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Simultaneous kinetic-spectrophotometric determination of periodate–bromate and iodate–bromate mixtures using the H-point standard addition method

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Received 10 September 2002; received in revised form 6 January 2003; accepted 10 January 2003

Abstract

The H-point standard addition method (HPSAM), based on spectrophotometric measurement, for simultaneous determination of periodate–bromate and iodate–bromate mixtures is described. This method is based on the difference between the rates of their reactions with iodide in acidic media. The results showed that simultaneous determinations could be performed with the ratio 1:15–12:1 for periodate–bromate and 15:1–1:15 for iodate–bromate. The proposed method was successfully applied to the simultaneous determination of periodate–bromate and iodate–bromate in water and synthetic samples.

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Keywords: Periodate; Iodate; Bromate; HPSAM

1. Introduction

Periodate, iodate and bromate are important oxidizing agents active on 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 contained in

water after 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 [4–7], and spectrophotometric [8–10], chromatographic [11,12] and polarographic [13] determination of iodate–bromate and periodate–bromate mixtures.

UV–Vis spectrophotometric methods are remarkable for their simplicity, versatility, sensitivity and precision. El-Shahawi [4] used the ion-associate of periodate with amiloride hydrochloride for

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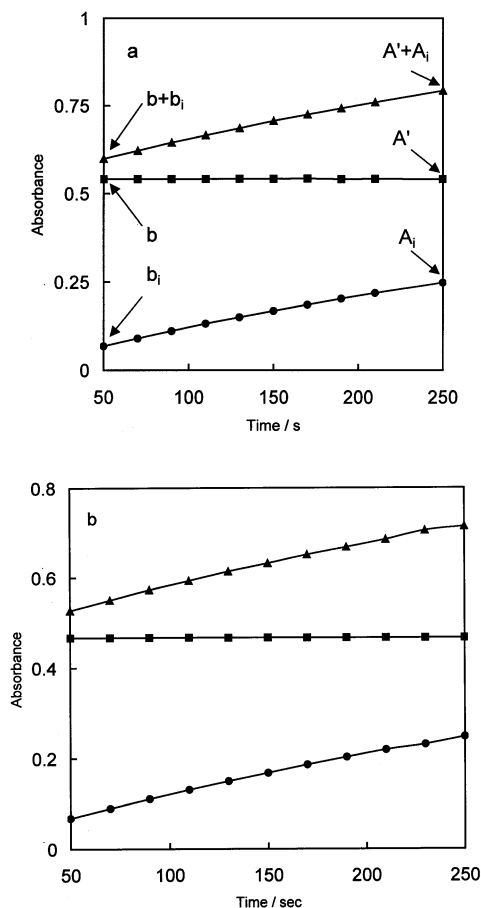


Fig. 1. Absorbance–time curves for (a) $0.5 \mu\text{g ml}^{-1} \text{IO}_4^-$ (■), $0.5 \mu\text{g ml}^{-1} \text{BrO}_3^-$ (●) and their mixture (▲); (b) $0.5 \mu\text{g ml}^{-1} \text{IO}_3^-$ (■), $0.5 \mu\text{g ml}^{-1} \text{BrO}_3^-$ (●) and their mixture (▲) in the presence 0.01 M iodide, 0.05 M sulphuric acid and at 30°C .

simultaneous spectrophotometric determination of periodate and iodate by liquid–liquid extraction. Periodate in the range $0.01\text{--}10.0 \mu\text{g ml}^{-1}$ was determined by this method. Iodate has been determined after prior oxidation to periodate with potassium peroxodisulphate. Ensafi and Bagherian Dehaghi [5] described a procedure for simultaneous spectrophotometric and spectrofluorometric determination of iodate and periodate. Periodate and iodate reacted with iodine to produce iodine that could be determined spectrophotometrically at 349 nm . The absorbance is proportional to the iodate and periodate concentrations. Periodate reacted with alizarin navy blue

to produce a fluorescent compound. They determined periodate by measuring the fluorescent intensity at 516 nm and then calculated iodate concentration by subtraction. They determined iodate and periodate in the range $1.0 \times 10^{-5}\text{--}2.0 \times 10^{-4}$ and $1.0 \times 10^{-5}\text{--}2.2 \times 10^{-4} \text{ M}$, respectively. Recently, we reported a spectrophotometric method at 665 nm for the determination of periodate and iodate in the range $0.1\text{--}1.0$ and $0.1\text{--}1.3 \mu\text{g ml}^{-1}$, respectively, based on their reaction with iodide in the presence of methylene blue [6]. Two sets of conditions were established that in one set of conditions only periodate reacted with iodide but in the other set both ions reacted with iodide during 3 min after initiation of the reaction. The data were evaluated by proportional equation. We also determined periodate, bromate and iodate mixtures spectrophotometrically at 352 nm based on their reaction with iodide. Three sets of conditions were developed [7]. In the first set of conditions, only periodate reacted with iodide, but in the second set periodate and iodate reacted with iodide and in the third set the three ions during the first 3 min after initiation of the reaction. The method could be used for the determination of periodate, iodate and bromate in the range $0.05\text{--}8.0$, $0.05\text{--}5.0$ and $0.2\text{--}12.0 \mu\text{g ml}^{-1}$, respectively.

Although the standard addition method could remove the error resulting from the sample matrix, it cannot remove the constant error resulting from other components in the system [14]. In 1988, Bosch-Reig and Campins-Falco [15] presented a new technique called the H-point standard addition method (HPSAM) that was based on the principle of dual-wavelength spectrophotometry and the standard addition method. The greatest advantage of HPSAM is that it can remove the presence of an interference and reagent blank [14]. HPSAM can determine the two components simultaneously with extensively or even coincident overlapping spectra [16].

The Bosch-Reig et al. [17] method was aimed at establishing the fundamentals for application of HPSAM to kinetic data for the simultaneous analysis of binary mixtures or the calculation of analyte concentrations completely free from biased error. For this purpose, they used two variants of HPSAM: one is applied when the reaction of one

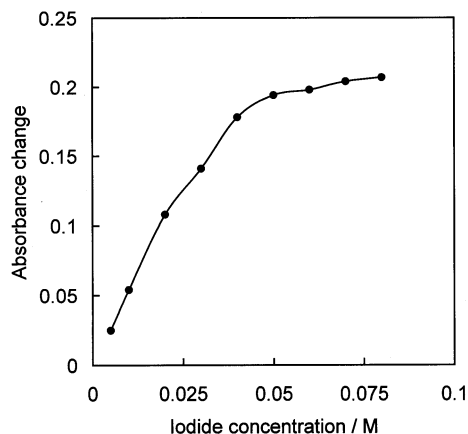


Fig. 2. Effect of iodide concentration on the reaction of $0.5 \mu\text{g ml}^{-1}$ each of periodate and bromate in the presence of 0.05 M sulphuric acid and at 30°C .

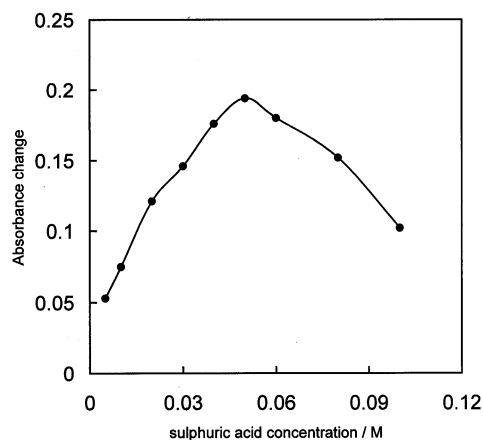


Fig. 3. Effect of sulphuric acid on the reaction of $0.5 \mu\text{g ml}^{-1}$ each of periodate and bromate in the presence of 0.01 M iodide and at 30°C .

component is faster than that of the other or the latter does not take place at all; the other is used when the rate constants of the two components are time-dependent.

In this paper, we describe a rapid, simple, precise and accurate method for the simultaneous determination of periodate–bromate and iodate–bromate using HPSAM. The method is based on the difference between the rate of the reaction of the investigated oxihalides with iodide in acidic media.

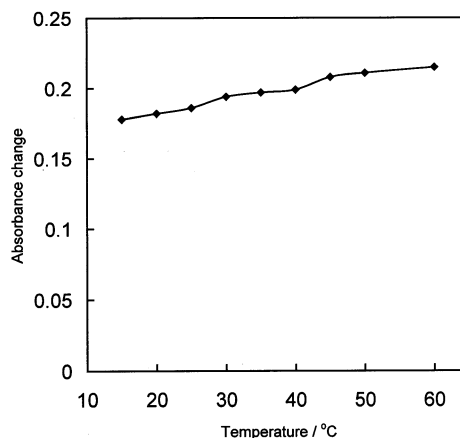


Fig. 4. Effect of temperature on the reaction of $0.5 \mu\text{g ml}^{-1}$ each of periodate and bromate in the presence of 0.01 M iodide and 0.05 M sulphuric acid.

2. Experimental

2.1. Apparatus

A Shimadzu model 3101PC UV–visible recording spectrophotometer with 1-cm glass cells was used for absorbance measurements.

2.2. Reagents

Triply distilled water and analytical-reagent grade chemicals were used. Standard solutions of periodate, iodate and bromate were prepared by dissolving appropriate amounts of sodium periodate, sodium iodate and potassium bromate (all from Merck) in water. A 0.1 M iodide solution was prepared by dissolving 3.75 g sodium iodide (Merck) in water and diluting to the mark in a 250-ml volumetric flask. A 0.5 M sulphuric acid solution was prepared with diluting concentrated sulphuric acid (Merck).

2.3. Procedure

Appropriate volumes of periodate and bromate or iodate and bromate standard solutions and 1 ml of 0.5 M sulphuric acid were added into a 10 ml volumetric flask. The solution was diluted to ca. 9 ml with water and 1 ml of 0.1 M iodide solution was added to initiate the reaction. A stopwatch

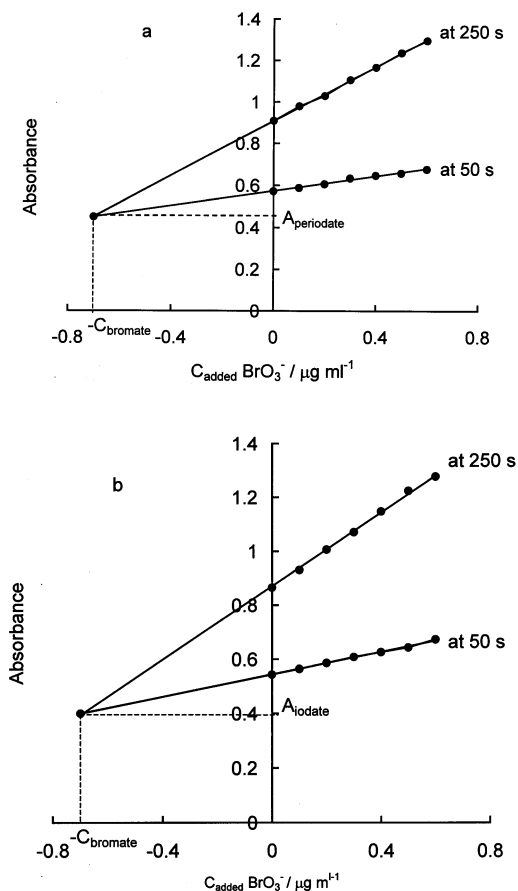


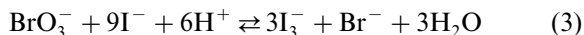
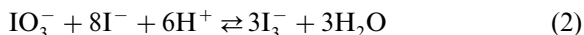
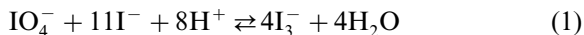
Fig. 5. Plot of HPSAM for simultaneous determination of the mixture of (a) $0.5 \mu\text{g ml}^{-1}$ each of periodate and bromate, and (b) $0.5 \mu\text{g ml}^{-1}$ each of iodate and bromate.

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 a 1-cm glass cell to measure the absorbance change with time at 352 nm. Synthetic samples containing different ratios of periodate and bromate or iodate and

bromate were prepared and standard addition of bromate (up to $1.0 \mu\text{g ml}^{-1}$) was made. After the addition of sulphuric acid and iodide solution as described above, the absorbance of the solution was measured at 50 and 250 s after initiation of the reactions for performing HPSAM in the proposed systems. Simultaneous determination could be performed with the ratio 1:15–12:1 for periodate–bromate and 15:1–1:15 for iodate–bromate. The concentration range of bromate for the construction of HPSAM calibration was 0.10 – $1.50 \mu\text{g ml}^{-1}$.

3. Results and discussion

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



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

It was observed that the reaction of periodate and iodate with iodide in acidic media was completed immediately after mixing, while the reaction of bromate with iodide in the same conditions is relatively slow (see Fig. 1a and b). Therefore, the systems seen to be appropriate for simultaneous determination of periodate–bromate and iodate–bromate mixtures by using HPSAM.

Table 1

Characteristics of calibration graphs for the determination of periodate, iodate and bromate by the proposed method

Ion	Slope ($\text{ml } \mu\text{g}^{-1}$)	Intercept	Correlation coefficient ($n = 11$)	Range ($\mu\text{g ml}^{-1}$)	Limit of detection ^a ($\mu\text{g ml}^{-1}$)
IO_4^-	1.0017	−0.0599	0.9998	0.1–1.2	0.01
IO_3^-	0.7844	0.01707	0.9997	0.1–1.5	0.02
BrO_3^-	0.362	0.00306	0.9994	0.1–1.5	0.04

^a Defined as $C_L = 3S_b/m$, where C_L , S_b and m are limit of detection, standard deviation of the blank signal and slope of the calibration graph, respectively [18].

Table 2

Results of several experiments for the analysis of periodate–bromate mixtures in different ratios

<i>A</i> – <i>C</i> equations	<i>r</i> (<i>n</i> = 6)	Present in sample ($\mu\text{g ml}^{-1}$)		Found ^a ($\mu\text{g ml}^{-1}$)	
		BrO_3^-	IO_4^-	BrO_3^-	IO_4^-
$A_{250} = 0.652C + 1.116$	0.9984	0.10	1.20	0.097 (97)	1.15 (96)
$A_{50} = 0.197C + 1.072$	0.9992				
$A_{250} = 0.814C + 1.215$	0.9996	1.50	0.10	1.50 (100)	0.095 (95)
$A_{50} = 0.256C + 0.407$	0.9997				
$A_{250} = 0.750C + 0.985$	0.9996	1.20	0.15	1.20 (100)	0.16 (107)
$A_{50} = 0.212C + 0.3487$	0.9991				
$A_{250} = 0.596C + 0.884$	0.9995	0.20	0.80	0.21 (105)	0.82 (103)
$A_{50} = 0.188C + 0.797$	0.9998				
$A_{250} = 984C + 0.9104$	0.999	0.90	0.10	0.88 (98)	0.095 (95)
$A_{50} = 0.328C + 0.333$	0.9991				
$A_{250} = 0.632C + 0.674$	0.9998	0.60	0.35	0.63 (105)	0.34 (97)
$A_{50} = 0.192C + 0.399$	0.9991				
$A_{250} = 0.577C + 0.680$	0.9992	0.30	0.60	0.29 (97)	0.57 (95)
$A_{50} = 0.168C + 0.561$	0.9996				
$A_{250} = 0.668C + 0.775$	0.9991	0.50	0.50	0.52 (104)	0.49 (98)
$A_{50} = 0.247C + 0.558$	0.9993				

^a Values of recovery are given in parentheses.

Table 3

Results of several experiments for the analysis of iodate–bromate mixtures in different ratios

<i>A</i> – <i>C</i> equations	<i>r</i> (<i>n</i> = 6)	Present in sample ($\mu\text{g ml}^{-1}$)		Found ^a ($\mu\text{g ml}^{-1}$)	
		BrO_3^-	IO_3^-	BrO_3^-	IO_3^-
$A_{250} = 0.728C + 0.199$	0.9987	1.50	0.10	1.50 (100)	0.096 (96)
$A_{50} = 0.204C + 0.403$	0.9994				
$A_{250} = 0.634C + 0.284$	0.9986	0.10	1.50	0.10 (100)	1.50 (100)
$A_{50} = 0.191C + 1.239$	0.9993				
$A_{250} = 0.678C + 0.835$	0.9991	0.80	0.40	0.76 (95)	0.39 (98)
$A_{50} = 0.211C + 0.480$	0.9993				
$A_{250} = 0.654C + 0.619$	0.9987	0.60	0.30	0.57 (95)	0.29 (97)
$A_{50} = 0.211C + 0.366$	0.9992				
$A_{250} = 0.618C + 0.8$	0.9991	1.0	0.20	1.00 (100)	0.21 (105)
$A_{50} = 0.182C + 0.363$	0.999				
$A_{250} = 0.593C + 0.728$	0.9993	0.50	0.50	0.52 (104)	0.52 (104)
$A_{50} = 0.173C + 0.512$	0.9991				
$A_{250} = 0.641C + 0.92$	0.9989	0.15	1.00	0.15 (100)	1.00 (100)
$A_{50} = 0.1911C + 0.852$	0.9993				

^a Values of recovery are given in parentheses.

3.1. Effect of variables

To take full advantage of the procedure, the reagent concentrations and the reaction conditions must be optimized. Various experimental parameters were studied in order to obtain an opti-

mized system. The parameters were optimized by studying their effects on the reaction of periodate–bromate binary mixtures.

The effect of iodide concentration on the rate of reaction was studied in the range 0.005–0.05 M. The results are shown in Fig. 2. As Fig. 2 shows,

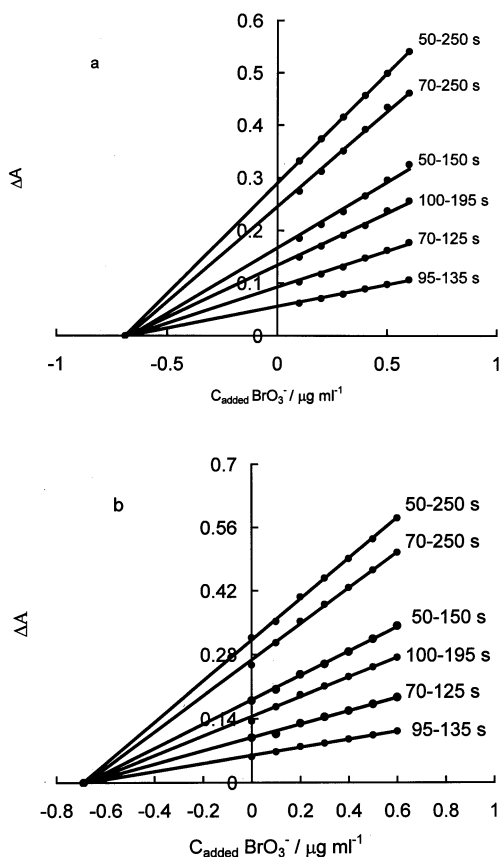


Fig. 6. ΔA vs. added bromate concentration for different time intervals at 352 nm for (a) $0.7 \mu\text{g ml}^{-1} \text{BrO}_3^-$ and $0.5 \mu\text{g ml}^{-1} \text{IO}_4^-$, and (b) $0.7 \mu\text{g ml}^{-1} \text{BrO}_3^-$ and $0.5 \mu\text{g ml}^{-1} \text{IO}_3^-$.

the absorbance change for binary mixture of periodate–bromate increased by increasing the iodide concentration up to 0.01 M and remained nearly constant at higher concentrations; therefore, 0.01 M iodide concentration was selected as the optimum concentration.

The effect of sulphuric acid concentration on the rate of reaction was studied in the range 0.01–0.1 M. The results are shown in Fig. 3. As Fig. 3 shows, the absorbance change for binary mixture of periodate–bromate increased by increasing sulphuric acid concentration up to 0.05 M and decrease at higher concentrations. Therefore, 0.05 M sulphuric acid concentration was selected as the optimum concentration.

The effect of temperature on the rate of reaction was studied in the range 15–60 °C. The results are

shown in Fig. 4. As Fig. 4 shows, the absorbance increased slowly by increasing the temperature between 15 and 60 °C. Therefore, 30 °C was used for routine works.

3.2. Requirements for applying HPSAM

The basis of the use of HPSAM for the treatment of kinetic data under the conditions that the reaction of one component is completed while that of other component is not completed yet is described below [17]. In this case, the variable to be fixed was the times 50 and 250 s at which the product of the reaction of periodate and iodate have the same absorbance over the range between these two times and also there is an appropriate difference between the slopes of the calibration lines.

Considering a binary mixture of periodate–bromate, e.g., assume that the absorbance of the produced triiodide at the reaction of bromate with iodide at 352 nm at times 50 and 250 s is b_i and A_i , respectively (see Fig. 1a and b), while those of the periodate–iodide reaction under the same conditions are b and A' , respectively. They are equal in this case. The following equations show the relation between them:

$$\text{(bromate): } A_i = b_i + m_i t_j, \quad (4)$$

$$t_1 \leq t_j \leq t_2, \quad i = 0, 1, n, \dots,$$

$$\text{(periodate): } A' = b + m t_j, \quad m = 0, \quad (5)$$

where the subscripts i and j denote the different solutions for n additions of the bromate concentration prepared to apply HPSAM and for a time comprised in the 50–250 s range, respectively.

Thus, the overall absorbance corresponding to periodate–bromate mixture at 50 and 250 s was $A_{50} = b_0 + b_i$ and $A_{250} = A' + A_i$, respectively.

Application of HPSAM at the two aforesaid times gives

$$A_{50} = b_0 + b + M_{50} C_i, \quad (6)$$

$$A_{250} = A_0 + A' + M_{250} C_i, \quad (7)$$

where M_{50} and M_{250} are the slopes of the standard addition calibration lines at 50 and 250 s, respectively. C_i is the concentration of added species, which intersect at point $H(C_H, A_H) \equiv (-C_{\text{bromate}},$

Table 4
Results of five replicate experiments for the analysis of IO_4^- – BrO_3^- mixtures

<i>A</i> – <i>C</i> equations	<i>r</i> (<i>n</i> = 6)	Present in sample ($\mu\text{g ml}^{-1}$)		Found ($\mu\text{g ml}^{-1}$)	
		BrO_3^-	IO_4^-	BrO_3^-	IO_4^-
$A_{250} = 0.67C + 0.903$	0.9993	0.70	0.50	0.68	0.51
$A_{50} = 0.18C + 0.572$	0.9994				
$A_{250} = 0.665C + 0.908$	0.999	0.70	0.50	0.69	0.51
$A_{50} = 0.177C + 0.572$	0.9993				
$A_{250} = 0.685C + 0.909$	0.9986	0.70	0.50	0.72	0.48
$A_{50} = 0.174C + 0.541$	0.9991				
$A_{250} = 0.693C + 0.876$	0.9991	0.70	0.50	0.68	0.47
$A_{50} = 0.186C + 0.531$	0.9994				
$A_{250} = 0.667C + 0.905$	0.9987	0.70	0.50	0.71	0.49
$A_{50} = 0.171C + 0.552$	0.999				
Mean				0.70	0.49
S.D.				0.018	0.018
RSD (%)				2.6	3.6

Table 5
Results of five replicate experiments for the analysis of IO_3^- – BrO_3^- mixtures

<i>A</i> – <i>C</i> equations	<i>r</i> (<i>n</i> = 6)	Present in sample ($\mu\text{g ml}^{-1}$)		Found ($\mu\text{g ml}^{-1}$)	
		BrO_3^-	IO_3^-	BrO_3^-	IO_3^-
$A_{250} = 0.7C + 0.864$	0.9984	0.70	0.50	0.67	0.48
$A_{50} = 0.217C + 0.543$	0.999				
$A_{250} = 0.694C + 0.872$	0.9993	0.70	0.50	0.71	0.50
$A_{50} = 0.2103C + 0.542$	0.9995				
$A_{250} = 0.695C + 0.870$	0.9986	0.70	0.50	0.68	0.51
$A_{50} = 0.222C + 0.548$	0.999				
$A_{250} = 0.702C + 0.896$	0.9991	0.70	0.50	0.71	0.52
$A_{50} = 0.215C + 0.564$	0.9993				
$A_{250} = 0.721C + 0.938$	0.999	0.70	0.50	0.72	0.51
$A_{50} = 0.216C + 0.5736$	0.9992				
Mean				0.70	0.50
S.D.				0.022	0.015
RSD (%)				3.1	3.0

$A_{\text{periodate}}$) (Fig. 5). At the intersect

$$b_0 + b + M_{50}(-C_{\text{H}}) = A_0 + A' + M_{250}(-C_{\text{H}}). \quad (8)$$

Hence

$$-C_{\text{H}} = \frac{(A' - b) + (A_0 - b_0)}{M_{50} - M_{250}}, \quad (9)$$

where A' and b are equal because of the fast reaction between periodate and iodide, hence

$$-C_{\text{H}} = \frac{A_0 - b_0}{M_{50} - M_{250}}, \quad (10)$$

which is equivalent to the existing $C_{\text{bromate}} (= b_0/M_{50} = A_0/M_{250})$.

Substitution of $C_{\text{periodate}}$ into Eqs. (6) and (7) yields $A_{\text{H}} = b$ and the overall equation for the absorbance at H-point simplifies to

$$A' = b = A_{\text{H}} = A_{\text{periodate}}. \quad (11)$$

Table 6

Determination of periodate and bromate mixtures in different samples using HPSAM

Sample	Spiked ($\mu\text{g ml}^{-1}$)		Found ^a ($\mu\text{g ml}^{-1}$)	
	BrO_3^-	IO_4^-	BrO_3^-	IO_4^-
Tap water	0.200	1.200	0.19 ± 0.01	1.20 ± 0.02
Synthetic sample ^b	1.000	0.250	1.03 ± 0.02	0.25 ± 0.02
Synthetic sample ^c	0.200	1.000	0.20 ± 0.02	0.99 ± 0.01

^a Mean \pm S.D. ($n = 3$).^b Contained: Cl^- , 1000 $\mu\text{g ml}^{-1}$; Br^- , 1000 $\mu\text{g ml}^{-1}$; ClO_3^- , 1000 $\mu\text{g ml}^{-1}$; ClO_4^- , 1000 $\mu\text{g ml}^{-1}$; SO_4^{2-} , 1000 $\mu\text{g ml}^{-1}$; SCN^- , 10 $\mu\text{g ml}^{-1}$.^c Contained: CO_3^{2-} , 1000 $\mu\text{g ml}^{-1}$; NO_3^- , 1000 $\mu\text{g ml}^{-1}$; Br^- , 1000 $\mu\text{g ml}^{-1}$; ClO_3^- , 1000 $\mu\text{g ml}^{-1}$; SO_4^{2-} , 1000 $\mu\text{g ml}^{-1}$; SCN^- , 5.0 $\mu\text{g ml}^{-1}$.

Table 7

Determination of iodate and bromate mixtures in different samples using HPSAM

Sample	Spiked ($\mu\text{g ml}^{-1}$)		Found ^a ($\mu\text{g ml}^{-1}$)	
	BrO_3^-	IO_3^-	BrO_3^-	IO_3^-
Tap water	0.200	1.500	0.21 ± 0.02	1.50 ± 0.03
Synthetic sample ^b	1.300	0.100	1.30 ± 0.02	0.10 ± 0.01
Synthetic sample ^c	0.300	1.200	0.32 ± 0.02	1.18 ± 0.02

^a Mean \pm S.D. ($n = 3$).^b Contained: Cl^- , 1000 $\mu\text{g ml}^{-1}$; Br^- , 1000 $\mu\text{g ml}^{-1}$; ClO_3^- , 1000 $\mu\text{g ml}^{-1}$; ClO_4^- , 1000 $\mu\text{g ml}^{-1}$; SO_4^{2-} , 1000 $\mu\text{g ml}^{-1}$; SCN^- , 10 $\mu\text{g ml}^{-1}$.^c Contained: CO_3^{2-} , 1000 $\mu\text{g ml}^{-1}$; NO_3^- , 1000 $\mu\text{g ml}^{-1}$; Br^- , 1000 $\mu\text{g ml}^{-1}$; ClO_3^- , 1000 $\mu\text{g ml}^{-1}$; SO_4^{2-} , 1000 $\mu\text{g ml}^{-1}$; SCN^- , 5.0 $\mu\text{g ml}^{-1}$.

The intercept of the straight lines represented by Eqs. (6) and (7) would thus, directly yield the unknown bromate concentration (C_{bromate}) and the analytical signal of species periodate ($A_{\text{periodate}}$) corresponding to 50 and 250 s in the original samples. The concentration of periodate was calculated from this analytical signal from a calibration graph (Table 1).

According to the theory of the proposed method, the absorbance values for the different mixtures of periodate and bromate solutions were measured at 50 and 250 s.

A summary of the obtained results for various analyte concentrations is given in Table 2. The concentration was calculated directly by solving the system of equations of two straight lines. The periodate concentrations were calculated from Beer's law at 352 nm and from the absorbance values (A_{H}) obtained from the solution of the cited

system of equations. As is shown in Table 2, C_{bromate} was independent of the concentration of periodate and the value of $C_{\text{periodate}}$ was independent of the amount of bromate in the sample. Similar procedure was applied for the binary mixtures of iodate and bromate. The results are given in Table 3.

The version of HPSAM involving the use of the absorbance increment as an analytical signal can be employed by use of $A_{t_1-t_2}$ to allow the analyte concentration to be calculated with no systematic, constant, or proportional error thanks to the intrinsic features of HPSAM and the nature of the method of standard addition (MOSA). This method can also be used to diagnose the occurrence of interference with a given analytical procedure as, in the absence of error, the plot of any $A_{t_1-t_2}$ against the added analyte concentration will have a constant point ($-C_{\text{H}}, 0$) [17].

Therefore, ΔA_{t1-t2} value obtained after each addition will be exclusively related to the bromate concentration as the periodate absorbance will be the same at both times, and so its contribution to ΔA_{t1-t2} will be zero. However, in order to ensure the absorbance of a constant and proportional error from the calculated concentration, all possible $\Delta A_{t1-t2} - C_{\text{added}}$ lines for bromate should intersect at the same point, namely that corresponding to the unknown concentration, C_H . Fig. 6 shows the results obtained from employing this version of HPSAM for periodate–bromate and iodate–bromate mixtures.

The results showed that the simultaneous determination of periodate, iodate and bromate could be performed in the range 0.1–1.2, 0.1–1.5 and 0.1–1.5 $\mu\text{g ml}^{-1}$, respectively.

3.3. Accuracy and precision of the method

Under the optimum conditions, simultaneous determination of different binary mixtures of periodate–bromate and iodate–bromate were made using HPSAM. As Tables 2 and 3 show, the values of recovery are in the range 95–107%, which indicates that the accuracy of the method is satisfactory, when the concentration ratio of periodate–bromate and iodate–bromate vary from 1:15 to 12:1 and 15:1 to 1:15, respectively.

To check the reproducibility of the method, five replicate experiments were performed and the relative standard deviation (RSD) was obtained for mixtures. The results are given in Tables 4 and 5. As the results show, the precision of the results is satisfactory.

3.4. Selectivity

To study the selectivity of the proposed method, the effect of various ions on the determination of a mixture of 0.5 $\mu\text{g ml}^{-1}$ of periodate and 0.5 $\mu\text{g ml}^{-1}$ of bromate was tested under the optimum conditions. The tolerance limit was defined as the concentration of added ion causing less than $\pm 3\%$ relative error. The results show that the ions CO_3^{2-} , ClO_4^- , ClO_3^- , SO_4^{2-} , citrate, tartarate,

NO_3^- , acetate, NH_4^+ , Cl^- and Br^- did not interfere, even when present in 2000-fold excess over periodate and bromate. Sulphide and sulphite ions interfered by competing with I^- in the reduction of periodate, iodate and bromate, and therefore caused negative interferences. MoO_4^{2-} , WO_4^{2-} and NO_2^- caused negative interference because of their reaction with iodide ion.

3.5. Application

The proposed method was successfully applied to the determination of mixtures of periodate–bromate, iodate–bromate after addition to water samples and in synthetic samples. The results are given in Tables 6 and 7. As can be seen, the results are all satisfactory.

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