

Spectrophotometric Determination of Periodate, Iodate and Bromate Mixtures Based on Their Reaction with Iodide

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A rapid, simple, precise and accurate method is proposed for the determination of ternary mixtures of periodate-iodate-bromate based on their reaction with iodide ion at different pH values. The absorbance was measured at 352 nm. Three sets of reaction conditions were developed. In the first set of conditions, only periodate reacted with iodide, but in the second set the periodate and iodate reacted with iodide and in the third set the three ions reacted with iodide during the first 3 min after initiation of the reaction. The method could be used for individual determinations of periodate, iodate and bromate in the concentration range of 0.05 – 8.0 µg/ml, 0.05 – 5.0 µg/ml and 0.2 – 12 µg/ml, respectively. The data were evaluated by simultaneous equations.

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Introduction

Periodate, iodate and bromate are important oxidants which can oxidize many inorganic and organic compounds. These ions have been extensively used as ingredients for indicators in catalytic-kinetic analysis involving redox processes. Iodate and bromate have been reported to be toxic ions.^{1,2} The major route of environmental exposure to these oxihalides is drinking water.³ Bromate is a by-product of bromide containing water ozonization. Iodide ions may be found in brackish water and, to a lesser extent, in freshwater, and may form iodate during ozonization. Therefore, their determinations are required for environmental protection.

Several methods have been reported for the determination of periodate, iodate and bromate in mixtures. These include the spectrophotometric determination of periodate-iodate mixtures,⁴⁻⁶ spectrophotometric,⁷⁻⁹ chromatographic^{10,11} and polarographic¹² determination of iodate-bromate and periodate-bromate mixtures. To the best of our knowledge, there is only one report concerning the determination of ternary mixture of periodate, iodate and bromate. Kavalentis¹³ determined periodate, iodate and bromate mixtures by means of 3,4-dihydroxybenzaldehyde guanylhydrazone (3,4-DHGB). Periodate, iodate and bromate oxidized 3,4-DHGB in slightly acidic medium, in 0.1 M HClO₄ medium and in 20% HClO₄, respectively. The absorbance of the oxidized 3,4-DHGB was measured at 420 nm. Periodate, iodate and bromate could be determined in the ranges of 1 – 30, 0.5 – 16 and 0.4 – 14 µg/ml, respectively.

In this paper we describe a rapid, simple, precise and accurate method for the spectrophotometric determination of periodate, iodate and bromate ions in mixtures. The method is based on the reaction of periodate, iodate and bromate with iodide in acidic media at three different pH values.

Experimental

Apparatus

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

Reagents

Triply distilled water and analytical-reagent grade chemicals were used.

Standard solutions of periodate, iodate and bromate were prepared by dissolving an appropriate amount of sodium periodate, sodium iodate and potassium bromate (all from Merck) in water. A 0.15 M iodide solution was prepared by dissolving 5.625 g sodium iodide (Merck) in water and diluting to the mark in a 50-ml volumetric flask. Citrate buffer solutions (0.1 M) of pH 6 and 3.3 were prepared from sodium citrate, sodium hydroxide and hydrochloric acid solutions and 0.1 M glycine buffer solution of pH 1 was prepared from glycine and hydrochloric acid solutions.

Procedures

Three runs were needed for each sample. In the first run, an aliquot of a solution containing 1.5 – 17 µg of periodate, 1.0 – 18 µg of iodate and 2.0 – 120 µg of bromate was transferred into a 10 ml volumetric flask. Then, a 2 ml volume of a pH 6.0 buffer solution was added. The solution was diluted to ca. 9 ml with water and 1.0 ml of a 0.15 M iodide solution was added. A stopwatch was started just after the addition of the iodide solution. The solution was diluted to the mark and a portion of it was transferred into 1-cm glass cell to measure the absorbance at 352 nm during the first 3 min after initiation of the reaction.

The dependence of the absorbance during the first 3 min on the concentration of periodate was found to conform to the following equation:

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

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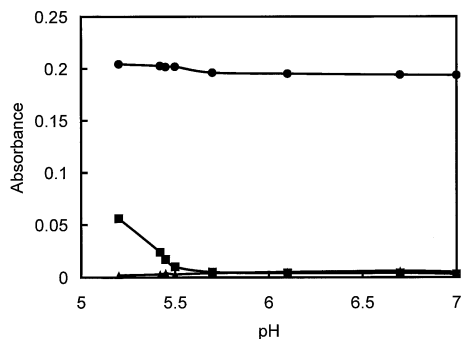


Fig. 1 Effect of the pH in the range of 5.2 - 7.0 on the reaction of 1.0 $\mu\text{g/ml}$ periodate (●), 100 $\mu\text{g/ml}$ iodate (■), and 100 $\mu\text{g/ml}$ bromate (▲) with 0.015 M iodide.

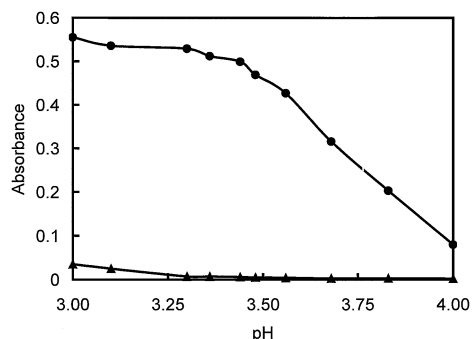


Fig. 2 Effect of the pH in the range of 3.0 - 4.0 on the reaction of 0.3 $\mu\text{g/ml}$ each of periodate and iodate (●), and 50 $\mu\text{g/ml}$ bromate (▲) with 0.015 M iodide.

The second run was performed as the first one, except that a 2 ml volume of a pH 3.3 buffer solution was used instead of 2 ml of a pH 6.0 buffer solution. The dependence of the absorbance during the first 3 min on the concentration of periodate and iodate was found to conform the following equation:

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

The third run was performed as the first one, except that 2 ml of a pH 1.0 buffer solution was used instead of a pH 6.0 buffer solution. The dependence of the absorbance during the first 3 min on the concentration of periodate, iodate and bromate was found to conform the following equation:

$$A_3 = a_3 + b_3 C_{\text{periodate}} + b'_3 C_{\text{iodate}} + b''_3 C_{\text{bromate}} \quad (3)$$

Results and Discussion

Periodate, iodate and bromate react with iodide in acidic media to produce triiodide according to the following reactions:



The reactions could be monitored spectrophotometrically by measuring the absorbance of the solutions at 352 nm, which is proportional to produced I_3^- concentration.

It was observed that the reaction of iodate and bromate with iodide showed induction periods that were dependent on the pH and reagent concentration. The induction period decreased by increasing the iodide, bromate or iodate concentration and increased by increasing the pH. Although bromate showed a longer induction period than iodate, the reaction of periodate initiated immediately after mixing with iodide in acidic and neutral media. Because of these differences periodate, iodate and bromate mixtures could be determined by choosing suitable conditions.

Three runs were used for each sample. All conditions were the same for three runs, except for the pH, which was different for each run. The pH for the first run was 6.0. At this pH only periodate reacted with iodide during the first 3 min after mixing. Therefore, the absorbance change during the first 3 min after mixing was proportional to periodate concentration. The pH for the second run was 3.3. At this pH, periodate and iodate reacted

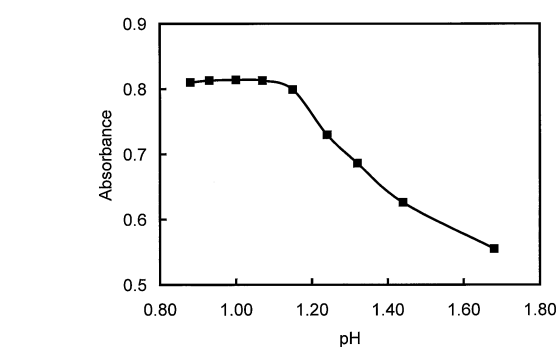


Fig. 3 Effect of the pH in the range of 0.9 - 1.7 on the reaction of 0.3 $\mu\text{g/ml}$ each of periodate and iodate and 1.5 $\mu\text{g/ml}$ bromate with 0.015 M iodide.

with iodide during the first 3 min after mixing. Therefore, the absorbance change during the first 3 min after mixing was proportional to periodate and iodate concentrations. The pH for the third run was 1.0. At this pH periodate, iodate and bromate reacted with iodine during the first 3 min after mixing. It must be noted that although the reactions of periodate and iodate were complete during the first 3 min after mixing, the reaction of bromate was not complete. The absorbance change during the first 3 min after mixing was proportional to periodate, iodate and bromate concentrations. The concentration of each anion was then calculated by three simultaneous equations.

Effect of variables

The effects of the pH on the reaction of periodate, iodate and bromate were studied. The results are shown in Figs. 1 - 3. As Fig. 1 shows, at pH values higher than 5.5, only periodate reacted with iodine during the first 3 min after mixing. Iodate and bromate did not react during the first 3 min after mixing, even when their concentrations were 100-fold excess over periodate. However, iodate reacted at pH values lower than 5.5. Therefore, a pH of 6 was selected as the optimum pH for the first run. Figure 2 shows the effect of the pH on the reaction of three investigated anions in the range of 3.0 - 4.0. As Fig. 2 shows, periodate and iodate reacted with iodide in this pH range. However, bromate did not react at pH values higher than 3.1 during the first 3 min after mixing, even when its concentration was 100-fold excess over iodate and periodate. Therefore, a pH of 3.3 was selected as the optimum pH for the second run. The effect of the pH on the reactions in the range of 0.9 - 1.7 is shown in Fig. 3. As Fig. 3 shows, the investigated

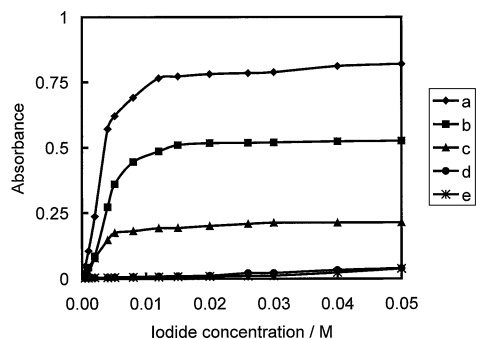


Fig. 4 Effect of iodide on the reaction of (a) 0.3 µg/ml each of periodate and iodate and 1.5 µg/ml bromate at pH 1, (b) 0.3 µg/ml each of periodate and iodate at pH 3.3, (c) 1.0 µg/ml periodate at pH 6, (d) 100 µg/ml iodate at pH 6 and (e) 100 µg/ml bromate at pH 3.3.

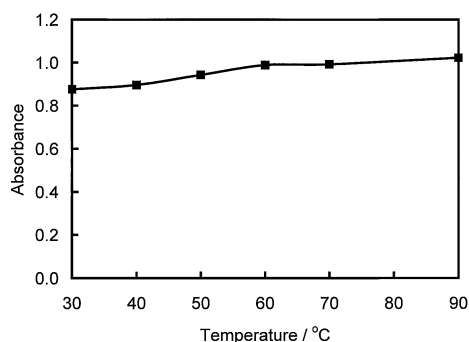


Fig. 5 Effect of the temperature on the reaction of 0.3 µg/ml each of periodate and 1.5 µg/ml bromate with 0.015 M iodide at pH 1.

anions reacted with iodide in this pH range during the first 3 min after mixing, but the reaction rate decreased at pH values higher than 1.2. Therefore, a pH of 1.0 was selected as the optimum pH for the third run.

The effect of the iodide concentration on the rate of the reactions was studied in the range of 0.005 – 0.5 M. The results are shown in Fig. 4. As Fig. 4 shows, at pH 1, the absorbance during the first 3 min after the initiation of a reaction for a mixture of periodate, iodate and bromate increased upon increasing the iodide concentration up to 0.012 M, and remained nearly constant at higher concentrations. The absorbance during the first 3 min after the initiation of the reaction for a mixture of periodate and iodate at pH 3.3 also increased upon increasing the iodide concentration up to 0.012 M, and remained nearly constant at higher concentrations. At pH 6, the absorbance of the periodate solution during the first 3 min after initiation of the reaction increased upon increasing the iodide concentration up to 0.006 M, and remained nearly constant at higher concentrations. Therefore, a 0.015 M iodide concentration was used for three runs. As is obvious from Fig. 4, at this concentration of iodide, iodate and bromate did not react at pH 6 and 3.3, respectively, during the first 3 min after mixing, even when present in high concentrations.

The effect of the temperature on the reactions of a mixture of periodate, iodate and bromate was studied in the range of 30 – 90°C. The results are given in Fig. 5. As Fig. 5 shows, increasing the temperature did not cause a considerable increase in the absorbance during the first 3 min after initiation of the

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

pH	Ion	Slope/ ml µg ⁻¹	Intercept	Correlation coefficient (n = 15)	Range	Limit of detection ^a / µg ml ⁻¹
1.0	IO ₄ ⁻	0.986	0.0148	0.9999	0.05 – 1.7	0.012
	IO ₃ ⁻	0.870	0.0178	0.9996	0.05 – 1.8	0.015
	BrO ₃ ⁻	0.141	0.0124	0.9997	0.20 – 12.0	0.086
3.3	IO ₄ ⁻	0.724	0.0205	0.9991	0.05 – 2.2	0.017
	IO ₃ ⁻	0.605	0.0963	0.9990	0.05 – 5.0	0.04
6.0	BrO ₃ ⁻	—	—	—	—	—
	IO ₄ ⁻	0.205	0.00612	0.9992	0.15 – 8.0	0.055
	IO ₃ ⁻	—	—	—	—	—
	BrO ₃ ⁻	—	—	—	—	—

a. Defined as $C_L = 3S_B/m^{14}$ where C_L , S_B and m are limit of detection, standard deviation of the blank signal and slope of the calibration graph, respectively.

Table 2 Tolerance limit of diverse ions on the determination of a mixture of 1.0 µg ml⁻¹ each of periodate, iodate and bromate

Ion	Tolerance limit/µg ml ⁻¹
CO ₃ ²⁻ , ClO ₄ ⁻ , ClO ₃ ⁻ , SO ₄ ²⁻ , citrate, tartrate	1000 ^a
NO ₃ ⁻ , acetate, NH ₄ ⁺	—
SCN ⁻ , Cl ⁻	20
Br ⁻ , NO ₂ ⁻ , SO ₃ ²⁻ , MoO ₄ ²⁻ , WO ₄ ²⁻	1

a. Maximum limit tested.

reaction. Therefore, 30°C was used for three runs.

Individual determination of periodate, iodate and bromate

Calibration graphs for individual determinations of periodate, iodate and bromate were obtained under the optimum conditions. The results are summarized in Table 1. As Table 1 shows, the method could be used for individual determinations of periodate, iodate and bromate in the concentration range of 0.05 – 8.0 µg/ml, 0.05 – 5.0 µg/ml and 0.2 – 12 µg/ml, respectively.

Determination of periodate-iodide-bromate mixtures

From Table 1 and taking into account that under the conditions of each run no synergic effects were observed between periodate, iodate and bromate, the following equations can be used for the determination of periodate, iodate and bromate in mixture:

$$A_1 = 0.00612 + 0.205C_{\text{periodate}}, \quad (7)$$

$$A_2 = 0.117 + 0.724C_{\text{periodate}} + 0.605C_{\text{iodate}}, \quad (8)$$

$$A_3 = 0.045 + 0.986C_{\text{periodate}} + 0.870C_{\text{iodate}} + 0.141C_{\text{bromate}}, \quad (9)$$

where A_1 , A_2 and A_3 are the absorbances after 3 min for the first, second and third runs, respectively, the concentrations are in µg/ml.

This method is also suitable for the determination of binary mixtures of iodate-periodate, bromate-periodate and iodate-bromate. The related equations can be obtained from the data in Table 1.

Table 3 Analyses of mixtures of periodate, iodate and bromate

Periodate/ $\mu\text{g ml}^{-1}$		Relative error, %	Iodate/ $\mu\text{g ml}^{-1}$		Relative error, %	Bromate/ $\mu\text{g ml}^{-1}$		Relative error, %
Taken	Found		Taken	Found		Taken	Found	
0.400	0.403	+0.75	0.200	0.195	-2.50	8.00	7.78	-2.75
0.600	0.606	+1.00	1.20	1.23	+2.50	1.00	0.969	-3.1
1.50	1.49	-0.67	0.200	0.178	2.17	1.00	0.970	-3.00
0.500	0.503	+0.63	0.700	0.681	-2.71	6.00	6.12	+2.00
0.800	0.808	+1.00	1.20	1.18	-1.67	0.800	0.803	+3.81
0.300	0.302	+0.67	1.00	1.03	+3.00	5.00	5.11	+2.20
0.500	0.496	-0.80	1.20	1.22	+1.67	0.300	0.313	+4.33
0.200	0.201	+0.53	4.00	4.03	+0.75	—	—	—
1.50	1.50	0.00	—	—	—	0.500	0.513	+2.60
0.500	0.498	-0.40	—	—	—	8.00	7.91	-1.13
—	—	—	1.50	1.49	-0.67	0.500	0.511	+2.20
—	—	—	0.800	0.807	+0.88	5.00	4.92	-1.60

Table 4 Determination of periodate, iodate and bromate in mixture in spring-water samples

Periodate/ $\mu\text{g ml}^{-1}$		Recovery, %	Iodate/ $\mu\text{g ml}^{-1}$		Recovery, %	Bromate/ $\mu\text{g ml}^{-1}$		Recovery, %
Taken	Found ^a		Taken	Found ^a		Taken	Found ^a	
0.500	0.505	101.0	0.400	0.385	96.3	2.00	1.92	96.0
0.800	0.813	101.6	1.00	1.01	101.2	0.800	0.821	102.6
1.00	0.980	98.0	0.500	0.519	103.8	4.00	4.02	100.5

a. Average of 5 determinations.

Precision

To evaluate the precision of the method, a series of independent samples was used. The relative standard deviations for seven determinations of samples containing 0.500 $\mu\text{g/ml}$ each of periodate, iodate and bromate were 1.85, 2.15 and 1.35% for periodate, iodate and bromate, respectively.

Selectivity

To study the selectivity of the proposed method, the effect of various ions on the determination of a mixture of each 1.0 $\mu\text{g/ml}$ of periodate, iodate and bromate was tested under the optimum conditions. The tolerance limit was defined as the concentration of added ion causing less than a $\pm 3\%$ relative error. The results are given in Table 2. As Table 2 shows, most of the ions did not interfere, even when present in 1000-fold excess over periodate, iodate and bromate. Sulfide and sulfite ions interfered by competing with I^- in the reduction of periodate, iodate and bromate, and therefore caused negative interference. MoO_4^{2-} , WO_4^{2-} and NO_2^- caused positive interference because of their reaction with I^- .

Determination of periodate, iodate, bromate in synthetic mixtures

Various synthetic mixtures of IO_4^- - IO_3^- - BrO_3^- , IO_4^- - IO_3^- , IO_4^- - BrO_3^- and IO_3^- - BrO_3^- were analyzed by the proposed method. The results are given in Table 3. As Table 3 shows, the relative error of the measurements were in the range of -3.1 to 4.33%. The maximum relative errors for periodate, iodate and bromate were +1.0, -2.5 and 4.33%, respectively.

As observed, the method is applicable to determination of mixtures having different proportions of these three anions.

Determination of periodate, iodate, bromate water samples

Different mixtures of periodate, iodate and bromate were

determined after addition to spring-water samples. Samples with various concentrations and various concentration ratios of ions were analyzed. Table 4 gives the results. The recoveries, being close to 100% indicate that there is no serious interference in such water samples.

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