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A novel spectrophotometric method for the simultaneous kinetic analysis of ternary mixtures by mean centering of ratio kinetic profiles

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Abstract

In this paper, a novel and very simple method was developed for the simultaneous spectrophotometric determination of ternary mixtures, without prior separation steps. The method is based on the mean centering of ratio kinetic profiles. The mathematical explanation of the procedure is illustrated. In order to investigate the applicability of the proposed method, it was applied to the simultaneous spectrophotometric determination of hydrazine, phenylhydrazine and acetylhydrazine based on their condensation reactions with *p*-(dimethylamino)benzaldehyde (DAB) and *p*-nitrobenzaldehyde (NB) in micellar sodium dodecyl sulfate (SDS) media as a typical ternary mixture. The analytical characteristics of the method such as accuracy, precision, relative standard deviation (R.S.D.) and relative standard error (R.S.E.) were calculated.

Keywords: Mean centering; Ratio kinetic profiles; Analysis of ternary mixtures

1. Introduction

Differences in kinetic behavior have been used extensively for the simultaneous determination of two or more components in mixtures. Many differential kinetic methods have been proposed for the analysis of mixtures of closely related species without prior separation. Application of kinetic–spectrophotometric methods of analysis to simultaneous determination have grown recently as the results of the incorporations of computerized data acquisition systems and the development of powerful mathematical treatments for processing the recorded information (e.g. multivariate calibration) [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 [2–6]. The simultaneous kinetic determination of such analytes is usually based on the difference in their reaction rate constants. The difference between the rate constants must be large enough for the differential kinetic methods to discriminate the rate constants and for successful handling of univariate data [7]. However, in the cases where the sample matrix is complex, the analytes are present at low concentration levels, their reaction rates might be very close to each other, and their similar chemical properties result in mutual interference, the selectivity of univariate approach is very low and the prediction is poor. Principal component regression (PCR) and partial least squares regression (PLS) are well known multivariate calibration procedures widely used in recent years for the simultaneous determination of analytes in mixtures by means of kinetic–spectrophotometric procedures [8].

Several methods based on the derivative of the ratio spectra have been reported for simultaneous determination of binary and ternary mixtures [9–17]. We proposed “the successive derivative ratio spectra” as a new spectrophotometric method for the simultaneous determination of ternary mixtures, without prior separation steps [18]. Unfortunately, the advantages

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of derivative spectra are at least partially offset by degradation in signal-to-noise ratio that accompanies obtaining derivatives.

We also proposed a novel and very simple method for the simultaneous determination of binary and ternary mixtures, without prior separation steps based on the mean centering of ratio spectra [19]. This method eliminates derivative steps and therefore signal-to-noise ratio is enhanced. After modeling procedure, the method has been successfully applied to the simultaneous analysis of binary mixtures of mefnamic acid and paracetamol and ternary mixtures of acetylsalysilic acid, ascorbic acid and paracetamol.

Recently, we applied mean centering of ratio kinetic profiles for the analysis of binary mixtures. The method has been successfully applied to the simultaneous analysis of binary mixtures of cobalt and nickel based on the kinetic profiles of their complexation reactions with 1-(2′-pyridylazo)-2-naphtol (PAN) in micellar media [20].

In the present work, we examined the applicability of the mean centering of ratio kinetic profiles for the analysis of ternary mixtures. The method was applied to the analysis of ternary mixtures of hydrazine, phenylhydrazine and acetylhydrazine based on their condensation reactions with *p*-(dimethylamino)benzaldehyde (DAB) and *p*-nitrobenzaldehyde (NB) in micellar sodium dodecyl sulfate (SDS) media as a typical real model and satisfactory results were obtained. The analytical characteristics of the method such as accuracy, precision, relative standard deviation (R.S.D.) and relative standard error (R.S.E.) show the applicability of the mean centering of ratio kinetic profiles for the analysis of ternary mixtures.

2. Theoretical background

Consider three analytes A, B and C that react with a common reagent to give the absorbing species to produce P_A, P_B and P_C, according to the following scheme:

$$A + R \xrightarrow{k_A} P_A \quad (1)$$

$$B + R \xrightarrow{k_B} P_B \quad (2)$$

$$C + R \xrightarrow{k_C} P_C \quad (3)$$

$$\frac{d[P]}{dt} = k_A C_A + k_B C_A + k_C C_C \quad (4)$$

where k_A, k_B, k_C and C_A, C_B, C_C are the rate constants and concentration amounts for A, B and C, respectively.

The reactions can be monitored by recording absorption spectra for products as a function of time or by measuring the absorbance with time at a fixed wavelength. It has been assumed that the reactions involved all processes to follow a first- or pseudo-first-order kinetics with respect to the analyte concentrations. If the absorbance is assumed to be proportional to the amount of product formed, then, in the absence of synergistic effects, the absorbance for the solution at time t is the sum of the absorbance obtained for each individual product:

$$A_{T(t)} = A_{P_{A,t}} + A_{P_{B,t}} + A_{P_{C,t}} \quad (5)$$

where $A_{P_{A,t}}$, $A_{P_{B,t}}$ and $A_{P_{C,t}}$ are the absorbances for the reaction products of analytes A, B and C, respectively. Eq. (5) can be rewritten as:

$$A_{T(t)} = \sum_i E_{(i,t)} C_i^0 \quad (6)$$

where C_i^0 is the initial concentration of the species i to be quantified and $E_{(i,t)} = \varepsilon_\lambda[1 - \exp(-kt)]$.

By analogy between $E_{(i,t)}$ and molar absorptivity (ε_λ) 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 ternary mixture of A, B and C, if Eq. (6) is divided by $E_{(c,t)}$ corresponding to the kinetic profile of a standard solution of C in a ternary mixture, the first ratio profile is obtained in the form of Eq. (7) (for possibility of dividing operation, the zero values of $E_{C(t)}$ should not be used in the divisor):

$$D = \frac{A_{T(t)}}{E_{C(t)}} = \frac{E_{A(t)} C_A}{E_{C(t)}} + \frac{E_{B(t)} C_B}{E_{C(t)}} + C_C \quad (7)$$

where $E_{A(t)}$ is the kinetic profile of A, $E_{B(t)}$ is kinetic profile of B and $E_{C(t)}$ is the kinetic profile of C. If Eq. (7) is mean centered (MC), since the mean center of a constant (C_c) is zero, Eq. (8) would be obtained:

$$MC(D) = MC\left[\frac{E_{A(t)} C_A}{E_{C(t)}}\right] + MC\left[\frac{E_{B(t)} C_B}{E_{C(t)}}\right] \quad (8)$$

By dividing Eq. (8) by $MC(E_{B(t)}/E_{C(t)})$, corresponding to the mean centering of the ratio of the kinetic profiles of B and C, the second ratio profile is obtained as Eq. (9) (as mentioned before, for possibility of dividing operation, the zero values of $MC(E_{B(t)}/E_{C(t)})$ should not be used in the divisor):

$$K = \frac{MC(D)}{MC(E_{B(t)}/E_{C(t)})} = \frac{MC(E_{A(t)} C_A / E_{C(t)})}{MC(E_{B(t)}/E_{C(t)})} + C_B \quad (9)$$

Now if Eq. (9) is mean centered, since the mean centering of a constant (C_B) is zero, Eq. (10) would be obtained:

$$MC(K) = MC\frac{MC(E_{A(t)} C_A / E_{C(t)})}{MC(E_{B(t)}/E_{C(t)})} \quad (10)$$

Eq. (10) is the mathematical foundation of multi-component analysis that permits the determination of concentration of each of the active compounds in the solution (A in this equation) without interfering from the other compounds of the ternary system (B and C in these equations). As Eq. (10) shows, there is a linear relation between the amount of MC(K) and the concentration of A in the solution.

A calibration curve could be constructed by plotting MC(K) against concentration of A in the standard solutions of A or in the standard ternary mixtures. For more sensitivity, the amount of MC(K) corresponding to maximum or minimum amount at time profile could be measured.

Calibration graphs for B and C could also be constructed as described for A.

3. Experimental

3.1. Apparatus

A Perkin-Elmer Lambda 45 UV/Vis spectrometer was used for recording and storage of UV–vis absorbance spectra and kinetic curves using quartz cells and slit width of 0.5 nm. A Metrohm model 713 pH-meter with a combined glass electrode was used for pH measurements. All calculations in the computing process were done in Matlab6.5 and Microsoft Excel for Windows. A simple program was written for this purpose in Matlab6.5.

3.2. Reagents

Triply distilled water and analytical-reagent grade chemicals were used. A stock solution of hydrazine (1000 $\mu g\,mL^{-1}$) was prepared by dissolving 0.4063 g of hydrazinium sulfate (Merck) in water and diluting to the mark with water in a 100-mL volumetric flask. A stock solution of phenylhydrazine (1000 $\mu g\,mL^{-1}$) was prepared by dissolving 0.1338 g of phenylhydrazinium chloride (Merck) in water and diluting to the mark in a 100-mL volumetric flask. A standard solution of acetylhydrazine (1000 $\mu g\,mL^{-1}$) was prepared by dissolving 0.1000 g of acetylhydrazine (Merck) in water and diluting to the mark in a 100-mL volumetric flask. A 0.2 M SDS was prepared by dissolving 14.4 g SDS (Merck) in water and diluting to the mark in a 250-mL volumetric flask. A stock solution of mixture of 0.01 M DAB and 0.025 M NB was prepared by dissolving 0.149 g DAB and 0.3775 g NB in ethanol and diluting to the mark with ethanol in a 100-mL volumetric flask. A 0.1 M HCl solution was prepared by diluting concentrated hydrochloric acid (Merck).

3.3. Procedure

A calibration graph for A is obtained by recording and storing the kinetic profile of standard solutions containing different concentrations of A, B and C. The stored kinetic profiles of the solutions of A are divided by standard kinetic profile of C according to Eq. (7). Then, mean centering of these vectors with respect to time are obtained according to Eq. (8) (for binary mixtures, the procedure was completed here and the minimum or maximum of these vectors with respect to time is used for the construction of calibration graph for A). After that, the residual vectors are divided by MC($E_{B(t)}/E_{C(t)}$) according to Eq. (9). The minimum or maximum of the mean centering of later profiles with respect to time (according to Eq. (10)) are used for the construction of calibration graph for A. For the prediction of concentration of A in synthetic ternary mixtures and real samples, the same procedure was used except that the kinetic profiles of the mixtures were used instead of the kinetic profiles of standard solution of A.

The construction of calibration curves for other active compounds and also their prediction step was performed as described for A.

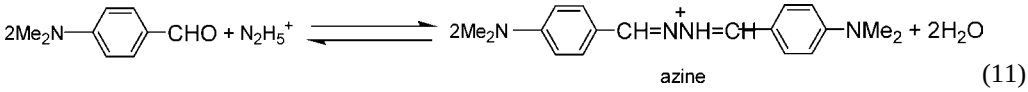
It should be noted that the data processing step is not time consuming and could be performed from kinetic profiles using a simple program stored in PC in few seconds.

The proposed method was used to simultaneous determination of ternary mixtures of hydrazine, phenylhydrazine and acetylhydrazine based on their condensation reactions with *p*-(dimethylamino)benzaldehyde in micellar sodium dodecyl sulfate media without any preliminary separation.

4. Results and discussion

4.1. Preliminary study of the system

In the SDS micellar media, the condensation reactions of aromatic aldehydes with hydrazine derivatives produce color products. Condensation reactions of hydrazine and acetylhydrazine with DAB and phenylhydrazine with NB affording azine, acethylhydrazone and phenylhydrazone products, respectively, proceed according to stoichiometric equations given below:



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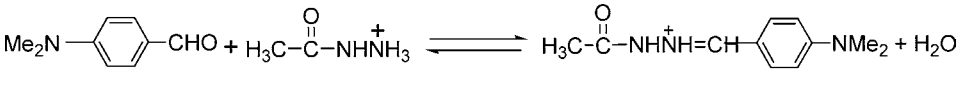

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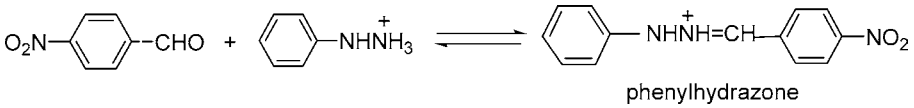

(13)

SDS micellar media strongly enhance the rate and equilibrium constants of the above reactions [21]. The reaction of phenylhydrazine with NB was completed at nearly 15 min in neutral media at 25 °C, while the reaction of hydrazine and acetylhydrazine with NB was very slow. But the reaction of hydrazine with DAB was very fast and completed by 5 min in acidic media at room temperature while the reaction of phenylhydrazine with NB was very slow. Also, acetylhydrazine reacts with DAB but its reaction is slower than hydrazine [22,23].

The spectra of the azine, phenylhydrazone and acetylhydrazone overlapped completely, and each compound interferes in the spectrophtometric determination of the others. The kinetic profiles for the condensation reaction of hydrazine, acethylhydrazine and phenylhydrazine with DAB and NB in micellar media (at 460 nm and 25 °C) are presented in Fig. 1. As Fig. 1 shows, the kinetic profiles of the condensation reaction of azine, phenylhydrazone and acetylhydrazone are different and could be used to their simultaneous determination by the proposed method.

We have previously reported the optimum conditions such as HCl concentration, DAB and NB concentration and temperature for the reactions of hydrazine, phenylhydrazone and acetylhydrazone with DAB and NB [22,23]. Therefore,

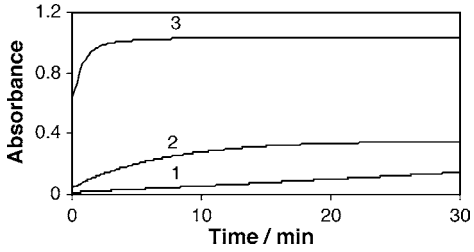

Fig. 1. Kinetic profiles for the condensation reaction of 5 μg mL^{-1} acetylhydrazine (1), 4 μg mL^{-1} phenylhydrazine (2) and 0.6 μg mL^{-1} hydrazine (3) with DAB and NB in micellar sodium dodecyl sulfate (SDS) media and 0.02 mol L^{-1} HCl at 460 nm.

optimum conditions for simultaneous determination of hydrazine, phenylhydrazine and acetylhydrazine were chosen as follows: the HCl concentration is 0.02 M, DAB concentration is 0.002 M, NB concentration is 0.0025 M, SDS concentration is 0.02 M and temperature is 25 °C.

4.2. Proposed method

The absorption kinetic profiles for the standard solutions of the hydrazine with different concentrations were recorded at 460 nm in the time range 0–30 min (Fig. 2a) with 10 s

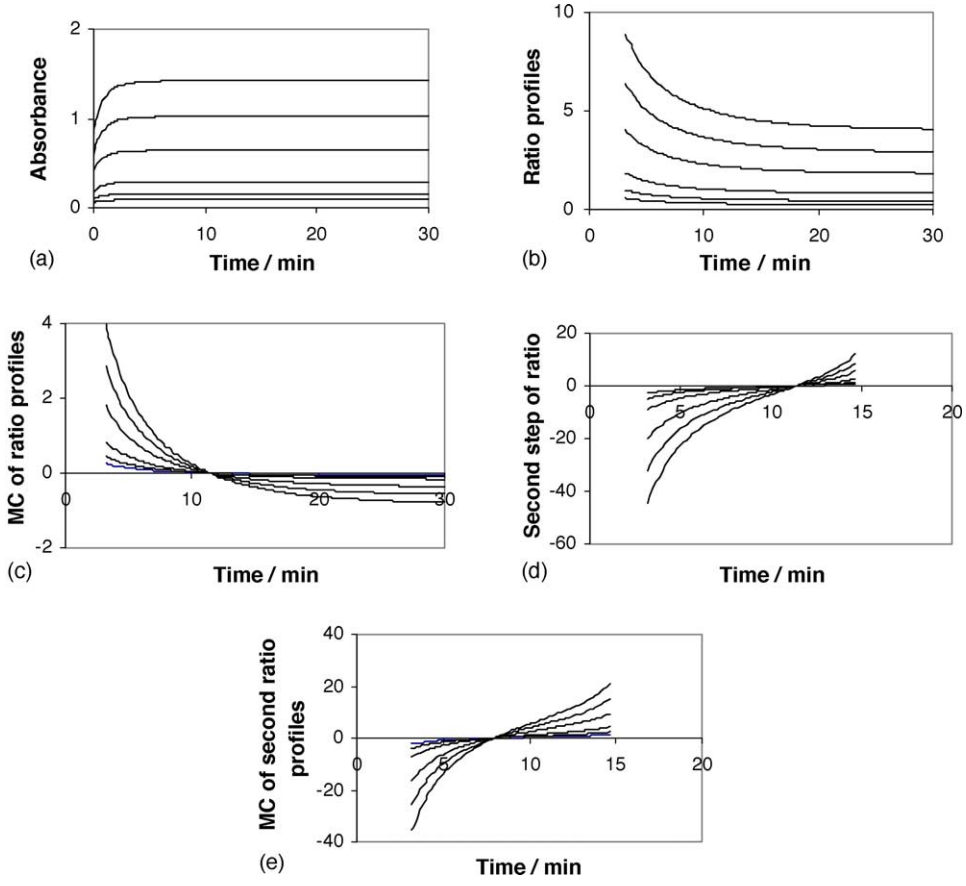

Fig. 2. The absorption kinetic profiles for the standard solutions of the hydrazine with different concentrations (0.05, 0.1, 0.2, 0.4, 0.6 and 0.8 μg mL^{-1}) at 460 nm (a), the ratio profiles obtained by dividing the normalized kinetic profile for the phenylhydrazine (b), the mean centering of ratio profiles (c), second ratio profiles (d) that were obtained by dividing the residual vectors by MC($E_{\mathrm{Phen}(t)}/E_{\mathrm{Acet}(t)}$) and MC of these vectors (e).

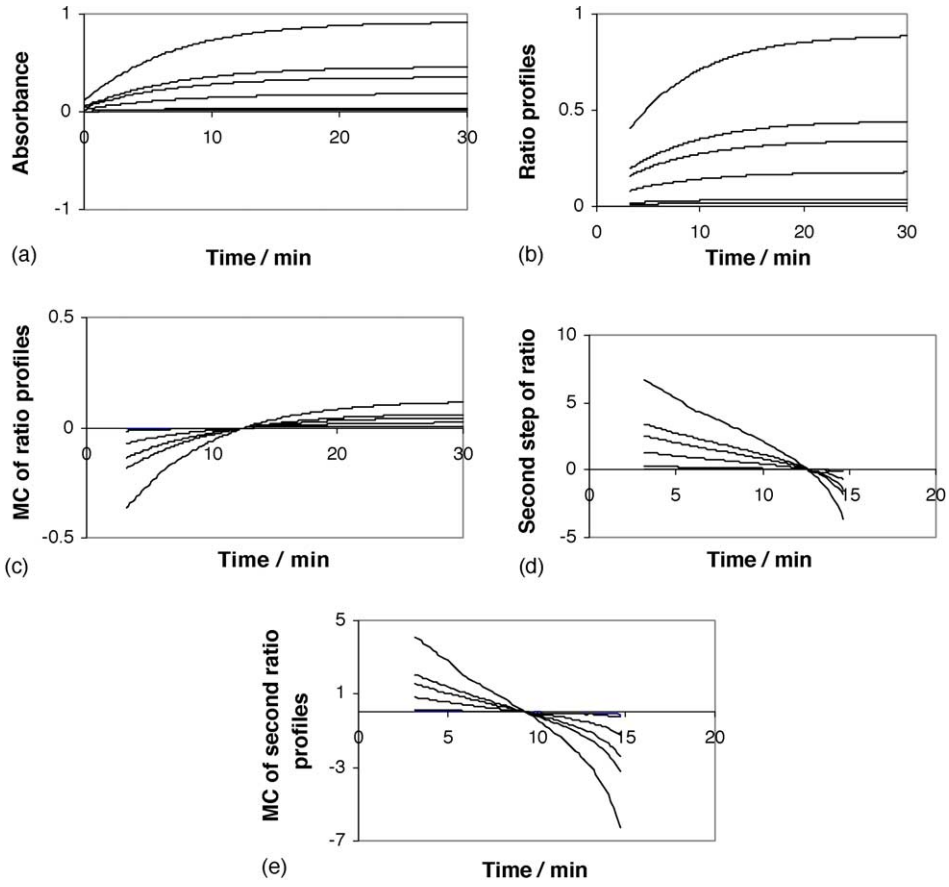

Fig. 3. The absorption kinetic profiles for the standard solutions of the phenylhydrazine with different concentrations (0.3, 0.5, 2.0, 4.0, 5.0 and 10.0 μg mL^{-1}) were recorded at 460 nm (a), the ratio profiles obtained by dividing the normalized kinetic profile of the hydrazine (b), the mean centering of ratio profiles (c), second ratio spectra (d) that were obtained by dividing the residual vectors by MC($E_{\mathrm{Acetyl}(t)}/E_{\mathrm{Hyd}(t)}$) and MC of these vectors (e).

intervals and divided by the normalized kinetic profile of the phenylhydrazine and the ratio profiles were obtained (Fig. 2b). Mean centering of the ratio profiles were obtained in the time range of 3–30 min (Fig. 2c). After that, the residual vectors are divided by MC($E_{\mathrm{Phen}(t)}/E_{\mathrm{Acet}(t)}$) corresponding to the MC of the ratio of the normalized kinetic profiles of phenylhydrazine and acetylhydrazine in the time range of 3–14 min and second ratio profiles according to Eq. (9) were obtained (Fig. 2d). MC of later profiles with respect to time according to Eq. (10) was obtained (Fig. 2e). The amount of hydrazine was determined by measuring the amplitude at 3 min corresponding to a minimum amount at time profile in the MC of second ratio profiles as shown in Fig. 2e. For the prediction of concentration of hydrazine in synthetic ternary mixtures and real samples, the same procedure was used except that the kinetic profiles of the mixtures were used instead of the kinetic profiles of standard solutions of hydrazine.

The absorption kinetic profiles for the standard solutions of phenylhydrazine with different concentrations were recorded at 460 nm in the time range 0–30 min (Fig. 3a) with 10 s intervals and divided by the normalized kinetic profile of the hydrazine and the ratio profiles were obtained (Fig. 3b). Mean centering of the ratio profiles were obtained in the time range of 3–30 min (Fig. 3c). After that the residual vectors are divided by MC($E_{\mathrm{Acetyl}(t)}/E_{\mathrm{Hyd}(t)}$) corresponding to the MC of the ratio of the normalized kinetic profiles of acetylhydrazine and hydrazine in the time range of 3–14 min and second ratio profiles according to Eq. (9) were obtained (Fig. 3d). MC of later profiles with respect to time according to Eq. (10) was obtained (Fig. 3e). The amount of phenylhydrazine was determined by measuring the amplitude at 3 min corresponding to a maximum amount at time profile in the MC of second ratio profiles as shown in Fig. 3e. For the prediction of concentration of phenylhydrazine in synthetic ternary mixtures

Table 1
Analytical characteristics for analysis of hydrazine, phenylhydrazine and acetylhydrazine in ternary mixtures by the proposed method

Analyte	Time (min)	Calibration equation[a]	(R^2)[b]	Linear range (μg mL^{-1})
Hydrazine	3	$Y = -44.644C + 0.8153$	0.9968	0.02–0.80
Phenylhydrazine	3	$Y = 0.4189C - 0.0636$	0.9994	0.3–10.0
Acetylhydrazine	10	$Y = 0.0622C - 0.0008$	0.9936	1.0–10.0

[a] C is the concentration of analyte in μg mL^{-1}.
[b] Determination coefficient.

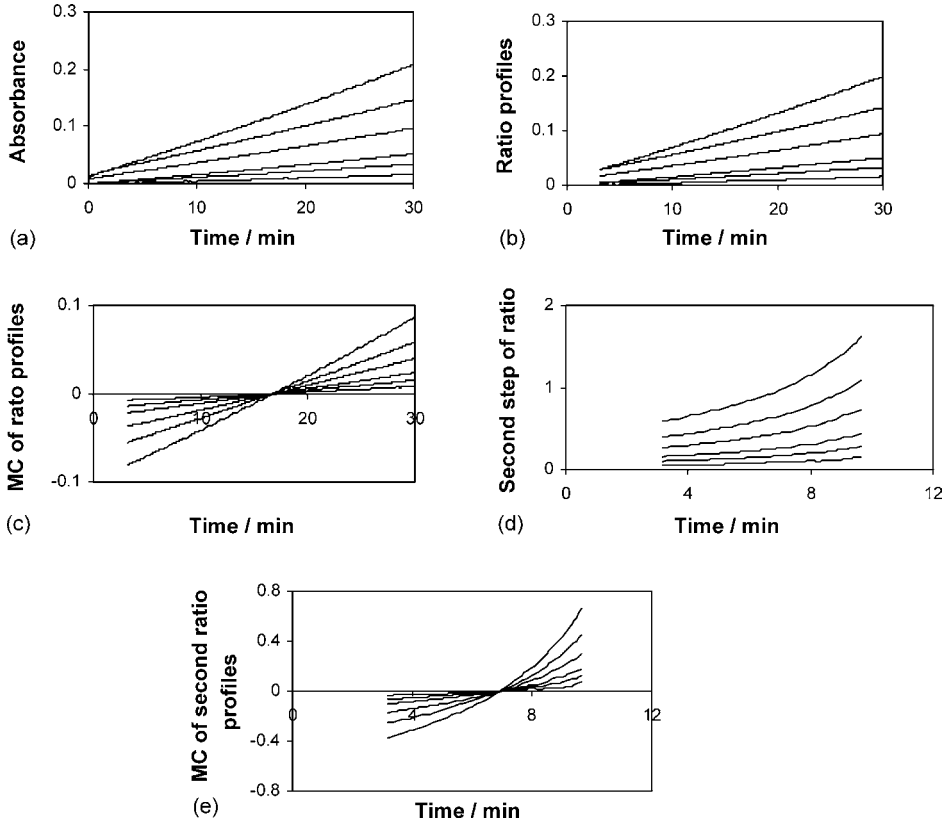

Fig. 4. The absorption kinetic profiles for the standard solutions of the acetylhydrazine with different concentrations (1.0, 2.0, 3.0, 5.0, 7.0 and 10.0 μg mL^{-1}) at 460 nm (a), the ratio profiles obtained by dividing the normalized kinetic profile of the hydrazine (b), the mean centering of ratio profiles (c), second ratio profiles (d) that were obtained by dividing the residual vectors by MC($E_{\mathrm{Hyd}(t)}/E_{\mathrm{Phen}(t)}$) and MC of these vectors (e).

and real samples, the same procedure was used except that the kinetic profiles of the mixtures were used instead of the kinetic profiles of standard solutions of phenylhydrazine.

The absorption kinetic profiles for the standard solutions of the acetylhydrazine with different concentrations were recorded at 460 nm in the time range 0–30 min (Fig. 4a) with 10 s intervals and divided by the normalized kinetic profile of the hydrazine and the ratio profiles were obtained (Fig. 4b). Mean centering of the ratio profiles were obtained in the time range of 3–30 min (Fig. 4c). After that, the residual vectors are divided by MC($E_{\mathrm{Hyd}(t)}/E_{\mathrm{Phen}(t)}$) corresponding to the MC of the ratio of the normalized kinetic profiles of hydrazine and

Table 2
Results for several experiments of analysis of hydrazine, phenylhydrazine and acetylhydrazine in ternary mixtures in different concentration ratios by proposed method

Taken (μg mL^{-1})			Found (μg mL^{-1})			Recovery (%)		
Hydrazine	Phenylhydrazine	Acetylhydrazine	Hydrazine	Phenylhydrazine	Acetylhydrazine	Hydrazine	Phenylhydrazine	Acetylhydrazine
0.22	1.0	3.5	0.21	1.11	3.5	95.5	111.0	98.7
0.07	2.0	4.0	0.07	2.03	3.9	100.0	101.5	97.5
0.4	0.6	5.0	0.41	0.59	4.7	102.5	98.3	93.5
0.6	0.5	3.0	0.62	0.53	3.2	103.3	106.0	106.1
0.8	1.0	3.0	0.83	1.01	3.4	103.8	101.0	112.0
0.21	4.0	8.0	0.22	3.89	7.6	104.8	97.3	94.7
0.1	6.0	7.5	0.11	5.98	7.4	110.0	99.7	98.4
0.04	0.3	5.0	0.04	0.33	4.9	100.0	110.0	98.1
0.11	9.0	5.0	0.1	9.13	5.1	90.9	101.4	102.4
0.08	5.0	1.0	0.08	4.94	0.9	100.0	98.8	90.0
0.22	1.0	3.5	0.21	1.11	3.5	95.5	111.0	98.7
0.07	2.0	4.0	0.07	2.03	3.9	100.0	101.5	97.5
Mean recovery						101.1	102.5	99.1
R.S.E. (%) single						1.70	3.60	4.50
R.S.E.$_t$ (%) total								3.66

phenylhydrazine in the time range of 3–10 min and second ratio profiles according to Eq. (9) were obtained (Fig. 4d). MC of later profiles with respect to time according to Eq. (10) was obtained (Fig. 4e). The amount of acetylhydrazine was determined by measuring the amplitude at 10 min corresponding to a maximum amount at time profile in the MC of second ratio profiles as shown in Fig. 4e. For the prediction of concentration of acetylhydrazine in synthetic ternary mixtures and real samples, the same procedure was used except that the kinetic profiles of the mixtures were used instead of the kinetic profiles of standard solutions of acetylhydrazine.

4.3. Analytical characteristics

In the proposed method, Beer's law was obeyed in the concentration range 0.02–0.8 μg mL^{-1} for hydrazine, 0.3–10.0 μg mL^{-1} for phenylhydrazine and 1.0–10.0 μg mL^{-1} for acetylhydrazine. Table 1 shows the linear regression parameters for calibration data for simultaneous determination of hydrazine, phenylhydrazine and acetylhydrazine in their ternary mixtures.

To check the reproducibility of the method five replicate resolving of hydrazine, phenylhydrazine and acetylhydrazine mixtures were performed. The relative standard deviation for five replicate measurements of 0.20 μg mL^{-1} of hydrazine, 1.0 μg mL^{-1} of phenylhydrazine and 3.5 μg mL^{-1} of acetylhydrazine was 5.00, 3.13 and 3.31%, respectively. The mean recoveries for simultaneous determination of these species in ternary mixtures were 100, 102 and 98.3% for hydrazine, phenylhydrazine and acetylhydrazine, respectively.

The selection of time range for the simultaneous determination of analytes and also for dividing steps by the proposed method is the main stage of the procedure. To select the appropriate range for using mean centering of ratio profiles, the following principles were applied. At this selected range, the analyte signals must be linear with concentrations, the analytical signal obtained from a mixture containing the analytes should be equal to the sum of the individual signals of the components. In addition, at selected range for possibility of dividing operation, the zero values of $E_{C(t)}$ and MC($E_{B(t)}/E_{C(t)}$) (according to Eqs. (7) and (9)) should not be used in the divisor. The selected time ranges regarding to these principals are shown in Figs. 2–4.

The effect of divisor concentration on the analytical parameters such as slope, intercept and correlation coefficient of the calibration graphs was also tested. It was observed that changing the concentration of divisors in their linear calibration range had no significant effect on the analytical parameters. Therefore, a normalized kinetic profile of each of the hydrazine, phenylhydrazine and acetylhydrazine was used as divisor profile in the proposed method.

In order to obtain the accuracy and precision of the method, several synthetic mixtures with different concentration ratios of hydrazine, phenylhydrazine and acetylhydrazine were analyzed using the proposed method. The results are given in Table 2. The prediction error of a single component in the

Table 3
Determination of hydrazine, phenylhydrazine and acetylhydrazine mixtures in different samples using proposed method

Sample	Taken (μg mL^{-1})			Found (μg mL^{-1})			Recovery (%)		
	Hydrazine	Phenylhydrazine	Acetylhydrazine	Hydrazine	Phenylhydrazine	Acetylhydrazine	Hydrazine	Phenylhydrazine	Acetylhydrazine
River water	0.20	1.0	2.0	0.19	1.02	1.8	95.0	102.0	90.0
	0.30	2.0	3.0	0.31	2.10	3.1	103.3	105.0	102.6
Spring water	0.10	1.0	1.5	0.11	0.94	1.5	110.0	94.0	100.0
	0.30	2.0	3.0	0.29	2.02	2.8	96.7	101.0	93.3
Well water	0.20	1.0	2.0	0.20	1.09	2.0	100.0	109.2	100.0
	0.30	2.0	4.5	0.31	1.92	4.6	103.3	95.8	101.5

mixtures was calculated as the relative standard error of the prediction concentration [21]. Table 2 also shows the reasonable single and total relative errors for such system.

4.4. Application

The proposed method was successfully applied to the determination of mixtures of hydrazine, phenylhydrazine and acetylhydrazine after addition to water samples. The results are given in Table 3. As it can be seen, the results are all satisfactory.

5. Conclusion

The proposed method for the resolving of ternary mixtures is simple, very sensitive and easy to understand and apply. The data processing step is not time consuming and could be performed in few seconds. Accuracy, precision, reproducibility, sensitivity and linear range for the proposed method are satisfactory. This approach can be used for the resolution of ternary mixtures with completely overlapped absorption spectra that show a difference in their rate constants in a given reaction.

References

[1] S.R. Crouch, J. Coello, S. Maspoch, M. Porcel, Anal. Chim. Acta 424 (2000) 115.
[2] A. Afkhami, A.R. Zarei, Talanta 53 (2001) 815.
[3] A. Afkhami, T. Madrakian, A.R. Zarei, Anal. Sci. 17 (2001) 1199.
[4] A. Afkhami, A.R. Zarei, Talanta 60 (2003) 63.
[5] E. Furusjo, L.G. Danielson, Anal. Chim. Acta 373 (1998) 83.
[6] L.J. Papa, J.H. Patterson, H.B. Mark, C.N. Reilley, Anal. Chem. 35 (1963) 1889.
[7] I.A. Pettas, M.I. Karayannis, Anal. Chim. Acta 491 (2003) 219.
[8] B.G.M. Vandeginste, D.L. Massart, L.M.C. Buydens, S. De Jong, P.J. Lewi, J. Smeyers-Verbeke, Handbook of Chemometrics and Qualimetrics, Elsevier, Amsterdam, 1998.
[9] F. Salinas, J.J. Berzas Nevado, S. Maspoch, J. Riba, Talanta 37 (1990) 347.
[10] J.J. Berzas Nevado, C.C. Guiberteau, F. Salinas, Talanta 39 (1992) 547.
[11] J.J. Berzas Nevado, C. Guiberteau Cabanillas, A.M. Contento Salcedo, Talanta 42 (1995) 2043.
[12] F. Onur, C. Yucesoy, S. Dermis, M. Katral, G. Kukdil, Talanta 51 (2000) 269.
[13] A. El-Gindy, B. El-Zeany, T. Awad, M.M. Shabana, J. Pharm. Biomed. Anal. 26 (2001) 203.
[14] E. Dinc, I.M. Palabyik, O. Ustundag, F. Yustsever, F. Onur, J. Pharm. Biomed. Anal. 28 (2002) 591.
[15] E. Erk, Y. Ozkan, E. Bannoglu, S.A. Ozkan, Z. Senturk, J. Pharm. Biomed. Anal. 24 (2001) 469.
[16] E. Dinc, Talanta 48 (1999) 1145.
[17] E. Dinc, E. Baydan, M. Kanbur, F. Onur, Talanta 58 (2002) 579.
[18] A. Afkhami, M. Bahram, Spectrochim. Acta Part A 61 (2005) 869.
[19] A. Afkhami, M. Bahram, Talanta 66 (2005) 712.
[20] A. Afkhami, M. Bahram, Anal. Chim. Acta 526 (2004) 211.
[21] A.K. Yatsimirsky, N.T. Yatsimirskaya, S.B. Kashina, Anal. Chem. 66 (1994) 2232.
[22] A. Afkhami, A.R. Zarei, Talanta 62 (2004) 559.
[23] A. Afkhami, A.R. Zarei, Anal. Sci. 20 (2004) 1199.