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# Simultaneous kinetic spectrophotometric determination of periodate and iodate based on their reaction with pyrogallol red in acidic media by chemometrics methods

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## Abstract

The univariate and multivariate calibration methods were applied for the simultaneous determination of iodate and periodate in water. The method is based on the reaction of periodate and iodate with pyrogallol red in sulfuric acid media. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of pyrogallol red at 470 nm. The calibration curve was linear over the concentration ranges of 0.1–12 and 0.1–14  $\mu\text{g ml}^{-1}$  for iodate and periodate, respectively. The experimental calibration matrix for partial least squares (PLS) and orthogonal signal correction (OSC–PLS) method was designed with 35 mixtures. The results obtained by the PLS and OSC–PLS were statistically compared. The effects of various cations and anions on iodate and periodate determination have been investigated.

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**Keywords:** Iodate; Periodate; Pyrogallol red; Spectrophotometric; PLS; OSC–PLS

## 1. Introduction

Iodate and periodate are exclusively associated with oxidation of metal ions, polyhydroxylated compounds and catalytic application at trace levels [1,2]. Thus, sensitive and selective determination of iodine compounds, particularly iodate and periodate is important in organic chemistry, biology and life science. Several spectrophotometric and spectrofluorimetric methods for the determination of both ions have been reported [3–5]. On the other hand, a few reports are present concerning the determination of iodate and periodate separately [6–11]. The aim of this present work was to develop a rapid, simple, sensitive and accurate method for the determination of iodate and periodate ions in water, based on the reaction of periodate and iodate with pyrogallol red (PGR) in acidic media. The system was monitored spectrophotometrically by measuring the decrease in absorbance of the dye at 470 nm. In spectroscopic calibra-

tions where a partial least squares (PLS) calibration model is used to predict a product quality such as a concentration [12–15], it is often encountered that the first component (or latent variable) accounts for a very high percentage of the variation in the spectral data  $\mathbf{X}$  and only a low percentage of variation of the product quality  $\mathbf{Y}$ . If more components are calculated the calibration model slowly improves. However, models with a large number of components are not desirable in terms of interpretability and robustness. Multivariate calibration is increasingly being used for developing quantitative relations between a set of calibration data usually digitized spectra contained in a data matrix  $\mathbf{X}$  and a set of concentrations or reference values of sample properties contained in a matrix  $\mathbf{Y}$ . Preprocessing the data before calibration is often employed in order to reduce the effect of systematic variations, which are not related to the measured parameters.

In 1998, Wold and coworkers published the original paper on orthogonal signal correction [16–20]. The objective was to construct a filter that removes from the spectral matrix ( $\mathbf{X}$ ) only the part that definitely is unrelated to  $\mathbf{Y}$ . It was followed by a number of different OSC filters. Svensson et al., Goicoechea and Olivieri and Trygg have reviewed

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and compared different OSC methods. The OSC component should fulfill three requirements simultaneously:

- it should contain (large) systematic variation in  $\mathbf{X}$ ;
- it should be predictable by  $\mathbf{X}$  (in order to be applied to future data);
- it should be orthogonal to  $\mathbf{Y}$ .

These requirements fit the description of structured noise in  $\mathbf{X}$ . Thus, the OSC filter can be used as a preprocessing step prior to latent variable regression modeling, e.g. PLS, to remove the structured noise in  $\mathbf{X}$ . The general, single-component OSC model of  $\mathbf{X}$  can be expressed by

$$\mathbf{X} = \mathbf{t}_{\text{osc}} \mathbf{p}_{\text{osc}}^T + \mathbf{E}$$

where  $\mathbf{t}_{\text{osc}} = \mathbf{X} \mathbf{w}_{\text{osc}}$  and  $\mathbf{Y}^T \mathbf{t}_{\text{osc}} = 0$ . Here  $\mathbf{t}_{\text{osc}}$ ,  $\mathbf{p}_{\text{osc}}$  and  $\mathbf{w}_{\text{osc}}$  represent the single OSC component.  $\mathbf{E}$  is the OSC-filtered matrix subsequently used in the latent variable regression model. More than one OSC component can be identified and removed from  $\mathbf{X}$ . For additional OSC components the filter is applied to the  $\mathbf{E}$  matrix. The OSC component is similar to the standard PLS component, as it has two sets of loading vectors, but with the difference that the score vector  $\mathbf{t}_{\text{osc}}$  is orthogonal to  $\mathbf{Y}$ . Comparisons between the results of different OSC filters are often made with regard to the number of OSC components removed. However, such comparisons are difficult to make, because one OSC component can be derived from different multicomponent prediction models.

In this paper, we wish to compare results of the PLS with and without preprocessing step using OSC in kinetic determination of two important anions.

## 2. Experimental

### 2.1. Reagents

All the chemicals used were of the analytical reagent grade. Doubly distilled water was used for the preparation of solutions. Stock solution of periodate ( $2000 \mu\text{g ml}^{-1}$ ) and iodate ( $2000 \mu\text{g ml}^{-1}$ ) was prepared by dissolving of 0.5 g  $\text{NaIO}_4$  (Merck) and 0.5 g  $\text{NaIO}_3$  (Merck) in water in 250 ml volumetric flasks. Pyrogallol red solution ( $2 \times 10^{-4} \text{ M}$ ) was prepared by dissolving 0.02 g of the dye (Merck) in a mixture of 1:1 EtOH/ $\text{H}_2\text{O}$  in a 250 ml volumetric flask.

### 2.2. Apparatus

Electronic absorption measurements were carried out on a CECIL 9000 spectrophotometer (slit width 0.2 nm and scan rate  $300 \text{ nm min}^{-1}$ ) using quartz cell of 1 cm path length.

### 2.3. Computer hardware and software

The absorbances versus time data from the spectrophotometer were collected with a laboratory-written program, in

QUICKBASIC, and transferred to Pentium IV computer for subsequent manipulation by PLS program. The data treatment was done with MATLAB for Windows (Mathworks, version 6.5). PLS and OSC-PLS programs (for calibration, prediction and experimental design) with PLS-toolbox (Eigenvector Company).

## 3. Procedure

In order to find the linear dynamic range of concentration of iodate and periodate, univariate calibration was performed for each anion. Different concentrations of solutions of iodate ( $10\text{--}1200 \mu\text{g ml}^{-1}$ ) and periodate ( $10\text{--}1400 \mu\text{g ml}^{-1}$ ) were prepared. A portion ( $20 \mu\text{l}$ ) of the solution containing iodate or periodate was injected into a quartz cell (containing 2 ml solution  $10^{-4} \text{ M}$  PGR and  $0.05 \text{ M}$   $\text{H}_2\text{SO}_4$ ) to measure the decrease in absorbance at 470 nm during 300 s. The calibration set contains 35 standard solutions. The concentration ranges of two analytes were between 0.5–12 and  $0.5\text{--}14 \mu\text{g ml}^{-1}$  for  $\text{IO}_3^-$  and  $\text{IO}_4^-$ , respectively. A validation set comprises of 12 synthetic mixtures containing various concentrations of two anions was also prepared by using the same stock solutions.

## 4. Results and discussion

The reaction between pyrogallol red (PGR) and mixture of iodate and periodate is fast in sulfuric acid media. PGR is a dye that can undergo oxidation and produce colorless compound. The system was monitored spectrophotometrically by measuring the decrease in absorbance of the dye at 470 nm (Fig. 1).

### 4.1. Effect of variables

The effect of temperature, ionic strength and concentration of  $\text{H}_2\text{SO}_4$  and PGR on reaction rate were studied separately for iodate and periodate and their optimum values were selected. The influence of temperature on reaction rate in the range of  $5\text{--}40^\circ\text{C}$  was studied under optimized conditions. The results show that the absorbance change increases with increasing temperature up to  $25^\circ\text{C}$ , and then levels off for the higher temperature. Therefore, a temperature of  $25^\circ\text{C}$  was selected (Fig. 2). The effect of ionic strength was investigated using  $0.05\text{--}0.5 \text{ M}$   $\text{NaNO}_3$  solution. This parameter had no effect on the reaction rate, then  $0.1 \text{ M}$  of  $\text{NaNO}_3$  was used. The reaction takes place in acidic media. The effect of  $\text{H}_2\text{SO}_4$  concentration in the range of  $0.01\text{--}0.1 \text{ M}$  on the reaction of iodate and periodate was studied separately. The results show that the absorbance change increased with  $\text{H}_2\text{SO}_4$  concentration up to  $0.03 \text{ M}$ , whereas greater amounts of the acid do not affect the absorbance change. Therefore,  $0.05 \text{ M}$   $\text{H}_2\text{SO}_4$  was selected for the subsequent studies (Fig. 3). The influence of PGR concentration on the reaction

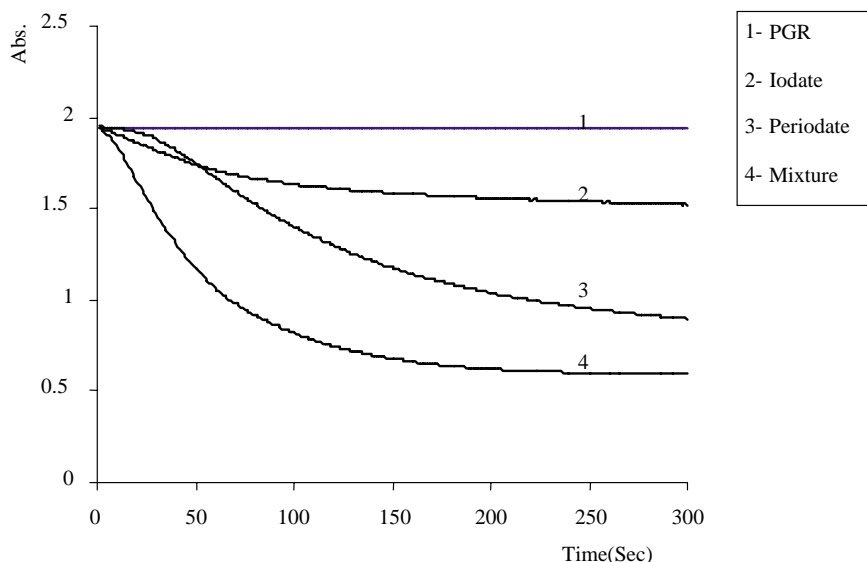


Fig. 1. Absorbance–time plot at 470 nm.

rate in the range of  $4 \times 10^{-5}$  to  $2.8 \times 10^{-4}$  M was studied. The results show that by increasing PGR concentration up to  $9 \times 10^{-5}$  M, the absorbance change increases and after that decreases (Fig. 4). The results show that the first 300 s was the best working time at which maximum rate of reaction was achieved.

#### 4.2. Univariate calibration

Under the optimum conditions the calibration graphs were obtained. The calibration graphs were constructed by plotting absorbance change values during first 300 s after initiation of reaction as a function of analyte concentration. The linear regression equation for the calibration graph for iodate for the concentration range of  $0.1\text{--}12 \mu\text{g ml}^{-1}$  was  $\Delta A =$

$0.005 + 0.0914C_{\text{IO}_3^-}$  ( $r^2 = 0.9945$ ,  $n = 16$ , Fig. 5) and for periodate in the concentration range of  $0.1\text{--}14 \mu\text{g ml}^{-1}$  was  $\Delta A = -0.0165 + 0.0778C_{\text{IO}_4^-}$  ( $r^2 = 0.9917$ ,  $n = 16$ , Fig. 6), where  $\Delta A$  is the absorbance change and  $C$  the iodate and periodate concentration in  $\mu\text{g ml}^{-1}$ .

#### 4.3. Multivariate calibration

Multivariate calibration methods such as PLS require a suitable experimental design of the standard belonging to the calibration set in order to provide good prediction. Two sets of standard solutions were prepared. The calibration set contains 35 standard solutions. The compositions of the calibration mixtures were selected at five levels for two anions (Table 1). For prediction set, it was used of 12 test mixtures.

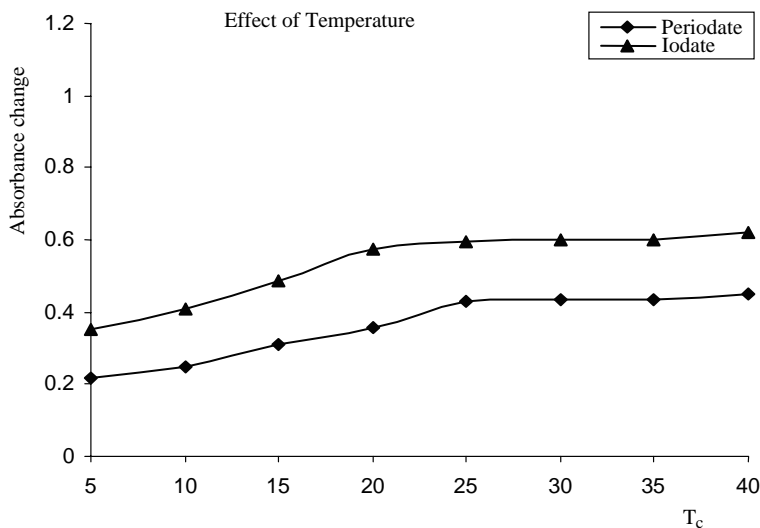


Fig. 2. Effect of temperature on the reaction rate. Condition:  $\text{H}_2\text{SO}_4 = 0.05$  M,  $\text{NaNO}_3 = 0.1$  M,  $\text{PGR} = 1.2 \times 10^{-4}$  M,  $\text{IO}_4^- = 5 \mu\text{g ml}^{-1}$  and  $\text{IO}_3^- = 5 \mu\text{g ml}^{-1}$ .

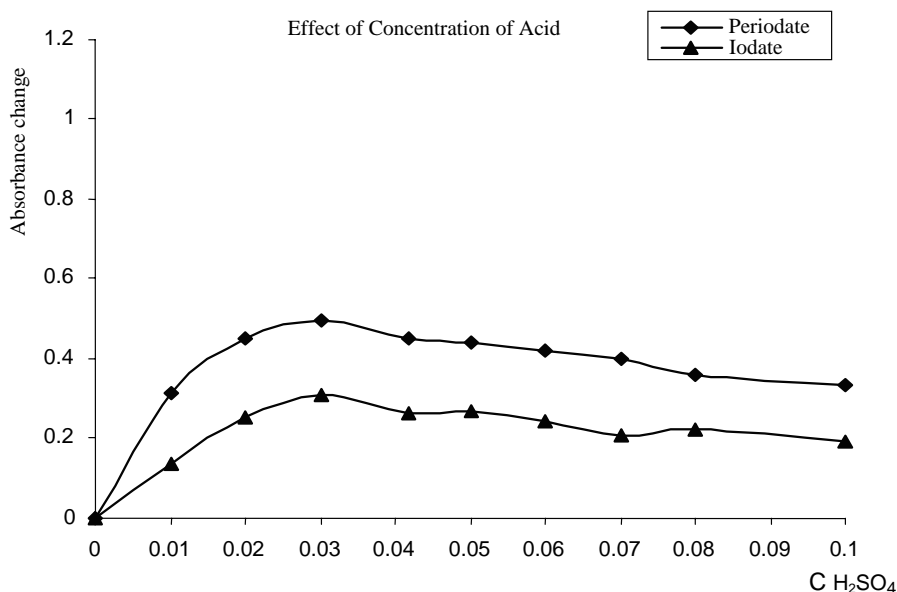


Fig. 3. Effect of acid concentration on the reaction rate. Condition: PGR =  $2.0 \times 10^{-4}$  M,  $\text{H}_2\text{SO}_4$  = 0.01–0.1 M,  $\text{IO}_4^-$  =  $8.0 \times 10^{-4}$  M,  $\text{IO}_3^-$  =  $8.0 \times 10^{-4}$  M,  $\text{NaNO}_3$  = 0.1 M and  $T = 25^\circ\text{C}$ .

The concentration of each anion solution was in the linear dynamic range of the anion for the prediction of each solution.

#### 4.3.1. Selection of optimum number of factors

To select the number of factors in PLS algorithm, in order to model the system without over fitting the concentration data, a cross-validation method, leaving out one sample at a time, was used [21–23]. Given the set of 35 calibration spectra, the PLS calibration on 34 spectra were performed, and using this calibration the concentration of the compounds in the sample left out during calibration was predicted. This process was repeated 35 times until each calibration sample had been left out once. The predicted concentration of the

compounds in each sample was compared with the known concentration of the compound in this reference sample and prediction error sum of squares (PRESS) was calculated. The PRESS was calculated in the same manner each time a new factor was added to PLS models. The maximum number of factors used to calculate the optimum PRESS was selected 18 (half the number of standard plus one). One reasonable choice for the optimum number of factors would be that number which yielded the minimum PRESS. However, using the number of factors that yields a minimum PRESS,  $h^*$ , leads to overfitting. A better criterion for selecting the optimum number of factors involves the comparison of PRESS from models with fewer than  $h^*$  factors. The  $F$ -statistic was used to determine significance. Haaland

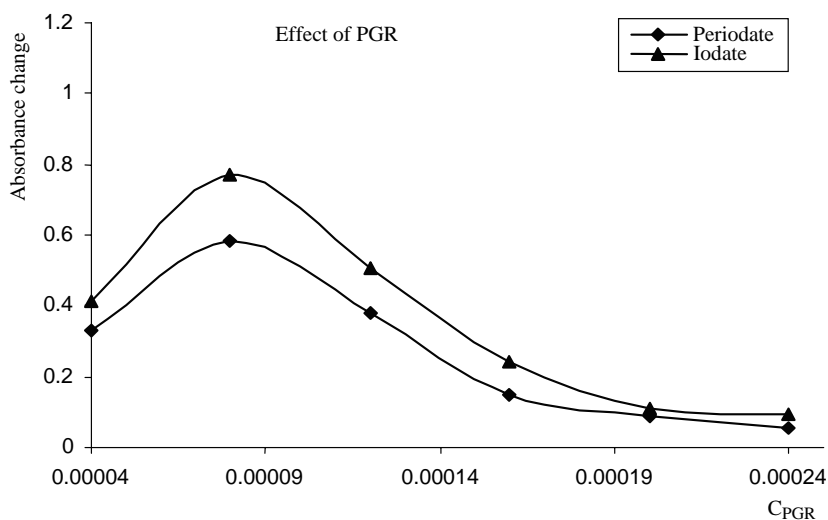


Fig. 4. Effect of PGR concentration on the reaction rate. Condition:  $\text{NaNO}_3$  = 0.1 M,  $\text{H}_2\text{SO}_4$  = 0.05 M,  $\text{IO}_4^-$  =  $5 \mu\text{g ml}^{-1}$ ,  $\text{IO}_3^-$  =  $5 \mu\text{g ml}^{-1}$  and PGR =  $4.0 \times 10^{-5}$  to  $2.4 \times 10^{-4}$  M.

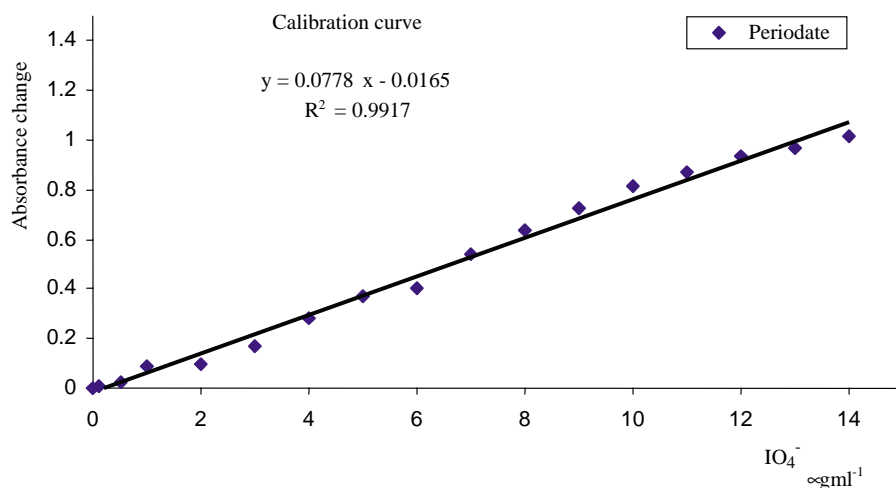


Fig. 5. Calibration curve of changing in absorbance vs. periodate concentration. Condition:  $\text{H}_2\text{SO}_4 = 0.05 \text{ M}$ ,  $\text{NaNO}_3 = 0.1 \text{ M}$ ,  $\text{PGR} = 1.0 \times 10^{-4} \text{ M}$ ,  $T = 25^\circ\text{C}$  and  $\text{IO}_4^- = 0.1\text{--}14 \text{ } \mu\text{g ml}^{-1}$ .

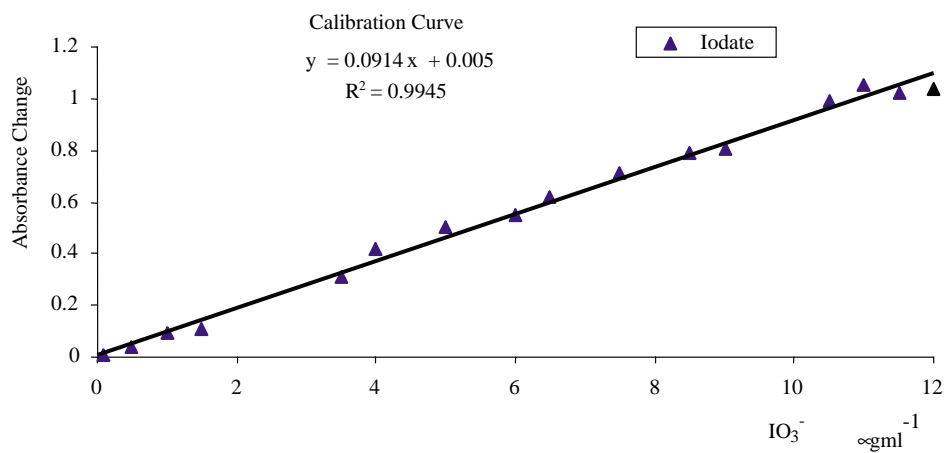


Fig. 6. Calibration curve of changing in absorbance vs. iodate concentration. Condition:  $\text{H}_2\text{SO}_4 = 0.05 \text{ M}$ ,  $\text{NaNO}_3 = 0.1 \text{ M}$ ,  $\text{PGR} = 1.0 \times 10^{-4} \text{ M}$ ,  $\text{IO}_3^- = 0.1\text{--}12 \text{ } \mu\text{g ml}^{-1}$  and  $T = 25^\circ\text{C}$ .

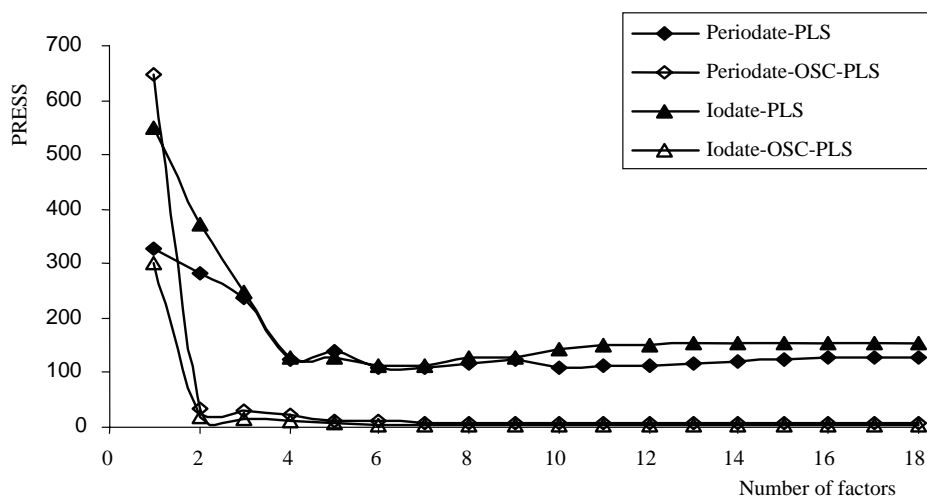


Fig. 7. Plot of PRESS vs. number of factors.

and Thomas empirically determined that  $F$ -ratio probability of 0.75 is a good choice [21–23]. So, we also selected the optimum number of factors for the PRESS values of the  $F$ -ratio probability, which drops below 0.75. The number of factors selected as optimums by this procedure were listed in Table 3 for periodate and iodate. In Fig. 7, the PRESS obtained by optimizing the calibration matrix of the absorbance data with PLS and OSC–PLS is shown. The results obtained by applying PLS and OSC–PLS methods to the 12 problem samples are listed in Table 2. Table 2 also shows the percentage error for prediction of two series of iodate and periodate.

The plot of the predicted concentration versus actual values are shown in Fig. 8 for periodate and iodate (line equations and  $R^2$  values are also shown).

#### 4.3.2. Statistical parameters

For the constructed model, four general statistical parameters were selected to evaluate the prediction ability of the model for simultaneous determination of periodate and iodate. For this case, the predicted concentrations of each sample in calibration step were compared with the actual concentrations. The first statistical parameter is the root mean square difference (RMSD). This parameter is an expression of the average error in the analysis for each component in training samples. The RMSD was obtained by the following formula:

$$\text{RMSD} = \left[ \frac{1}{n} \sum_{i=1}^n (\hat{c}_i - c_i)^2 \right]^{0.5} \quad (1)$$

The second statistical parameter was relative error of prediction (REP) that shows the predictive ability of each component, and is calculated as

$$\text{REP} (\%) = \frac{100}{\bar{c}} \left[ \frac{1}{n} \sum_{i=1}^n (\hat{c}_i - c_i)^2 \right]^{0.5} \quad (2)$$

Table 1

Composition of a training set containing two anions

Mixture no.	Periodate	Iodate
1	0.5	0.0
2	0.0	0.5
3	0.5	0.5
4	0.5	3.0
5	0.5	6.0
6	0.5	9.0
7	0.5	12.0
8	4.0	0.0
9	0.0	3.0
10	4.0	0.5
11	4.0	3.0
12	4.0	6.0
13	4.0	9.0
14	4.0	12.0
15	7.0	0.0
16	0.0	6.0
17	7.0	0.5
18	7.0	3.0
19	7.0	6.0
20	7.0	9.0
21	7.0	12.0
22	10.0	0.0
23	0.0	9.0
24	10.0	0.5
25	10.0	3.0
26	10.0	6.0
27	10.0	9.0
28	10.0	12.0
29	14.0	0.0
30	0.0	12.0
31	14.0	0.5
32	14.0	3.0
33	14.0	6.0
34	14.0	9.0
35	14.0	12.0

The predictive applicability of a regression model is described in various ways. The most general expression is the standard error of prediction (S.E.P.) and standard error of calibration denoted by SEC which is given in the following

Table 2

Prediction set composition and their predicted value for the determination of periodate and iodate by PLS and OSC–PLS

Added mixture ( $\mu\text{g ml}^{-1}$ )		PLS				OSC–PLS			
Periodate	Iodate	Found		Error (%)		Found		Error (%)	
		Periodate	Iodate	Periodate	Iodate	Periodate	Iodate	Periodate	Iodate
4.0	3.0	3.5	2.5	−12.5	−16.7	4.0	3.0	0.0	0.0
4.0	12.0	4.0	12.5	0.0	4.2	4.0	12.0	0.0	0.0
7.0	9.0	7.0	9.5	0.0	5.5	6.9	9.0	−1.4	0.0
14.0	6.0	11.5	8.0	−17.8	33.3	14.1	6.1	0.7	1.6
5.0	7.0	5.0	6.5	0.0	−7.1	5.2	7.1	4.0	1.4
10.0	6.0	10.0	7.5	0.0	25.0	10.0	6.0	0.0	0.0
8.0	8.0	8.0	8.5	0.0	6.2	8.1	8.1	1.3	1.3
10.0	12.0	10.5	11.5	5.0	−4.2	10.0	12.0	0.0	0.0
14.0	6.0	13.5	5.5	−3.6	−8.3	14.0	6.0	0.0	0.0
14.0	9.0	13.5	9.0	−3.6	0.0	14.1	9.1	0.7	1.1
7.0	12.0	9.0	12.0	28.6	0.0	7.0	12.0	0.0	0.0
4.0	6.0	3.0	5.5	−25.0	−8.3	3.9	6.0	2.5	0.0

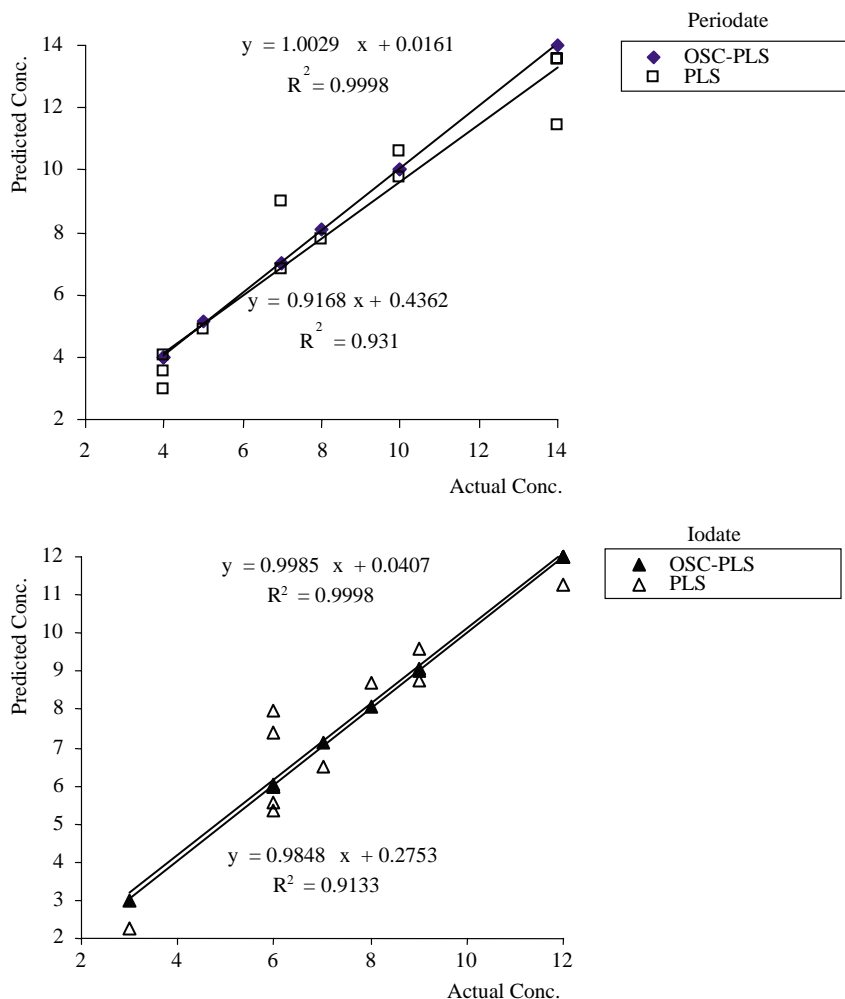


Fig. 8. Plots of predicted concentration vs. actual concentration for periodate and iodate by PLS and OSC-PLS.

formula:

$$\text{SEP (SEC)} = \left[ \frac{\sum_{i=1}^n (\hat{c}_i - c_i)^2}{n - 1} \right]^{0.5} \quad (3)$$

The square of the correlation coefficient ( $R^2$ ), which is indicated the quality of fit of all the data to a straight line is calculated for the checking of each calibration, and is calculated as

$$R^2 = \frac{\sum_{i=1}^n (\hat{c}_i - \bar{c})^2}{\sum_{i=1}^n (c_i - \bar{c})^2} \quad (4)$$

where  $c_i$  is the actual concentration of the analyte in the sample  $i$ ,  $\hat{c}_i$  the predicted concentration of the analyte in the sample  $i$ ,  $\bar{c}$  the mean of true concentration in the prediction set and  $n$  is the total number of samples used in the prediction set. The statistical results (RMSD, REP, SEP,  $R^2$ ) are summarized in Table 3.

#### 4.3.3. Effect of foreign ions

The interference due to several cations and anions was studied in detail. For these studies different amounts of the

ionic species were added to a mixture of periodate and iodate containing  $2.0 \mu\text{g ml}^{-1}$  of each. The starting point was  $2000 \mu\text{g ml}^{-1}$  of interference to mixture of anions, and if the interference occurred the concentration of interference was progressively reduced until interference ceased. The tolerance limits were taken as those concentrations causing changes not greater than  $\pm 5\%$  in the concentration of analytes. The tolerance limits for the different ions studied are listed in Table 4.

Table 3  
Statistical parameters obtained by applying the PLS and OSC-PLS methods to the synthetic mixtures

Parameter	PLS		OSC-PLS	
	Periodate	Iodate	Periodate	Iodate
RMSD	1.0104	0.9487	0.0866	0.0577
REP (%)	12.004	9.8821	1.0289	0.7217
SEP	1.0553	0.9874	0.0905	0.0603
$R^2$	0.8978	0.9707	0.9809	0.9914
No. of factors	6	4	4	3



Table 4

The maximum tolerance value of various cations and anions on the measurement of mixture periodate and iodate containing 2 and 2  $\mu\text{g ml}^{-1}$ , respectively

Interfering ions	Tolerance limit ( $\mu\text{g ml}^{-1}$ )
$\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{Br}^-$ , $\text{SO}_4^{2-}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$	1000
$\text{Ni}^{2+}$ , $\text{Cd}^{2+}$	800
$\text{CN}^-$ , $\text{CO}_3^{2-}$ , $\text{Zn}^{2+}$ , $\text{Co}^{2+}$	500
$\text{CH}_3\text{COO}^-$ , $\text{F}^-$ , $\text{C}_2\text{O}_4^{2-}$ , $\text{B}_4\text{O}_7^{2-}$ , $\text{Cu}^{2+}$	400
$\text{Al}^{3+}$ , $\text{BrO}_3^-$	200
$\text{Ba}^{2+}$ , $\text{Fe}^{2+}$	10
$\text{I}^-$ , $\text{WO}_4^{2-}$ , $\text{Hg}^{2+}$	<1

## 5. Conclusion

Determination of periodate and iodate based on the addition reaction of mixture two anions with PGR with the PLS and OSC–PLS modeling was established, with good prediction ability in the synthetic mixtures. Results show that OSC–PLS is an excellent calibration method to determination of periodate and iodate by kinetic procedures without the need of any previous knowledge about rate constants values. Analysis of the results for the two-component system revealed the differences in the accuracy of prediction between the two procedures for periodate and iodate. The best recovery values are obtained by the application of OSC–PLS model for absorbance data. The good agreement clearly demonstrates the utility of this procedure for the simultaneous determination of periodate and iodate in synthetic mixtures.

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