Variation of ratio kinetic profiles as a simple and novel spectrophotometric method for the simultaneous kinetic analysis of binary mixtures

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Abstract: In this paper, a new and very simple kinetic – spectrophotometric method is developed for the simultaneous determination of binary mixtures without prior separation steps. The method is based on the calculation of the variation of ratio kinetic profiles. The mathematical explanation of the procedure is also illustrated. The proposed method can be used for the simultaneous determination of two analytes A and B that react with the same reagent to give the same absorbing species. In order to evaluate the applicability of the method, theoretical and experimental data were tested. The results from experimental data relating to the simultaneous spectrophotometric determination of Co(II) and V(IV) based on their oxidation reactions with Fe (III) in the presence 1,10-phenanthroline (Phen) in micellar media are presented as a real model for the resolution of the binary systems. The applicability of the method to tap water and synthesized alloy samples was also assessed by spiking experiments with different amounts of Co(II) and V(IV).

Keywords: kinetic analysis; binary mixture; variation of ratio kinetic profiles; spectrophotometry.

INTRODUCTION

The spectrophotometric analysis of multicomponent mixtures shows that the quantification of compounds continues to be a difficult problem when there is no spectral difference between the components. Kinetic – spectrophotometric methods are good alternatives in such cases.[1] A number of differential kinetic methods have been developed for resolving mixtures of analytes with similar or identical spectra that cannot be resolved by equilibrium-based methods.[2–5] The simultaneous kinetic determination of such analytes is usually based on the diffe-

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rence in their reaction rate constants. The difference between the rate constants must be large enough for differential kinetic methods to discriminate the rate constants and for a successful handling of the univariate data.[6] However, in cases where the sample matrix is complex or the analytes are present at low concentration levels, their reaction rates might be very similar and their similar chemical properties result in mutual interference. Under such conditions, the selectivity of the univariate approach is very low and the prediction is poor.[7]

Recently, different two-way and three-way chemometric methods were used for multicomponent determination using kinetic – spectrophotometric data.[8–10] Chemometric methods have been used for the determination of different analytes and several reviews have been published on the subject.[11–13] However, the development of a simple method is very important. Afkhami and Bahram developed a new method for the simultaneous determination of binary mixtures of analytes with different kinetic profiles. The method is based on the mean centering (MC) of ratio kinetic profiles.[7]

Bosch-Reig *et al*. established the fundamentals for the application of the H--point standard addition method (HPSAM) to kinetic data,[14] for the simultaneous determination of binary mixtures or for the calculation of analyte concentrations completely free from bias errors. For these purposes, there are two variants of the HPSAM. One is applied when the reaction of one component is faster than that of the other or when the latter does not occur at all; this variant of the method is based on the assumption that only analyte X evolves with time and the other species Y or interferents do not evolve with time or have the same absorbance over the study interval. The other variant of the method is used when the rate constants of the two components are time-dependent. In this case, the two species in a mixture of X and Y evolve with time, c_X (concentration of analyte) and A_Y (the absorbance of the interferent) can be calculated by plotting the analytical signal ΔA_{t1-t2} against the added concentration of X at two wavelengths λ_1 and λ_2. The absorbances of the Y component provided at these two wavelengths are the same (A_Y), and, thus, so are the ΔA_{t1-t2} values.[14–16] However, when X and Y react with the same reagent to give the same absorbing species, this variant of HPSAM cannot be applied.

So far, a considerable amount of research effort has been devoted towards introducing and exploiting the concept of variation for analyzing kinetic systems.[17,18] The variation of signals is obtained by subtracting the zero-point signal (first signal) from each signal at each time. The contribution of inert compounds, compounds with constant signal over a period of time, can be easily removed in the calculation of variation. This approach can be useful for eliminating the interference from signal-stable components.

In the present work, variation of the ratio profiles was used for binary kinetic profiles resolution as well as the simultaneous determination of binary mixtures.

The mathematical explanation of the procedure is also demonstrated. After a modeling procedure, the method was successfully applied to the simultaneous analysis of binary mixtures of cobalt and vanadium based on their oxidation reactions with Fe(III) and 1,10-phenantroline in micellar media without any preliminary separation. The resolution procedure was based on the reaction rate differences.

EXPERIMENTAL

Apparatus and software

The absorption measurements were realized on a Shimadzu UV-1650 PC spectrophotometer, using 1.0 cm quartz cells. All spectra were saved in ASCII format and transferred to a PC computer for subsequent manipulation. The data were handled using Microsoft Excel and Matlab software (version 7.1).

Reagents and solutions

All experiments were performed with analytical grade chemicals and doubly distilled water. A stock Fe(III) solution (7.14×10^{-3} mol dm^{-3}) was prepared by dissolving 0.144 g of Fe(NO$_3$)$_3$·9H$_2$O (Merck) in water and diluting to 50 ml. Stock solutions of Co(II) (1.69×10^{-3} mol dm^{-3}) and V(IV) (1.96×10^{-3} mol dm^{-3}) were prepared by dissolving appropriate amounts of Co(NO$_3$)$_6$·4H$_2$O and VOSO$_4$·5H$_2$O (Merck), respectively, in water. A stock solution of 1,10-phenantroline (0.04 mol dm^{-3}) was prepared by dissolving 0.369 g of the hydrochloride form of the compound in 2–3 ml ethanol in a 50 ml volumetric flask and dilution to the mark with double-distilled water. Acetate buffer solution (0.1 mol dm^{-3}) of pH 3.5 was prepared from sodium acetate and acetic acid. A cetyl trimethyl ammonium bromide (CTAB) stock solution (0.05 mol dm^{-3}) was prepared by dissolving 0.456 g of the compound in double-distilled water.

Procedure

The proposed method was used for the simultaneous determination of cobalt and vanadium based on the different rates of their oxidation reaction with Fe(III) in the presence of 1,10-phenanthroline (phen) in micellar media without any preliminary separation.

Two ml buffer solution (pH 3.5), 0.50 ml of Phen stock solution, 0.2 ml of CTAB stock solution, 1.0 ml of Fe(III) and appropriate volumes of V(IV) and Co(II) were added to a 5.0 ml volumetric flask and made up to the mark with water. For each measurement, about 2.0 ml of the above solution was transferred to a spectrophotometric cell and the kinetic profile *vs.* time was recorded at 510 nm in the time range 10–300 s.

RESULTS AND DISCUSSION

Theoretical background

Consider two analytes, X and Y, that react with the same reagent to give the same absorbing species, P, according to the following scheme:

$$X + R \xrightarrow{k_X} P \tag{1}$$

$$Y + R \xrightarrow{k_Y} P \tag{2}$$

$$\frac{d[P]}{dt} = k_X c_X + k_Y c_Y \tag{3}$$

where, k_X, k_Y and c_X, c_Y are the rate constants and concentrations for X and Y, respectively.

The formation of the product, P, can be monitored by recording its absorption spectrum as a function of time or by measuring the absorbance at a fixed wavelength. It is assumed that the reactions involved in both processes follow first or pseudo-first order kinetics with respect to the concentrations of the analytes. If the absorbance is assumed proportional to the amount of formed product, then, in the absence of interactions, between the kinetics of both analytes, it will be given by:

$$A_t = \varepsilon \sum_i E_{(i,t)} c_i^0 \qquad (4)$$

where, c^0 is the initial concentration of the specie i to be quantified for first-order reactions and E is the kinetic profile, which can be given as:

$$E_{(i,t)} = \varepsilon(1 - \exp(-k_i t)) \qquad (5)$$

By analogy between $E_{(i,t)}$ and the molar absorptivity in the Beer–Lambert Law in spectrophotometric determinations, the variation of the absorbance as a function of time at a given wavelength can be used to construct a "kinetic profile", $A_{t1}, A_{t2}, ..., A_{tn}$ at times $t_1, t_2, ..., t_n$.

For a binary mixture of X and Y, if Eq. (4) is divided by $E_{Y(t)}$, corresponding to the kinetic profile of a standard solution of Y in a binary mixture, the ratio profile (R) is obtained in the form of Eq. (6) (to enable the dividing operation, zero values of $E_{Y(t)}$ should not be used in the divisor):

$$R = \frac{A_{(t)}}{E_{Y(t)}} = \frac{E_{X(t)} C_X}{E_{Y(t)}} + C_Y \qquad (6)$$

where $E_{X(t)}$ and $E_{Y(t)}$ are the kinetic profiles of X and Y, respectively. If the variation of R is calculated (by subtracting the zero-point signal (first signal) from each signal at each time), since the variation of a constant C_Y is zero, Eq. (7) is obtained:

$$\mathrm{Var}(R) = \mathrm{Var}\left(\frac{E_{X(t)} C_X}{E_{Y(t)}} \right) \qquad (7)$$

Equation (7) is the mathematical foundation of the multi-component analysis that enables the determination of the concentration of each of the active compounds in the solution (X in this equation) without interference from the other compound of the binary system (Y in these equations). As Eq. (7) shows, a linear relation exists between the magnitude of $\mathrm{Var}(R)$ and the concentration of X in the solution.

A calibration curve can be constructed by plotting Var(R) against the concentration of X in standard solutions of X or in standard binary mixtures. For more sensitivity, the magnitude of Var(R) corresponding to maximum time can be measured.

Calibration graphs for Y are constructed as described for X.

Simulations

With the view of evaluating the performance of the proposed method for the analysis of a binary mixture, several sets of synthetic data were created to model the spectrophotometric data of two kinetic reactions (X and Y) with overlapping kinetic profiles (Fig. 1A). The use of simulated data enabled the effect of each variable on the performance of the considered method to be determined. The data were generated under a known model, *i.e.*, a first order kinetic reaction, and artificial noise was added. The kinetic profiles were created for six different samples with different concentrations of X, shown in Fig. 1B. The ratio profiles were obtained were obtained by dividing the kinetic profiles of the samples by the kinetic profile of B (Fig. 1C). Then, the variation of the ratio profiles was obtained by subtraction of the magnitude of the first point from the magnitude at each time (Fig. 1D). Finally, the concentration of compound X was determined by measuring the magnitude of the resulting profiles at 300 s, corresponding to the maximum on the time profile shown in Fig. 1D.

The obtained model can be validated with a series of 8 synthetic mixtures, containing the considered concentrations of components X and Y in different proportions those are randomly selected. The kinetic profiles of these samples are created (Fig. 2A). To predict the concentration of compound X in these synthetic binary mixtures, the kinetic profiles of the binary mixtures are divided by kinetic profile of Y, whereby the ratio profiles are obtained (Fig. 2B). Finally, variations of ratio profiles for these mixtures are obtained (Fig. 2C). In this step, the effect of the compound Y is removed from the profiles of the mixtures. The concentration of X in these synthetic mixtures was determined by measuring the magnitude at 300 s, corresponding to the maximum in the time profile. Plotting the actual *vs.* the predicted concentration of analyte in eight mixture samples was used to show the average error analysis and the quality of all data to a straight line (Fig. 2D). As can be seen, good agreement between both the actual and predicted concentrations is evident. The results unveil the applicability of the method for sample mixtures.

Preliminary study of the system

1,10-Phenanthroline (Phen) is frequently used for the spectrophotometric determination of bivalent iron.[19] In the presence of 1,10-phenanthroline, Fe(III) becomes a stronger oxidant and can easily oxidize some metal cations. The reduced
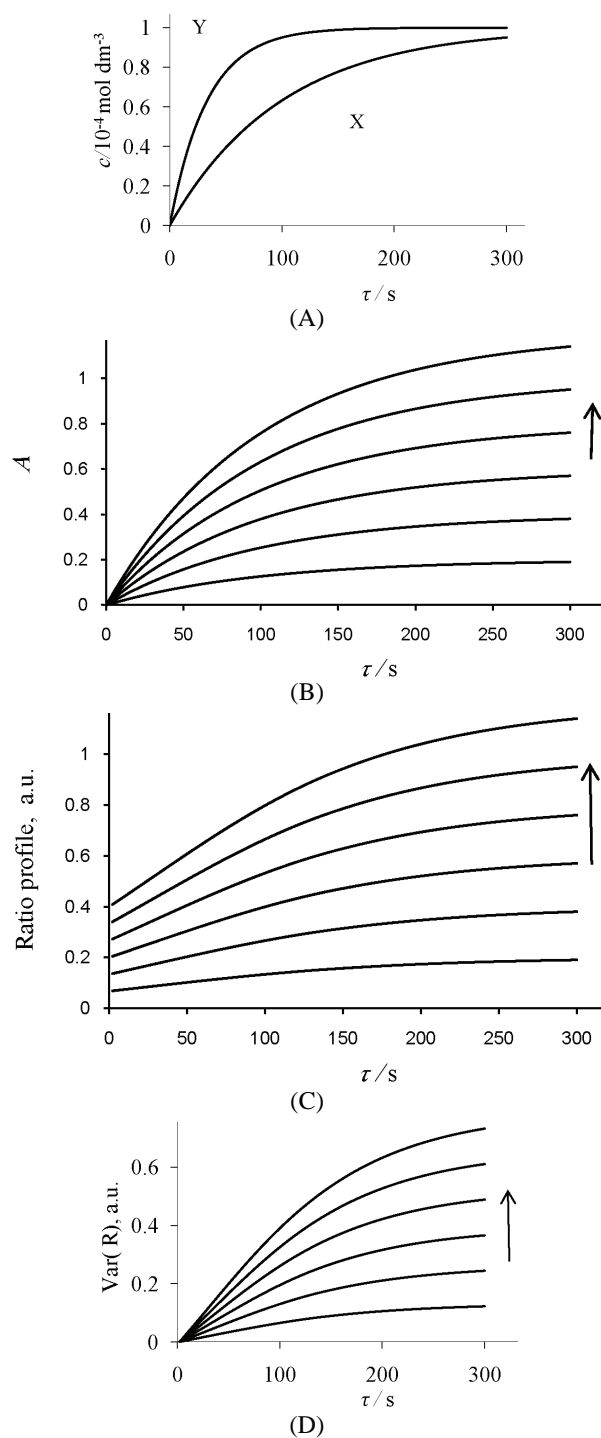
Fig. 1. The simulated pseudo--first order kinetic profiles of compounds X and Y (A), the simulated kinetic profiles of 2×10^{-5}–2×10^{-4} mol dm^{-3} of X (B), the ratio profiles that were obtained by dividing the kinetic profiles of X by the kinetic profile of Y (C), and variation of the ratio profiles (D).
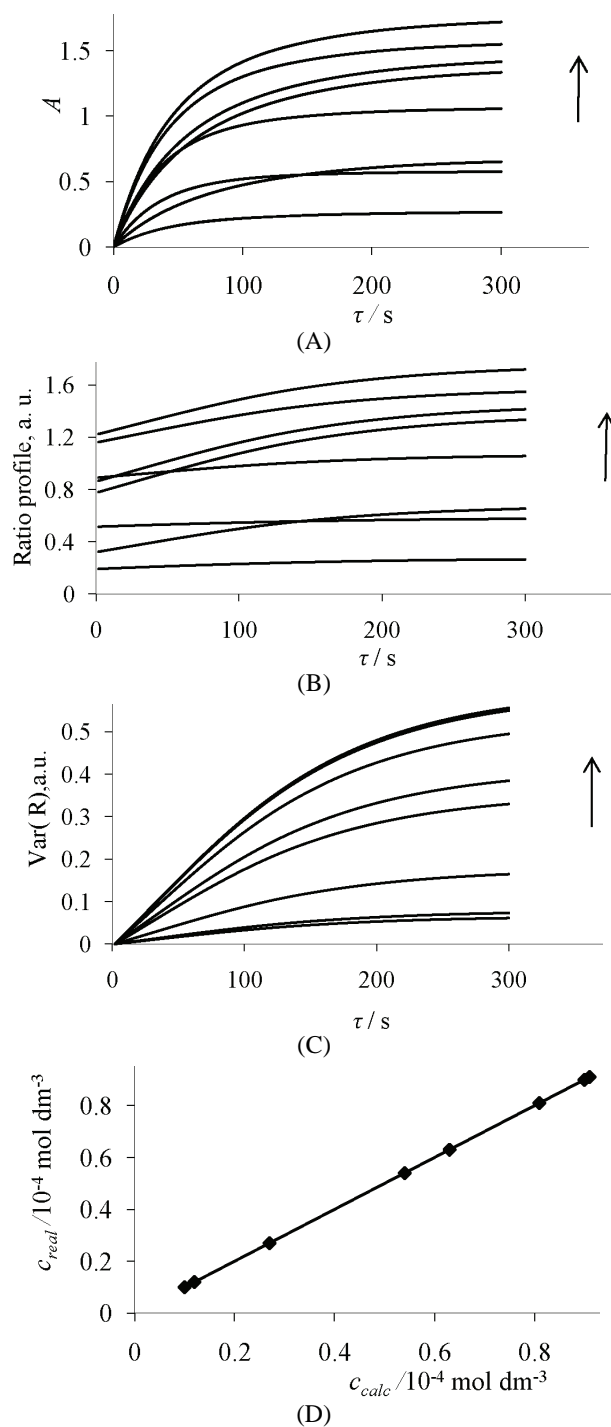
(A)

(B)

(C)

(D)

Fig. 2. The simulated kinetic profiles of randomly selected mixtures of X and Y (A), the ratio profiles that were obtained by dividing the kinetic profiles of the mixtures by the kinetic profile of Y (B), variation of the ratio profiles (C) and plots of the real values of concentration of X *vs.* the values found by proposed method (D).

product of the reaction, Fe (II), can form a colored complex with Phen. Its spectrum is shown in Fig. 3A. Thus, a visible spectrophotometric signal for the indirect monitoring the concentration of oxidizable analytes is formed.[20,21] Preliminary investigations showed that at pH 3.5 and 0.01 M cationic micellar solution of CTAB, V(IV) and Co(II) can be oxidized by Fe(III) in the presence of Phen at different rates. The common product in these reactions is the Fe(II)–Phen complex. The oxidation of V(IV) and Co(II) can be indirectly monitored by recording the absorbance at 510 nm, the λ_{max} of the Fe(II)–Phen complex. As Fig. 3B shows, the kinetic profiles of the oxidation reactions of Co(II) and V(IV) are different and hence can be used to their simultaneous determination.
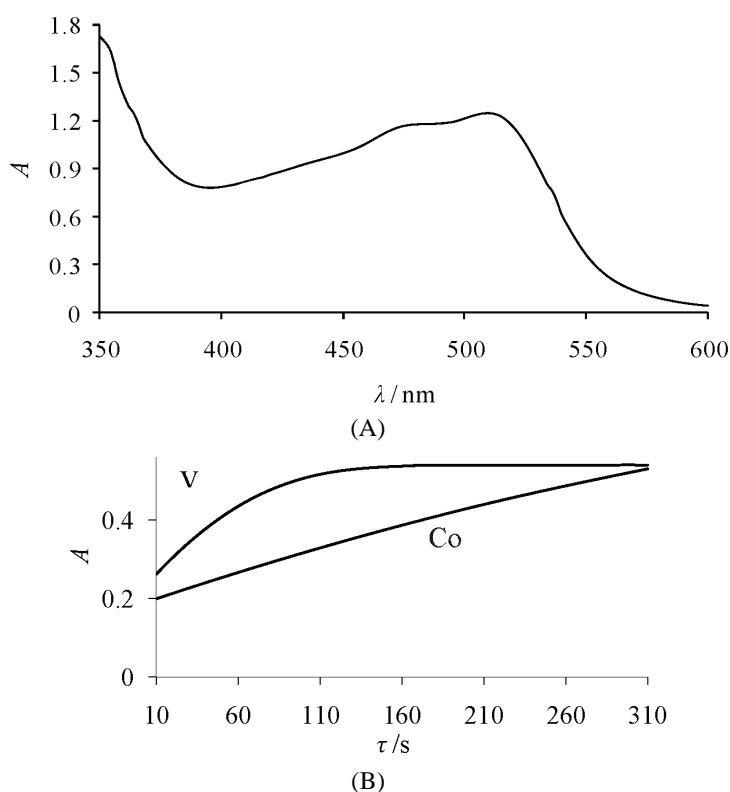

Fig. 3. Kinetic profiles of oxidation reaction of Co(II) (5×10^{-5} mol dm^{-3}) and V(IV) (5×10^{-5} mol dm^{-3}) with Fe(III) and Phen in micellar media, observed at 510 nm.

A 2×10^{-3} mol dm^{-3} Phen and 1.25×10^{-3} mol dm^{-3} Fe(III) solution (at least a 15-fold excess over the maximum concentration of the metal ions) was applied to obtain a pseudo-first order reaction with respect to the each of analyte concentrations.

Proposed method

The absorption kinetic profiles of standard Co(II) solutions of different concentrations were recorded at 510 nm in the time range 10–300 s (Fig. 4A) at 2 s
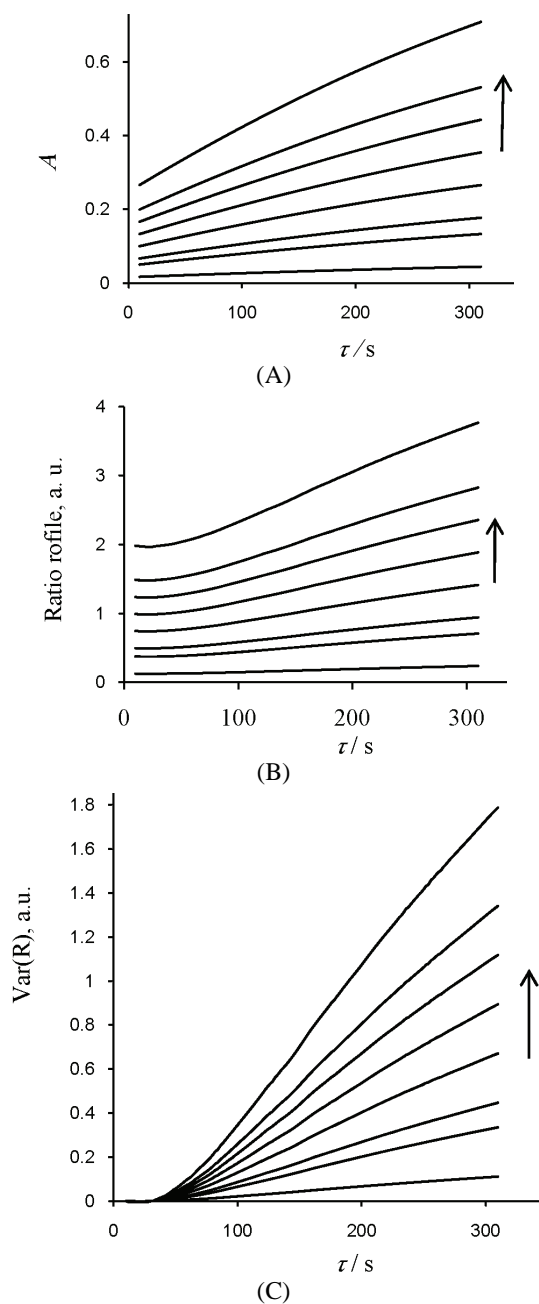

Fig. 4. The absorption kinetic profiles of standard solutions of Co(II) of different concentrations (A), the ratio profiles that were obtained by dividing the kinetic profiles of Co(II) by the kinetic profile of V(IV) (B) and the variation of the ratio profiles (C).

intervals and divided by the normalized kinetic profile of V(IV), whereby the ratio profiles were obtained (Fig. 4B). The variations of the ratio profiles were obtained by subtraction of the magnitude of the first point from all the other points of the ratio kinetic profile (Fig. 4C). The concentration of Co(II) was determined by measuring the magnitude at 300 s, corresponding to the maximum time shown in Fig. 4C. For the prediction of the concentration of Co(II) in synthetic binary mixtures and real samples, the same procedure was applied except that the kinetic profiles of the mixture were used instead of the kinetic profiles of a standard solution of Co(II).

For determination of V(IV) in the presence of Co(II), the same procedure was used except that the kinetic profiles were divided by the normalized kinetic profile of Co(II).

Analytical characteristics

Calibration curves of both components were obtained by plotting the magnitude of variation at 300 s against the concentration of the analytes and evaluation by linear regression. The characteristics of the calibration graph and the statistical parameters for determination of Co(II) and V(IV) are summarized in Table I.

TABLE I. Analytical characteristics of the analysis of Co(II) and V(IV) in binary mixtures by the proposed method

Analyte	Linear range mol dm^{-3}	Equation	Squared correlation coefficient (R^2)	Limit of detection (*LOD*) mol dm^{-3}
Co(II)	8.50×10^{-6}–1.35×10^{-4}	$Y = 1.30\times10^4 c + 0.0025$	0.9983	2.30×10^{-6}
V(IV)	9.80×10^{-6}–1.56×10^{-4}	$Y = 9.25\times10^3 c + 0.0063$	0.9958	4.11×10^{-6}

The model obtained in the calibration step was validated by the analysis by the proposed method of ten randomly selected synthetic mixtures containing different proportions of Co(II) and V(IV). The obtained results are given in Table II. The values of the root mean square difference (*RMSD*), the square of the correlation coefficient obtained when plotting the actual *vs.* the predicted concentrations (R^2), and the relative error of prediction (*REP*) for each component in the ten synthetic samples are included in Table II to show the average error in the analysis and the fitting quality of all data to a straight line.

Interference studies

For studying interferences, the influence of several ions was tested, including those that most frequently accompany Co(II) and V(IV) in real samples. The effect of interfering ions at different concentrations on the kinetic curve of the absorbance of a solution containing 5×10^{-5} mol dm^{-3} of each analyte was studied. An ion was considered as an interferent when its presence produced a variation in the absorbance of the sample greater than 5 %.

TABLE II. Statistical parameters of the analysis of Co(II) and V(IV) in the validation set by the proposed method ($RMSD = [(\text{sum}(c_{\text{real}}-c_{\text{found}})^2)/\text{sum}(c_{\text{found}})^2]^{1/2}$; $REP = 100\times \times[(\text{sum}(c_{\text{real}}-c_{\text{found}})^2)/n]^{1/2}$; R^2: correlation coefficient for the plot of c_{real} *vs.* c_{found})

Parameter	Co(II)	V(IV)
Recovery, %	101.04	98.01
RMSD	0.08	0.15
REP	3.52	5.18
R^2	0.9941	0.9915

Among the interfering ions tested, Mn(II), Ni(II), V(V), As(V), Cu(II), Cd(II), Zn(II), Al(III), Bi(III), Ce(III), Te(IV), Se(IV), Se(VI), Pb(II), Na(I), K(I), Ca(II) and the anions HSO_3^-, SO_4^{2-}, SO_3^{2-}, F^-, Cl^-, CO_3^{2-}, MoO_4^{2-}, CH_3COO^-, NO_3^- and I^- did not interfere at concentrations 1000 times higher than those of the analytes. However, Sn(II) and Sb(III) interfered at levels similar to those of Co(II) and V (IV) as they can also be oxidized by the Fe(III) and Phen system. The kinetic profiles of the oxidation reaction of Sn(II) and Sb(III) with Fe(III) and Phen in micellar media are shown in Fig. 5.
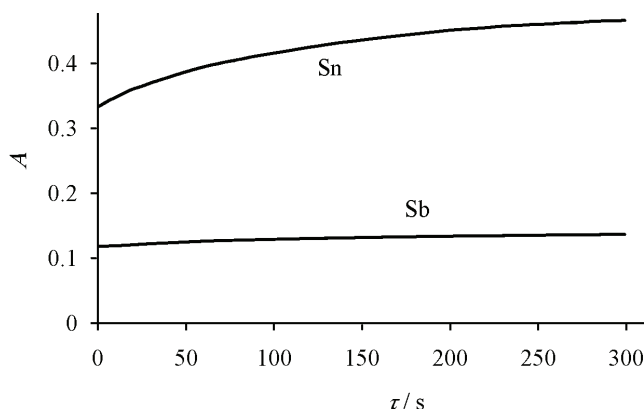

Fig. 5. Kinetic profiles of the oxidation reaction of Sn(II) and Sb(III) with Fe(III) and Phen in micellar media, observed at 510 nm.

Application

In order to assess the applicability of the proposed method, it was applied to the simultaneous determination of Co(II) and V(IV) in two samples: 1) a synthetic alloy sample and 2) tap water. The synthetic alloy sample contained Mn(II), Ni(II), V(V), Mo(VI), Al(III), Co(II) and V(IV). Moreover, the proposed method was applied for the simultaneous determination of Co(II) and Ni(II) in this synthetic sample. The results are given in Table III. The good agreement between the obtained results and known values indicate the successful application of the proposed method for simultaneous determination of Co(II) and Ni(II) in complex samples.

TABLE III. Statistical parameters of the analysis of Co(II) and V(IV) in real samples by the proposed method

Parameter	Co(II)		V(IV)	
	Synthetic alloy sample	Tap water	Synthetic alloy sample	Tap water
Recovery, %	104.21	102.14	106.31	97.62
RMSD	0.17	0.12	0.21	0.16
REP	3.67	2.09	6.75	5.58
R^2	0.9912	0.9938	0.9913	0.9926

Tap water samples were spiked with Co(II) and V(IV) and the proposed method was applied to determine the analytes. The accuracy of the proposed method was validated by a recovery method. As can be judged from Table III, the results can be considered acceptable.

CONCLUSIONS

A very simple and easy to understand method was proposed for resolving binary mixtures. Inert interferon (species having constant signal during the time range) do not interfere in the analysis. The proposed method is suitable for the analysis of binary mixtures with completely overlapping absorption spectra (same product formed in different reactions) that show a difference in their rate constants in a given reaction.

The proposed method is superior to other methods for the analysis of binary mixtures, namely: multivariate calibration methods (partial least square (PLS), net analyte signal (NAS) and artificial neural networks (ANN)) and the HPSAM. In comparison with multivariate calibration methods (PLS, NAS and ANN), the proposed method is simple, rapid and easy to understand and apply. In comparison with the HPSAM, the proposed method is simpler and more rapid and the presence of species with a constant absorbance at the measuring wavelength during the time of the experiment cannot interfere, while they interfere in the HPSAM. In addition, the proposed method eliminates the necessity of searching to find suitable wavelength. Furthermore, when both analytes react with the same reagent to give the same absorbing species but at different rates, the proposed method can be used for determining the analytes, whereas the HPSAM cannot be applied.

И З В О Д

ВАРИЈАЦИЈА ОДНОСА КИНЕТИЧКИХ ПРОФИЛА КАО ЈЕДНОСТАВАН НОВИ СПЕКТРОФОТОМЕТРИЈСКИ МЕТОД ЗА СИМУЛТАНУ КИНЕТИЧКУ АНАЛИЗУ БИНАРНИХ СМЕША

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У раду је развијен нови једноставан кинетички спектрофотометријски модел за одређивање бинарних смеша, без њихове предходне сепарације. Метод је заснован на израчунавању промене односа кинетичког профила. Приказано је математичко објашњење процедуре. Предложени метод може бити коришћен за симултано одређивање два аналита, А и Б, који реагују са истим реагенсом а који даје исту абсорбујућу врсту. Да би се испитала применљивост методе, модел је тестиран експериментално. Експериментални резултати се односе на симултано одређивање Co(II) и V(IV) базирано на њиховој оксидацији са Fe(III) у присуству 1,10-фенантролина у мицеларном медијуму који представља реални модел за раздвајање бинарних система. Применљивост методе је оцењивана у узорцима воде за пиће и синтетисаним легурама који су имали различит садржај Co(II) и V(IV).

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