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Spectrophotometric Simultaneous Kinetic Determination of Iodide and Iodate Using Partial Least-Squares Calibration Method in a Single Kinetic Run

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Abstract

A rapid, sensitive and versatile kinetic method is presented for the simultaneous spectrophotometric determination of iodide and iodate by partial least-squares regression (PLS) using original and derivate data named as absorbance and rate data. The method is based on the catalytic effect of the cited anions on the reaction rate between Ce(IV) and As(III) in 2 mol l^{-1} sulfuric acid medium. The Savitzky-Golay convolution method is used for calculating and smoothing the rate data. Results show that PLS is an excellent calibration method to resolve the mixtures of two anions by first-order or pseudo first-order kinetic procedures without any previous knowledge about rate constant values. The 26 calibration solutions were made of iodide and iodate in the range of 10-48 and 55-235 ng ml^{-1}. The RMSEP calculated for 12 test solutions are 0.1756, 0.5074 and 0.2327, 0.9197 for the absorbance and rate data for iodide and iodate respectively. The application of the method was confirmed by analysis of these anions in real matrix samples.

Keywords: Simultaneous determination; Iodide; Iodate; Kinetic; Spectrophotometric

1. Introduction

The resolution of mixtures from differences in the reaction rate with a common reagent is very commonplace in analytical laboratory [1-5]. The different techniques and procedures associated with these types of methods have been reviewed [6-10].

Iodide and iodate are anions, which appear together in many real samples. Several techniques such as chromatography [11], high performance liquid chromatography [12], neutron activation analysis [13,14], *etc.*, have been used for the simultaneous determination of these anions in different samples.

Nowadays the simultaneous determinations of the desired constituents in the real samples are of interest and there are several reports on the resolution of multi-component systems [15-18]. Especially by appearance and development of the new instrument with the high technological facility to gather spectral information in a short time domain, the demand to have facile methods to handle these massive data is relevant. So the multivariate statistical analysis methods gain precise

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focus to overcome these requisites. The application of these new developed methods are started from the middle of the 1980 and increased day to day until this time. Thus the precise understandings of these new approaches are essential for accurate applications to solve the analytical problems and also other sub-branch of the related topics. According to these findings the appearance of a new interdisciplinary field like chemometrics is inevitable.

The theory and uses of multivariate calibration in the analytical chemistry are by now solidly established and have been subject of the several reviews and monographs [19-27], therefore only a brief outline of the method are described here.

The partial least squares (PLS) is a quantitative spectral decomposition technique that is closely related to principal component regression (PCR). However, in PLS the decomposition is performed in a slightly different fashion. Instead of firstly decomposing the spectral matrix into a set of eigenvectors and scores, and regressing them against the concentrations as a separate step, PLS actually uses the concentration information during the decomposition process. This causes spectra containing higher constituent concentrations to be weighted more heavily than those with low concentrations. Thus, the eigenvectors and scores calculated using PLS is quite different from those of PCR. The main idea of PLS is to get as much concentration information as possible into the first few loading vectors.

There are actually two versions of PLS algorithm; PLS-1 and PLS-2. The differences between these methods are subtle but have very important effects on the results. In PLS-1, a separate set of scores and loading vectors is calculated for each constituent of interest. In this case, the separate set of scores and loading vectors are specifically tuned for each constituent, and therefore, should give more accurate predictions than PCR or PLS-2. In this paper, the PLS-1 and PLS was written in MATLAB and used to determine the concentration of iodide and iodate in synthetic and real samples according to algorithms described in references [19-29].

In the present study in continuation our efforts to apply chemometrics methods in solving some problems in the universe of the analytical methods [30-37] a kinetic method for simultaneous determination of iodide and iodate in mixtures in a single kinetic run was developed on the basis of partial least-squares (PLS) using the original absorbance and first derivative named as rate data. The method is based on the catalytic effect of the iodide and iodate on the reaction between Ce(IV) and As(III).

2. Experimental

2.1. Instruments and Software

A 662 probe type photometer (Metrohm) and model D1 thermostatically controlled bath (HAAKE) were used.

The absorbance *versus* time data from photometer were collected through a laboratory-written program, in QuickBasic, and transferred to a Pentium II computer for subsequent manipulation by PLS program. Data processing (PLS calibration method and calculating and smoothing the rate) were performed using laboratory-written program in MATLAB for windows (Mathworks, Version 5.3).

2.2. Reagents

The entire chemicals used were of analytical-reagent grade. Triple distillated water was used throughout. Stock solution (1000 $\mu g\,ml^{-1}$) of each anion was prepared from KI and KIO_3 (Merck). The working solutions were obtained by dilution of the stock solutions as required before use. A stock As(III) solution (0.20 $mol\,l^{-1}$) prepared by dissolving 4.95 g of As_2O_3 (Merck) in 20 ml of 1 $mol\,l^{-1}$ NaOH (Merck) then diluted using appropriate amount of H_2SO_4. The concentration of the H_2SO_4 in the final solution was checked to be 2 $mol\,l^{-1}$. A stock Ce(IV) solution (0.04 $mol\,l^{-1}$) was prepared by dissolving $(NH_4)_4Ce(SO_4)_4.2H_2O$ (Merck) in 2 $mol\,l^{-1}$ H_2SO_4.

2.3. Procedure

A 5 ml portion of Ce(IV) solution was mixed with 1 ml portion of As(III) solution. The resulting solution was diluted to 10 ml by H_2SO_4 (final concentration 2 $mol\,l^{-1}$). The solution was placed in a jacketed glass cell and the photometers probe was immersed into the solution and fixed by using a suitable holder. The solution was thermostated at the 25°C, while a magnetic stirrer was mixing it continuously. Then a given amount of the mixture of iodide and iodate was injected instantaneously through a syringe with the photometer on and absorbance-time data at 430 nm was collected by a microprocessor system.

3. Results and Discussion

In the absence of iodide or iodate, the reaction between Ce(IV) and As(III) was very slow. However, when traces amounts of the cited anions is present, the reaction will occur in a few minutes and the color of Ce(IV) fades quickly.

3.1. Effect of Variables

The effect of temperature, acidity and concentration of reactants on reaction rate were studied. The effect of temperature on the rate reaction with and without cited anions were studied. The reaction rate was found to increase with the increasing temperature. Therefore, 25°C was chosen as an adequate temperature.

The Effect of acidity of medium on the rate of reaction was investigated by addition of H_2SO_4 solution with different concentrations to the reaction medium. The optimum result was obtained at the range 1.5-2.5 mol l^{-1} of H_2SO_4. The effect of concentration of As(III) on the reaction rate was studied, in the range 0.01-0.02 mol l^{-1} of As(III), the reaction rates were almost unchanged with respect to the concentration of As(III) for both iodide and iodate; thus 0.015 mol l^{-1} As(III) was used in the procedure. The reaction rate decreased with the decrease in Ce(IV) concentration for both iodide and iodate, particularly for iodide. To have a compromise for both reactions the concentration of Ce(IV) was specified at 4×10^{-5} mol l^{-1}.

3.2. Linear Calibration Range

Under these optimum-working conditions the linear calibration range of iodide and iodate were investigated. The linear ranges were checked by using the fixed time and slope methods. Iodide and iodate showed linear behavior at concentration ranges 10-50 and 50-250 ng ml^{-1}, respectively.

The absorbance *versus* time plot and the first derivative or ν (rate) *versus* time plot for the reaction between As(III) and Ce(IV) in the absence and presence of iodide, iodate and their mixtures are shown in Figure 1. The variation in the absorbances for each solution was recorded at 400 nm in 1 second intervals (~300 data point in 300 sec).

The Savitzky-Golay convolution method was used for calculating rate and smoothing rate data [28]. The 17-point method was selected for this work. After data collection, the variables were mean centered (zero mean) for subsequent manipulation by PLS program.

3.3. Multivariate Calibration

To perform the simultaneous determination of iodide and iodate, a PLS calibration method was trained by training set solutions for the resolution of the mixtures of iodide and iodate in future test solutions (prediction set). For this purpose a synthetic set of 38 solutions of mixtures of cited anions were prepared in the linear range as stated above. The compositions of calibration and prediction standards are summarized in Tables 1 and 2, respectively. The concentrations of the entire solutions were selected from the random generated routine in the Microsoft Excel. From the series, 26 solutions were chosen for calibration, and the other 12 solutions were used as prediction solutions. The selection of the test or prediction solutions were performed on the basis of their distributions in the plot of the first principal component *versus* second principal component (score plot), shown in Figure 2. As it is wise from the analytical point of view the geometrical location of the prediction set are inside the calibration set, *i.e.* all the variation in the prediction set are spanned by the calibration set in the constructing the calibration model.

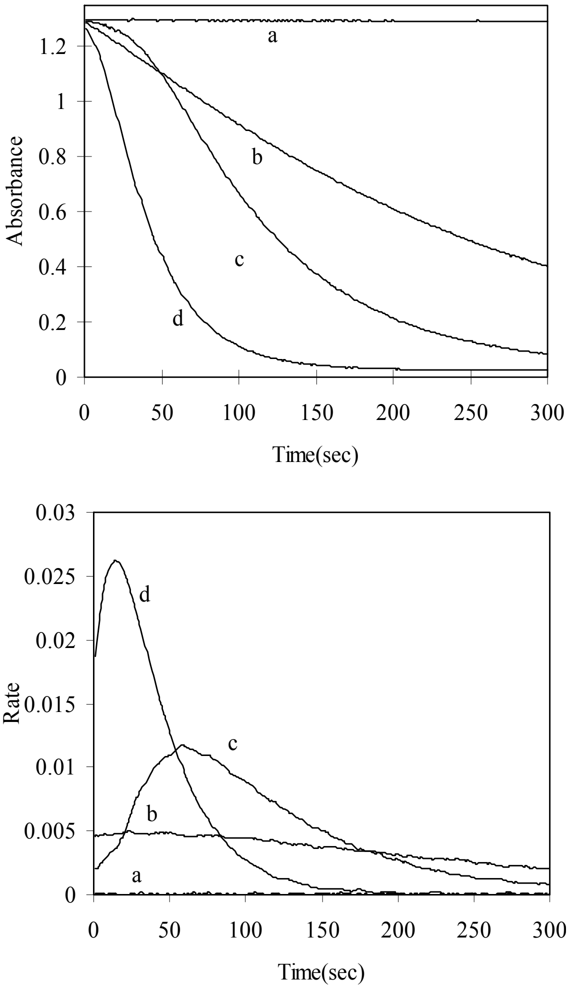

Figure 1. Absorbance-time plot (up) and rate-time plot (bottom): (a); blank, (b); Pure iodide (35 ppb), (c); Pure iodate (160 ppb), (d); Mixture of iodide (35 ppb) and iodate (200 ppb), Ce(IV) (0.00098 M); As(III) (0.015 M); H_2SO_4 (2 M).

Table 1. Calibration set composition

Solution number	Iodide (ng ml^{-1})	Iodate (ng ml^{-1})
1	48	170
2	18	60
3	20	95
4	30	142
5	38	195
6	20	112
7	22	205
8	12	110
9	18	140
10	25	85
11	37	140
12	13	60
13	35	185
14	44	122
15	28	105
16	26	175
17	21	145
18	10	135
19	12	60
20	20	170
21	17	235
22	31	110
23	25	55
24	30	155
25	40	175
26	25	88

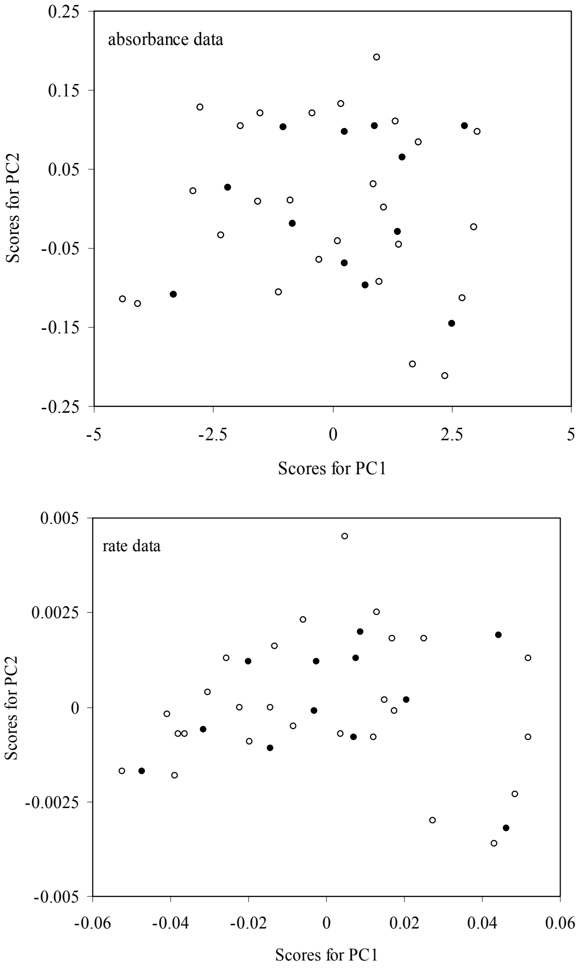

Figure 2. Distribution of iodide and iodate for the synthetic series on score plots. ○; Calibration, ●; Prediction. Top: Absorbance-time data, Bottom: Rate-time data.

3.3.1. Selection of Optimal Number of Factors

To select the number of factors in the PLS algorithm, in order to model the system without overfitting the concentration data, a cross-validation method [38], leaving out one sample at a time, was used. Given the set of 26 calibration spectra, the PLS-1 calibration on 25 calibration spectra were performed, and using this calibration, the concentrations of the compounds, in each sample were compared with the known concentrations of the compounds in this reference sample and the prediction error sum of squares (PRESS) was calculated. The PRESS was calculated in the same manner each time a new factor was added to the PLS model. According to the Haaland and Thomas criterion [39], the maximum number of factors was allowed for obtaining the optimum numbers of factors which was 14 factors (half the number of total standards plus one). The PRESS's are minimum values at the number of factors 9 and 10 for absorbance data and 11 and 11 for rate data for iodide and iodate, respectively. The large number of significant factors at optimum PRESS reveals that there is some nonlinearity in the system. To tackle this problem the nonlinear calibration methods like artificial neural network or fuzzy logic can be applied. The application of a more simple calibration method like PLS in the present study has priority over nonlinear and complex ones. The plot of the PRESS *versus* number of factors for two anions for the two types of data, original and first derivative data are shown in Figure 3.

Table 2. Prediction set composition and their predicted values

	Actual value (ng ml^{-1})		**Predicted value (ng ml^{-1})**							
			Absorbance		*Recovery (%)*		*Rate*		*Recovery (%)*	
Mixture	Iodide	Iodate	Iodide	Iodate	Iodide	Iodate	Iodide	Iodate	Iodide	Iodate
P1	23	90	23.0	90.7	100.0	100.8	23.0	88.8	100.0	98.7
P2	22	150	21.9	149.1	99.5	99.4	21.8	149.5	99.1	99.7
P3	12	70	11.9	70.2	99.2	100.3	11.8	70.1	98.3	100.1
P4	35	130	34.5	129.6	98.6	99.7	34.7	129.5	99.1	99.6
P5	32	160	32.2	160.5	100.6	100.3	32.1	160.8	100.3	100.5
P6	45	155	45.1	155.5	100.2	100.3	45.0	155.5	100.0	100.3
P7	25	230	25.1	230.3	100.4	100.1	24.8	228.1	99.2	99.2
P8	15	135	15.0	135.5	100.0	100.4	14.9	136.1	99.3	100.8
P9	30	135	30.1	134.3	100.3	99.5	30.0	134.0	100.0	99.3
P10	27	150	26.9	150.5	99.6	100.3	27.1	150.1	100.4	100.1
P11	24	95	24.1	95.0	100.4	100.0	24.4	93.8	101.6	98.7
P12	20	170	20.1	169.9	100.5	99.9	20.5	170.2	102.5	100.1

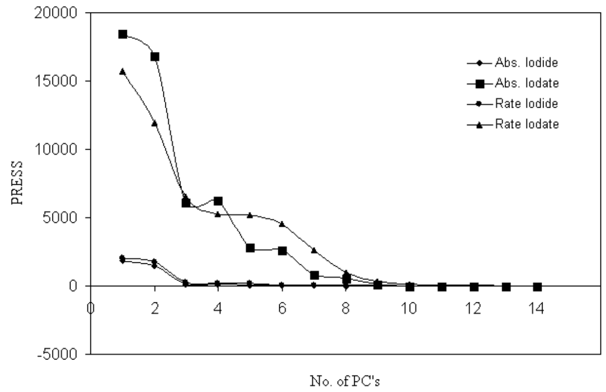

Figure 3. The PRESS *versus* number principal components for two type data for iodide and iodate in prediction set.

The results obtained by applying PLS algorithm to the 12 prediction solutions are listed in Table 2. Table 2 also shows the recovery for prediction series of iodide and iodate mixtures. The recoveries were also quite acceptable. The range of the recovery percent values for iodide and iodate are: 98.6-100.6%, 99.4-100.8% and 98.3-102.5%, 98.7-100.8%, by using absorbance and rate data, respectively.

One of the good tools which commonly is used to show the ability of the calibration model to predict the concentration of the involved species in the unknown solutions is the plot of the calculated concentrations *versus* experimental in the prediction set. As shown in the Figure 4 plots there are good correlations between the calculated against analytical concentration for the two anions and using two type of the kinetic data. The line equations and also R^2 are shown in the Figure 4.

3.3.2. Statistical Parameters

For the optimized model two parameters were calculated, as some type of figures of merit, to assess the prediction ability of the model for absorbance and rate data. The first is the root mean square difference (RMSEP), which is an indication of the average error in the analysis, for each component:

$$\mathrm{RMSEP} = \left[\frac{1}{n}\sum_{i=1}^{n}(\hat{x}_i - x_i)^2\right]^{0.5}$$

The RMSEP values are an estimate of the absolute error of prediction for each component. The second is the square of the correlation coefficient (R^2), which is an indication of the quality of fit of all data to a line;

$$R^2 = \sum_{i=1}^{n}\left(\hat{x}_i - \bar{x}\right)^2 / \sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2$$

where x_i is the true concentration of the analyte in the sample i, $\hat{x}_i$ represents the estimated concentration of the analyte in the sample i, $\bar{x}$ is the mean of the true concentration in the prediction set, and n is the total number of sample used in the prediction sets. The number of factors, PRESS at the optimum number of

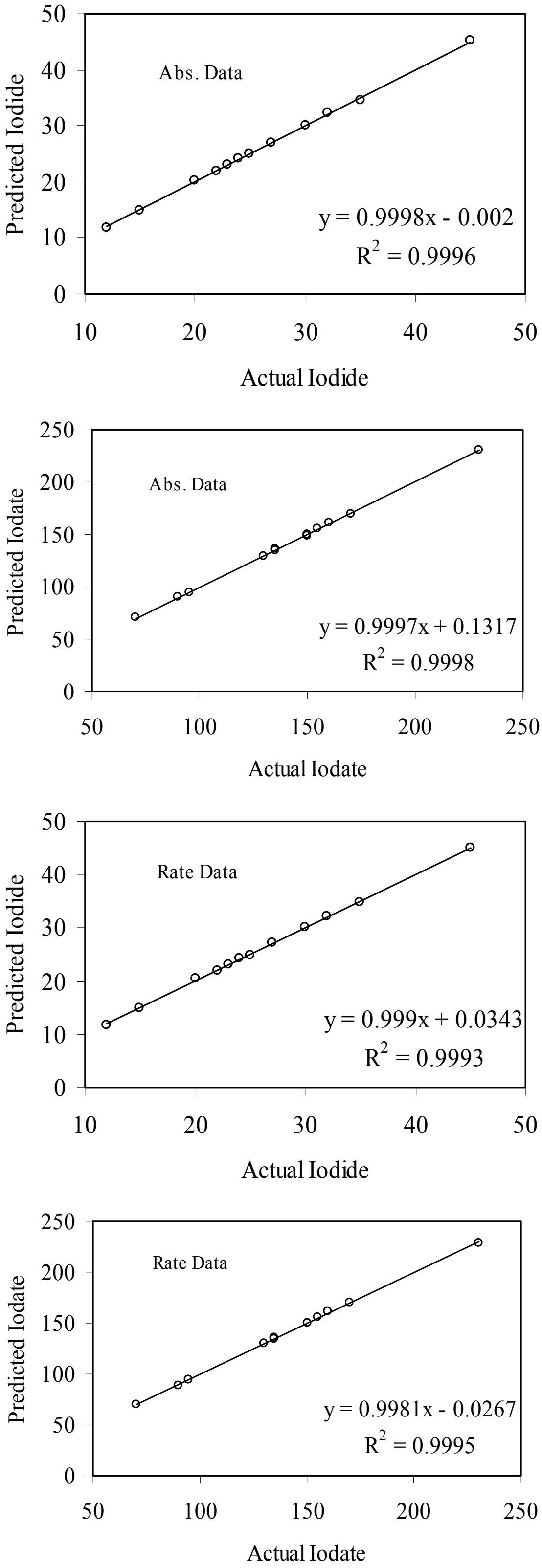

Figure 4. Plots of predicted concentration *versus* actual concentration for iodide and iodate in the prediction set.

Table 3. Statistical parameters in determination of iodide and iodate for prediction set

Type	**Absorbance**		**Rate**	
Anions	*Iodide*	*Iodate*	*Iodide*	*Iodate*
NPC*	9	10	11	11
PRESS	1.9	1.5	53	61
RMSEP	0.1756	0.5074	0.2327	0.9197
R^2	0.9999	0.9996	0.9987	0.9967

*Number of principal components

factors, RMSEP and R^2 were calculated for the iodide and iodate concentration in prediction set are summarized in Table 3. It is noteworthy to mention that the two kinds of data, original kinetic curve and the first derivative, the rate data, did not show any superiority over each other and the difference more or less are within the effect of the random error effects in the measurement.

3.4. Effect of Foreign Ions

Most of the common anions and cations had no interfering effect in this study. It was found that 100-fold excess of K(I), Ca(II), Mg(II), Co(II), Mn(II), Fe(III), Pb(II), SO_4^-, NO_3^-, Cl^- and Br^- had no interference effect in the determination of the two anions. It was found that Cd(II), Pd(II) and $S_2O_3^{-2}$ interfered when present 4 or 5 fold excess and Hg(II), Ag(I) interfered seriously when present even at 1 fold excess of the cited anions.

3.5. Method Applicability

In order to test the accuracy and applicability of these methods, the optimized calibration model was applied in the analysis of the real samples with different matrices, urine sample, a fontal sample, Taq-e-Bostan and a vegetable juice sample. Table 4 shows the results obtained for the analysis of these real matrix samples. As the result shows the calibration model constructed by PLS and kinetic data is able to predict the concentrations of iodide and iodate in real samples.

4. Conclusion

The salient features of the proposed procedure for the determination of iodide and iodate in synthetic and real samples are simplicity, high sensitivity and precision of the method. The method can be easily adapted for handling large numbers of samples and there is also

Table 4. Application of the optimized model for the analysis of real sample

			Absorbance				Rate			
Real matrix	*Added (ng ml^{-1})*		*Found (ng ml^{-1})*		*Recovery (%)*		*Found (ng ml^{-1})*		*Recovery (%)*	
	Iodide	Iodate	Iodide	Iodate	Iodide	Iodate	Iodide	Iodate	Iodide	Iodate
Urine	35	140	34.5	139.6	98.6	99.7	35.0	141.1	100.0	100.8
Water (Taq-e-Bostan)	25	100	25.0	101.6	100.0	101.6	24.8	103.4	99.2	103.4
Vegetable juice	25	75	24.9	73.7	99.6	98.3	24.8	70.4	99.2	93.9

potential for automation. The good results obtained with this procedure, calibration model and PLS, demonstrate that this procedure could be a useful tool for simultaneous determination of iodide and iodate in synthetic and real samples. As the effect of the iodide and iodate as catalysts on the oxidation of the As(III) by Ce(IV) in acidic medium is clear, it is interesting to determine iodide and iodate in a single kinetic run. Since the catalytic effect on the reaction rate is just due to changing the rate constants and the simultaneous effect of the two catalysts generates a collinear problem and prevents the direct determination of the two species. So in the present case, probably there are some sources that cause PLS modeling can differentiate between two species as catalysts and leave the determination with acceptable level of the errors.

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