 ml of 3.2×10^{-2} M iodide solution

was added. The solution was diluted to the mark with water. The stopwatch was started just after the addition of iodide. A portion of the solution was transferred in to a glass cell to measure the decrease in absorbance at 665 nm during 20–180 s after initiation of the reaction. The dependence of the absorbance change during 20–180 s on the concentration of periodate was found to conform to the following equation:

$$\Delta A_1 = a_1 + b_1 C_{\text{periodate}} \qquad (1)$$

2.3.2. Procedure 2

A aliquot solution containing 1.0–10 µg of periodate and 1.0–13 µg of iodate was transferred in to a 10 ml volumetric flask containing 1.5 ml of 1.0×10^{-2} M sulfuric acid and 1 ml of 2.19×10^{-4} M methylene blue solution. The solution was diluted to ca 9 ml with triply distilled water and then 1 ml of 1.6×10^{-2} M iodide solutions was added. The solution was diluted to the mark with water. The stopwatch was started just after the addition of iodide solution. A portion of the solution was transferred into a glass cell to measure the decrease in absorbance at 665 nm during 20–180 s on the concentration of periodate and iodate was found to conform to the following equation:

$$\Delta A_2 = a_2 + b_2 C_{\text{periodate}} + b'_2 C_{\text{iodate}} \qquad (2)$$

3. Results and discussion

3.1. Preliminary investigations

Periodate and iodate react with iodide in acidic media to liberate iodine:

$$11I^- + IO_4^- + 8H^+ \leftrightarrows 4I_3^- + 4H_2O$$

$$8I^- + IO_3^- + 6H^+ \leftrightarrows 3I_3^- + 3H_2O$$
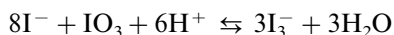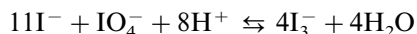
The produced triiodide forms an ion pair with methylene blue and decolourize it. Therefore the reactions could be monitored spectrophotometrically by measuring the decrease in the absorbance of the solution at 665 nm.

It was observed that the reaction of iodate with iodide showed an induction period that was de-

pendent on acid concentration. This induction period increased by decreasing acid concentration. But the reaction of periodate initiated immediately after mixing with iodide in acidic media. Because of this difference, periodate and iodate would be determined by choosing suitable conditions. Two simultaneous equations were solved to give the periodate and iodate concentrations.

3.2. Effect of variables

The effect of reaction variables was studied separately for periodate and iodate and their opti-
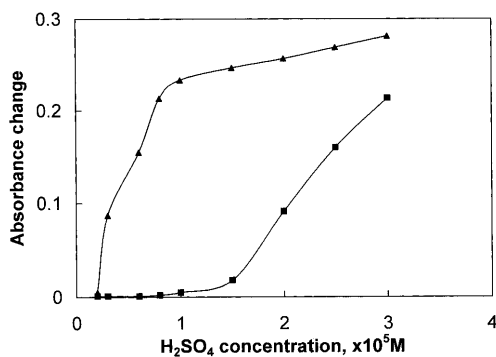

Fig. 1. Effect of sulfuric acid concentration in the range of 1.0×10^{-6}–3.1×10^{-5} M on periodate (▲) and iodate (■) reaction rate. Conditions: periodate, 1.00 μg ml^{-1}; iodate, 80 μg ml^{-1}; I$^-$, 3.2×10^{-2} M; and methylene blue, 2.19×10^{-4} M.
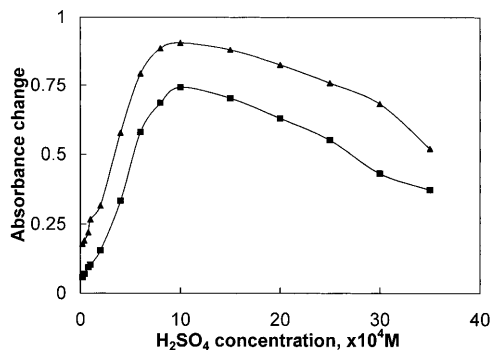

Fig. 2. Effect of sulfuric acid concentration in the range of 2×10^{-5}–3.5×10^{-3} M on periodate (▲) and iodate (■) reaction rate. Conditions: periodate, 1.0 μg ml^{-1}; iodate, 1.0 μg ml^{-1}; I$^-$, 1.60×10^{-2} M; and methylene blue, 2.14×10^{-4} M.

mum values were selected. Two sets of conditions must be fulfilled. In the first (Section 2.3.1) only periodate reacted and in the second (Section 2.3.2) both the iodate and periodate reacted.

3.2.1. Effect of sulfuric acid concentration

The reactions take place in acidic media. The effect of sulfuric acid concentration on the reaction of periodate and iodate was studied separately. The results are given in Figs. 1 and 2. As Fig. 1 shows, in dilute acidic media only periodate reacted with iodide and iodate did not react even when its concentration was 80-fold excess over periodate. The absorbance change for periodate reaction rapidly increased by increasing sulfuric acid concentration up to 1.0×10^{-5} M and slowly increased at higher concentrations. Therefore, a final concentration of 1.0×10^{-5} M sulfuric acid was optimum for Section 2.3.1. Fig. 2 shows the effect of sulfuric acid concentration on both the reactions in the range of 2×10^{-5}–3.5×10^{-3} M. As Fig. 2 shows the absorbance change for both the reactions increased by increasing sulfuric acid concentration up to 1.5×10^{-3} M and decreased at higher concentrations. Therefore, a final concentration of 1.5×10^{-3} M sulfuric acid was optimum for Section 2.3.2.

3.2.2. Effect of iodide concentration

Effect of iodide concentration on both the reactions at 1×10^{-5} and 1.5×10^{-5} M sulfuric acid was studied separately. The results are shown in Figs. 3 and 4. As Fig. 3 shows, at 1×10^{-5} M sulfuric acid concentration, the absorbance change for periodate reaction increased with increasing iodide concentration up to 3.15×10^{-3} M and remained nearly constant at higher concentrations. But at the same concentration of acid iodate did not react with iodide up to 6.3×10^{-3} M even when its concentration was 80-fold excess over periodate.

Therefore, 3.20×10^{-3} M iodide concentration was selected as optimum concentration for Section 2.3.1. As Fig. 2 shows at 1.5×10^{-3} M sulfuric acid the absorbance change for both the reactions increased up to 1.4×10^{-3} M and remained nearly constant at higher concentrations. Therefore, a final concentration of 1.6×10^{-3} M
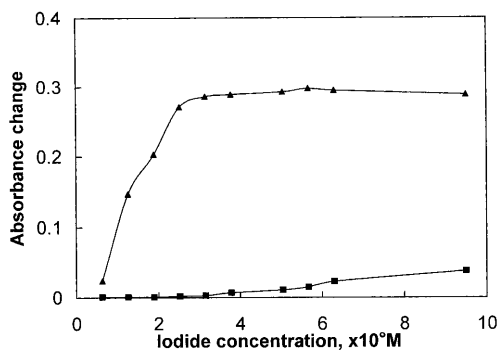
Fig. 3. Effect of iodide concentration in the range of 5×10^{-4}–9.5×10^{-3} M on periodate (▲) and iodate (■) reaction rate. Conditions: periodate, 1.0 µg ml^{-1}; iodate, 80 µg ml^{-1}; H$_2$SO$_4$, 1.0×10^{-5} M; and methylene blue, 2.19×10^{-4} M.
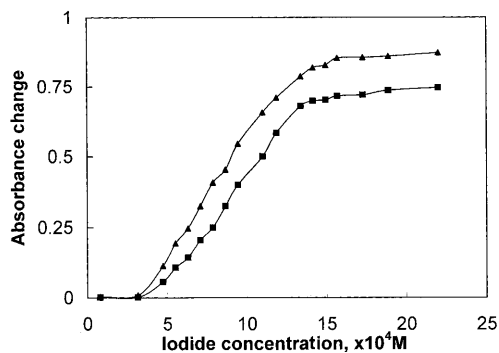

Fig. 4. Effect of iodide concentration in the range of 7.87×10^{-5}–2.20×10^{-3} M on periodate (▲) and iodate (■) reaction rate. Conditions: periodate, 1.0 µg ml^{-1}; iodate, 1.0 µg ml^{-1}; H$_2$SO$_4$, 1.5×10^{-3} M; and methylene blue, 2.19×10^{-4} M.

iodide was selected as optimum concentration for Section 2.3.2.

3.2.3. Effect of methylene blue concentration

The effect methylene blue concentration on both the reactions was studied in the range of 3.75×10^{-6}–3.0×10^{-5} M. As Fig. 5 shows the absorbance change for both the reactions increased by increasing methylene blue concentration up to 2.25×10^{-5} M and remained nearly constant at higher concentrations. A concentration of 2.19×10^{-5} M methylene blue was chosen for both the procedures.

3.2.4. Effect of temperature

Effect of temperature on both the reactions was studied in the range of 25–55°C. The results are given in Fig. 6. Increasing temperature had no effect on both the reactions in the range of 25–35°C. But the absorbance change for both the reactions decreased at higher temperatures probably due to the instability of the product of methylene blue-iodine reaction. The same temperature, 25°C, was chosen for both the procedures.

3.2.5. Effect of iodate on the reaction of periodate under the conditions of procedure 1

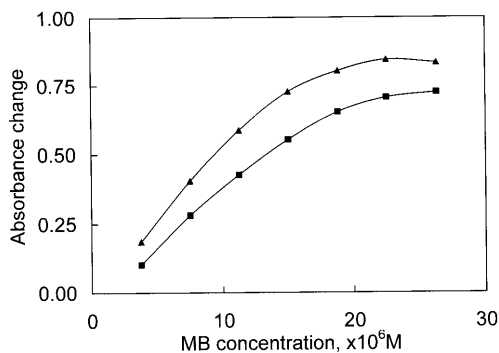The effect of iodate concentration of the reaction of 1 µg ml^{-1} periodate under the conditions

Fig. 5. Effect of methylene blue concentration on periodate (▲) and iodate (■) reaction rate. Conditions: periodate, 1.0 µg ml^{-1}; iodate, 1.0 µg ml^{-1}; H$_2$SO$_4$, 1.5×10^{-3} M; and I$^-$, 1.6×10^{-2} M.
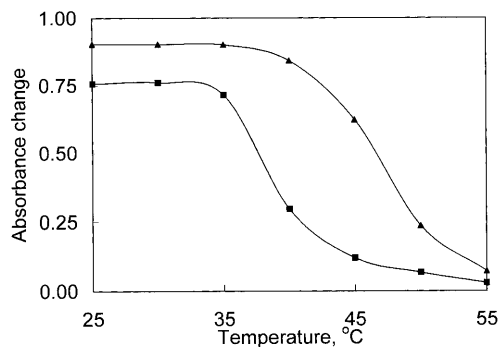

Fig. 6. Effect of temperature on periodate (▲) and iodate (■) reaction rate. Conditions: periodate, 1.0 µg ml^{-1}; iodate, 1.0 µg ml^{-1}; H$_2$SO$_4$, 1.5×10^{-3} M; I$^-$, 1.6×10^{-2} M; and methylene blue, 2.19×10^{-4} M.
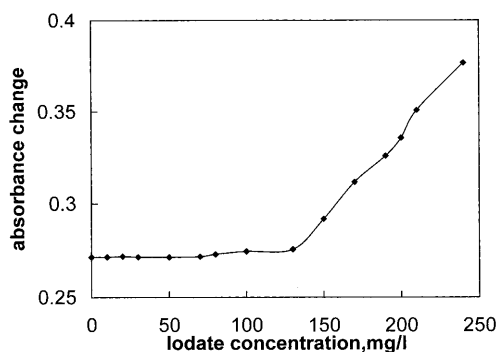
Fig. 7. Effect of iodate on the reaction rate of periodate. Under the conditions of procedure 1. Conditions: periodate, 1.0 µg ml^{-1}; H$_2$SO$_4$, 1.5×10^{-3} M; I$^-$, 3.2×10^{-2} M; and methylene blue, 2.19×10^{-4} M.

of Section 2.3.1 was studied in the range of 0.0–240 µg ml^{-1}. The results are given in Fig. 7. As Fig. 7 shows iodate had no effect on the reaction of 1 µg ml^{-1} periodate up to 100 µg ml^{-1} and caused a positive interference at higher concentrations.

3.3. Analytical parameters

Under the optimum conditions used in each procedure the calibration graphs were obtained. The calibration graphs were constructed by plotting absorbance change values during 20–180 s after initiation of reaction as a function of analyte concentration. The calibration graphs for the individual determinations were linear in the range of 0.10–3.5 µg ml^{-1} for periodate under the conditions of the Section 2.3.1 and 0.10–1.0 µg ml^{-1} for periodate and 0.1–1.3 µg ml^{-1} for iodate under the conditions of Section 2.3.2. Iodate had no contribution in absorbance change under the conditions of Section 2.3.1. The results are sum-marized in Table 1. The absence of synergistic effects ensured that the absorbance changes for a mixture of two analytes under the conditions of Section 2.3.2 were the sum of the absorbance changes obtained for each individual analyte. Therefore the following equations can be used for the determination of periodate and iodate in mixture.

$$\Delta A_1 = -0.0335 + 0.3436 C_{\text{periodate}} \tag{3}$$

$$\Delta A_2 = -0.1651 + 1.0148 C_{\text{periodate}} + 0.8196 C_{\text{iodate}} \tag{4}$$

Where ΔA_1 and ΔA_2 are the absorbance changes for Sections 2.3.1 and 2.3.2, respectively, and the concentrations are in µg ml^{-1}.

To evaluate the precision and the detection limit, a series of independent standard samples was used. The relative standard deviation for five replicate measurements of 0.5 µg ml^{-1} of periodate and iodate was 1.30 and 1.13% in a 1:2 mixture.

The limit of detection which can be calculated on the basis of $Y_{\text{LOD}} = Y_{\text{B}} + 3S_{\text{B}}$ [16], in which Y_{LOD}, Y_{B} and S_{B} are signal of limit of detection, signal of blank and, standard deviation of blank, signal of blank and, standard deviation of blank, respectively was 0.090 µg ml^{-1} for periodate under the conditions of Section 2.3.1 and 0.05 and 0.07 µg ml^{-1} for periodate and iodate, respectively, under the conditions of Section 2.3.2.

3.4. Selectivity

To study the selectivity of the proposed method, the effect of various ions on the determination of a mixture of 0.7 µg ml^{-1} periodate and 0.7 µg ml^{-1} iodate was tested under the optimum conditions. The results are given in Table 2. The

Table 1
Characteristics of the calibration graphs for the determination of periodate and iodate

Ion	Procedure	Range (µg ml^{-1})	Slope (ml µg^{-1})	Intercept	Correlation coefficient ($n = 11$)
IO$_4^-$	1	0.1–3.5	0.3436	−0.0335	0.9995
	2	0.1–1.0	1.0148	−0.08767	0.9992
IO$_3^-$	1	–	–	–	–
	2	0.1–1.30	0.8196	0.07745	0.9997

Table 2
Tolerance limit of diverse ions on the determination of a mixture of 0.7 µg ml^{-1} periodate and 0.7 µg ml^{-1} iodate

Ion	Tolerance limit (µg ml^{-1})
BrO_3^-, ClO_4^-, ClO_3^-, SO_4^{-2}, citrate, tartrate	1000[a]
NO_3^-	500
Br^-, Cl^-	400
NO_2^-	10

[a] Maximum limit tested.

tolerance limit was defined as the concentration of added ion causing less than $\pm 3\%$ relative error.

3.5. Determination of periodate and iodate in synthetic mixtures

Various mixtures of standards of IO_4^- and IO_3^- solutions were prepared and tested according to the recommended procedure. The test was carried out covering concentrations within the dynamic ranges of the species, using different concentration ratio of these ions. The results are given in Table 3. As Table 3 shows the relative error of measurements were $\leq 5\%$. The maximum relative errors for periodate and iodate were 2.5 and 5%, respectively.

As it is observed the method is applicable for the determination of IO_4^- and IO_3^- in the mixtures contain 1:2–2:1 proportions of these two anions.

3.6. Application

Different mixtures of periodate and iodate were determined after addition to water samples. Table 4 shows the results. The recoveries being close to 100% indicating that there is no serious interference in such water samples.

Table 3
Analyses of mixtures of periodate and iodate

Periodate:iodate	Periodate (µg ml^{-1})		Relative error (%)	Iodate (µg ml^{-1})		Relative error (%)
	Taken	Found		Taken	Found	
1:2	0.300	0.305	+1.66	0.600	0.630	+5
3:2	0.600	0.591	−1.52	0.400	0.386	−3.5
2:3	0.400	0.410	+2.50	0.600	0.593	−1.2
2:2.5	0.400	0.397	−0.70	0.500	0.517	+3.4
2:7	0.200	0.203	+1.50	0.700	0.697	−0.4
2:1	0.600	0.603	+0.50	0.300	0.288	−4
1:2	0.400	0.410	+2.50	0.800	0.791	−1.1

Table 4
Determination of periodate and iodate in mixture in water samples

Sample	Periodate (µg ml^{-1})		Recovery (%)	Iodate (µg ml^{-1})		Recovery (%)
	Taken	Found[a]		Taken	Found[a]	
Tap water	0.300	0.308	102.7	0.700	0.712	101.7
	0.600	0.592	98.7	0.600	0.608	101.3
	0.400	0.400	100	0.300	0.245	98.3
Spring water	0.400	0.415	103.8	0.400	0.392	98
	0.600	0.590	98.3	0.500	0.510	102
	0.500	0.512	102.4	0.600	0.615	102.5

[a] Average of five determinations.

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