



Simultaneous Spectrophotometric determination of Metal Ions in Aqueous Solutions Using a Simple Spectra Ratio Method

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Abstract

A simple spectrophotometric method was developed for the simultaneous determination of Ni, Co, Pd, Cu, Zn, and Fe without the need for any prior separation steps. The method is based on the differences of absorbance ratios in two and/or three wavelengths. The mathematical model of the method was first presented, then applied to the modelled data with adding random noise, finally applied to the spectrophotometric data of ions in binary and ternary liquid mixtures. The spectrophotometric analysis based on the complexation reaction of these cations with 1-(2-pyridylazo)-2-naphthol (PAN). Under the optimum condition, the calibration curve was linear over the concentration ranges from 0.1 to 5 µg/L with the RSDs under 4.21%. The results indicated that the proposed method is relatively simple and rapid for the analysis of binary and ternary mixtures with a satisfactory precision and accuracy.

Keywords: Spectrophotometry; Multicomponent analysis; Ratio spectra; Metal ions; Data modeling;

1. Introduction

Simultaneous multicomponent analysis has always been important for analytical chemists. Because real samples have a complex composition and measuring one compound in the presence of other compounds is of great value. simultaneous determination of salinity, carbonate and ammoniacal nitrogen in waters using flow injection coupled dual-channel detection cell [1], multicomponent analysis of mixture of vitamins and pharmaceuticals in tablets and capsules by Multivariate Curve Resolution [2], removal of Cr(VI) and phenol using tea waste biomass [3], determination of two PAHs by kinetic-spectroscopic 3D chemiluminescence [4], and determination of six synthetic dyes by HPLC-UV-DAD [5] are examples

of multicomponent analysis reported in the literatures.

Spectrophotometric multi-component analysis, recording and mathematically processing of absorption spectra, is one of the most extensively used tools by analysts for quantitative and qualitative analysis. Wavelet transform as one of the popular signal processing methods for separation of overlapping signals has been used for UV spectroscopic analysis of pharmaceuticals [6]. Continuous wavelet transform (CWT), the integral transformation of the absorbance data vectors followed the construction of calibration graphs by measuring CWT amplitudes, was applied for the simultaneous determination of chemical species in binary mixtures [7]. A derivative method developed by using CWT with a Haar wavelet function was

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applied for detection and control of trace amounts of copper, cobalt, and nickel in purification process of zinc hydrometallurgy [8].

Obtaining ratio spectra followed by applying different calculating techniques are one of the common procedures in multicomponent analysis. Derivative ratio spectra method as an alternative method to derivative spectrophotometry was utilized for resolving binary and ternary mixtures [9,10]. In quantitative analysis, derivative spectra enlarge difference between spectra to resolve overlapping bands. Derivative spectroscopy uses first or higher derivatives of absorbance with respect to wavelength for qualitative analysis and for quantification [11,12]. An unwanted effect of the derivatization process is the decrease in S/N with higher orders of derivatives. This decrease follows from the discrimination effect and from the fact that noise always contains the sharpest features in the spectrum [13]. Mean centering of ratio spectra is another method which introduced for the simultaneous determination of binary and ternary mixtures. This method recently was utilized for resolution of severely overlapped binary mixture of Ibuprofen and Paracetamol in pharmaceutical dosage form [14]. 'Double divisor-ratio spectra derivative method [15], double divisor mean centering of ratio spectra [16], ratio difference method [17,18], successive-ratio derivative spectra method [19], and ratio H-point standard addition method [20] are other approaches to treat spectrophotometric spectra in order to multicomponent analysis of a mixture.

Due to the harmful effects of heavy metals, there are growing public health concerns about water pollutions [21] and thus proposing fast, simple and accurate detection methods for metal ions in water samples has become a critical issue [22,23]. Considering the simplicity of spectrophotometric methods and the advantages of spectral ratio methods, in this work a rapid and simple method has been developed for the simultaneous determination of binary and ternary mixtures of metal ions in water samples. The method is rapid and easy to operate only based the subtraction of absorbance ratio values in two and/or three wavelengths without any additional operations such as derivatization, mean centering or applying Fourier function. The mathematical model of the method was first utilized to the analysis of binary and ternary mixtures of

modeled data and then for the simultaneous spectrophotometric determination of six heavy metal ions in their synthetic mixtures in tab water.

2. Theory

2.1. The theoretical background

Consider a mixture of two compounds X and Y. If there is no interaction among the compounds the relevant form of the Beer's law is as in Eq. (1):

$$(1) \quad A_m = \alpha_X C_X + \alpha_Y C_Y$$

where A_m is the absorbance of the mixture, α_X and α_Y are the molar absorptivity and C_X and C_Y are the concentrations of X and Y, respectively. If Eq. (1) is divided by α_Y corresponding to the absorbance of a standard solution of Y at the same wavelength, the absorbance ratio (B) is obtained. If B is obtained in two different wavelengths, the difference of B values is proportional only to C_X as shown in Eq. (2):

$$(2) \quad B_1 - B_2 = \left(\frac{\alpha_{X1}}{\alpha_{Y1}} - \frac{\alpha_{X2}}{\alpha_{Y2}} \right) C_X$$

where α_{X1} , α_{X2} , α_{Y1} , and α_{Y2} are the molar absorptivity of X and Y in wavelengths of 1 and 2. For more sensitivity and obtaining positive values for B, it is recommended to select maximum absorption wavelength of X and Y as 1 and 2 wavelengths.

Briefly for the ternary mixture (X, Y and Z) analysis, the absorption of mixture is obtained in three wavelengths corresponding to maximum absorption wavelengths of X, Y and Z marked as 1, 2 and 3, respectively. If B is obtained in three wavelengths, Eqs. (3-5) can be written as:

(3)

$$C_1 = B_1 - B_3 = \left(\frac{\alpha_{X1}}{\alpha_{Z1}} - \frac{\alpha_{X3}}{\alpha_{Z3}} \right) C_X + \left(\frac{\alpha_{Y1}}{\alpha_{Z1}} - \frac{\alpha_{Y3}}{\alpha_{Z3}} \right) C_Y$$

(4)

$$C_2 = B_1 - B_2 = \left(\frac{\alpha_{X1}}{\alpha_{Z1}} - \frac{\alpha_{X2}}{\alpha_{Z2}} \right) C_X + \left(\frac{\alpha_{Y1}}{\alpha_{Z1}} - \frac{\alpha_{Y2}}{\alpha_{Z2}} \right) C_Y$$

$$(5) \quad D = \frac{C_1}{\begin{pmatrix} \alpha_{Y1} - \alpha_{Y3} \\ \alpha_{Z1} \quad \alpha_{Z3} \end{pmatrix}} - \frac{C_2}{\begin{pmatrix} \alpha_{Y1} - \alpha_{Y2} \\ \alpha_{Z1} \quad \alpha_{Z2} \end{pmatrix}} = \left(\frac{\begin{pmatrix} \alpha_{X1} - \alpha_{X3} \\ \alpha_{Z1} \quad \alpha_{Z3} \end{pmatrix}}{\begin{pmatrix} \alpha_{Y1} - \alpha_{Y3} \\ \alpha_{Z1} \quad \alpha_{Z3} \end{pmatrix}} - \frac{\begin{pmatrix} \alpha_{X1} - \alpha_{X2} \\ \alpha_{Z1} \quad \alpha_{Z2} \end{pmatrix}}{\begin{pmatrix} \alpha_{Y1} - \alpha_{Y2} \\ \alpha_{Z1} \quad \alpha_{Z2} \end{pmatrix}} \right) C_X$$

where α_{X1} , α_{X2} , α_{X3} , α_{Y1} , α_{Y2} , α_{Y3} , α_{Z1} , α_{Z2} , and α_{Z3} are the molar absorptivity of X, Y and Z in wavelengths of 1, 2 and 3, respectively. Eq. (5) is the mathematical foundation of multi-component analysis that permits the determination of concentration of X in the solution without interference of Y and Z in the mixture of them. A calibration curve could be constructed by plotting D against concentration of X in the standard ternary mixture solutions.

2.2. Modeling

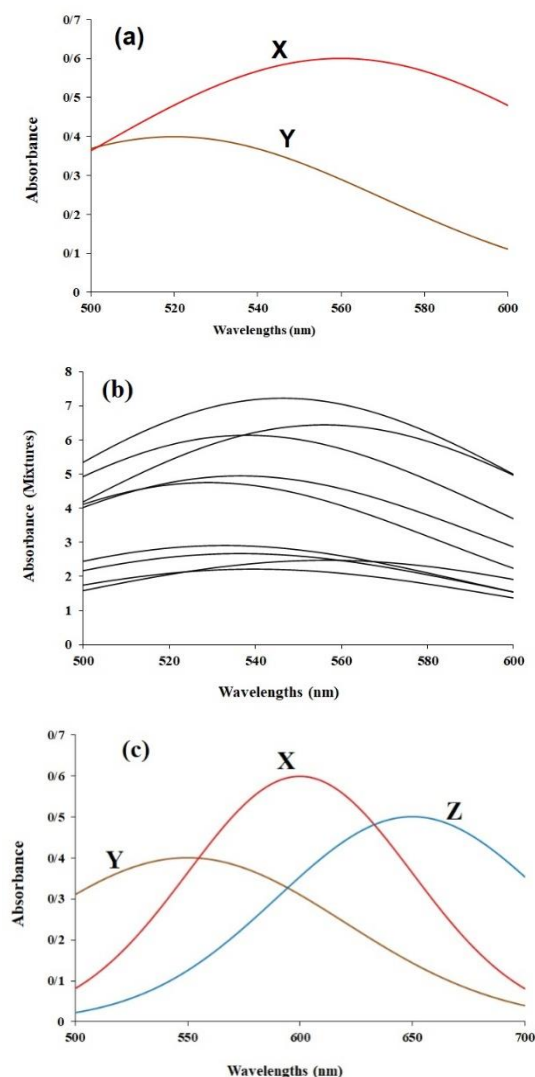
The analytical applicability of the proposed method was validated using modeled data. In the designed model for binary mixture two curves were created which demonstrate two compounds X and Y with the maximum absorption wavelengths 560 and 520 nm respectively (Fig. 1a). The absorption spectra for different concentrations of X in the presence of Y were created (Fig. 1b) and divided by the spectrum of Y and the ratio spectra were obtained. The concentration of compound X was determined by measuring the difference of amplitudes of the resulting absorbance ratio at two different wavelengths (maximum absorption wavelengths of X and Y).

In the designed model for ternary mixture three curves related to the three components X, Y and Z, with the maximum absorption wavelengths 600, 550 and 650 nm respectively, (Fig. 1c) were created. The absorption spectra created for different concentrations of X in the presence of Y and Z (Fig. 1d) were divided by the spectrum of Y and the ratio spectra were obtained. On the other hand, by dividing the spectrum of Z by the spectrum of Y the ratio spectrum of Z/Y was obtained.

Three wavelengths (e.g. maximum absorption wavelengths of each three components) were selected and the ratio of amplitudes in each wavelength was obtained. The difference of the values is proportional to the X concentration according to Eq. (5). To predict the concentration of compound X in these

synthetic binary and ternary mixtures the proposed procedures were performed. From the results obtained (Table 1), it is clear that the effects of the components X and Y have been eliminated.

In order to test the robustness of the method, random noise was added to the generated set of artificial data. In this procedure random noise of ± 0.005 absorbance unit was added to each spectrum and then the proposed method was performed as explained above. It was found that the obtained values for X concentration have a good agreement with expected values even in the noisy signal of the mixtures (Table 1). The results obtained compared with those obtained by mean centering method. It was found that the proposed method was more robust than mean centering method in the relatively high level of noise. The modeling procedure was implemented using the MATLAB software version 8.2.



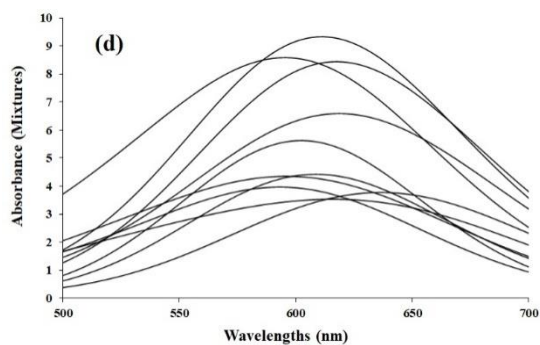


Fig. 1. (a) The modeled spectra of compound X and Y. (b) The modeled absorption spectra of different concentration of X in the presence of Y. (c) The modeled spectra of compound X, Y and Z. (d) The modeled absorption spectra of different concentration of X in the presence of Y and Z.

3. Experimental

3.1. Reagents and apparatus

A SHIMADZU UV-1650 PC double beam spectrophotometer was used for all absorbance measurements and spectra recordings; a Shimadzu AA-6300 type flame atomic absorption

spectrophotometer was used for comparing the results. All chemicals reagent was of analytical grade or the highest purity available. A solution of 1-(2-pyridylazo)-2-naphthol (PAN) as a 0.050% (w/v) in ethanol was prepared and used. A standard palladium(II) solution (1000 $\mu\text{g}/\text{mL}$) as a stock solution was prepared by dissolving 0.166 g of palladium(II) chloride (Fluka) in 10 mL of an aqueous solution containing 2 mL of concentrated hydrochloric acid, and then adjusting the volume of the solution in a 100 mL volumetric flask. Standard nickel(II) solution (1000 $\mu\text{g}/\text{mL}$) as a stock solution was prepared by dissolving 0.495 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water and then adjusting the volume in a 100 mL volumetric flask. Stock solutions of Co(II), Zn(II), Fe(III) and Cu(II) as 1000 $\mu\text{g}/\text{mL}$ was prepared by dissolving appropriate amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ respectively in 100 mL volumetric flask similar to

Table 1. The analysis of modelling data for X, Y and Z mixtures by the proposed method to predict values of X.

Sample number	Composition of synthetic mixtures			Predicted values of X	
	X	Y	Z	Noise free	± 0.005 noise
1	0.50	4.20	-	0.50	0.52
2	2.00	2.40	-	2.00	2.05
3	1.50	6.00	-	1.50	1.51
4	5.00	3.00	-	5.00	5.03
5	6.00	4.50	-	6.00	6.08
6	2.50	8.50	8.20	2.50	2.45
7	3.50	4.30	3.50	3.50	3.58
8	5.50	7.50	7.40	5.50	5.37
9	7.50	5.70	9.50	7.50	7.38
10	9.00	5.80	6.22	9.00	9.31
11	0.50	3.00	2.55	0.50	0.48
12	1.50	1.00	8.00	1.50	1.54
13	4.50	7.00	5.70	4.50	4.53
14	8.50	2.70	8.50	8.50	8.57
15	6.5	4.3	3.5	6.5	6.46

preparation of nickel(II) solution. Triton X-100 solution as 5.0% (v/v) was prepared in by dissolving 5 mL of Triton X-100 in 100 mL volumetric flask. An acetate buffer solution of pH 4.5 was prepared by mixing sodium acetate (0.10 M) and acetic acid (0.10

M) and adjusting the pH of the solution using a pH-meter (Metrohm 744). Other solutions prepared by dissolving appropriate amounts of their chemicals in doubly distilled water. All chemicals purchased from Merck.

3.2. Individually determination of cations

1.5 mL Buffer solution and 3 mL Triton X100 solutions were added to a 10 mL volumetric flask contains required volumes of Ni, Co, Cu, Pd, Zn and/or Ni solutions. Finally, 2 mL PAN solution was added and the absorbance of colored obtained solutions recorded in 3-10 min after adding PAN solution at the corresponding maximum wavelengths (581 nm for Co-PAN, 617 nm for Pd-PAN, 556 nm for Cu-PAN, 555 nm for Zn-PAN, 550 nm for Fe-PAN and 569 nm for Ni-PAN).

3.3. Simultaneous determination of cations

In binary mixture analysis the absorbance of the mixture was measured in two wavelengths (e.g. maximum wavelengths of two cation-PAN complexes) and then each absorbance value was divided by the absorbance of a standard sample solution of interferent (divisor) at the same wavelength. The analyte content of the sample was determined from the difference of the two values obtained. In ternary mixture analysis the obtained absorbance of the mixture in three wavelengths (e.g. maximum wavelengths of three cation-PAN complexes) were divided by the absorbance of a standard sample of one of interferents at the same wavelengths followed by dividing the results by the absorbance ratio of two interferents at the same wavelength. The analyte content of the sample was calculated from difference of three resultant values as described in theoretical background section.

4. Results and discussion

4.1. Wavelengths selection

PAN reacts with a wide variety of metal ions to form colored water insoluble chelates [24]. In micellar media, these complexes become soluble and highly absorbing substances in the visible region of the spectrum (Fig 2). Experiments show that the spectra of metal ion-PAN complexes are pH dependent on and solution pH 4-6 is commonly used range [25]. According to the results of our experiments which are confirmed by those in the literature, pH 4.5 was best for the investigated complexes (Fig. 3). The spectra of complexes presented in Fig. 2 was recorded at pH 4.5 in Triton X100 micellar media. Pd-PAN shows an

absorption maximum at $\lambda = 617$ nm and a shoulder at $\lambda = 665$ nm. Co-PAN complex shows an absorption maximum at $\lambda = 581$ nm and a shoulder at about $\lambda = 621$ nm. Ni-PAN shows two absorption maximums at $\lambda = 569$ nm and 530 nm. Zn-PAN complex shows an absorption maximum at $\lambda = 555$ nm and a shoulder at about $\lambda = 520$ nm. Cu-PAN and Fe-PAN complexes show absorption maximum at $\lambda = 556$ nm and $\lambda = 550$ nm respectively. Because of highly spectral overlapping, univariate calibration methods cannot be applied for the simultaneous determination of these metal ions. Hence, the proposed method was used for obtaining quantitative information from spectral data.

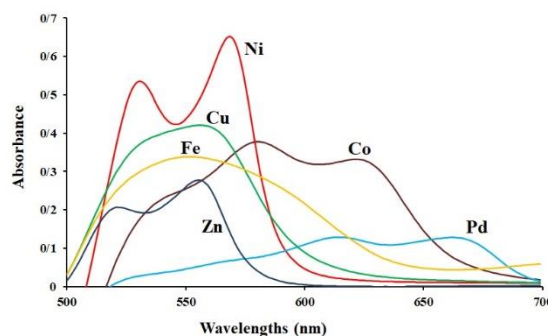


Fig. 2. Absorption spectra of metal ion-PAN Complexes at pH 4.5, in Triton X100 micellar media. Concentration of cations is 1.0 $\mu\text{g/mL}$

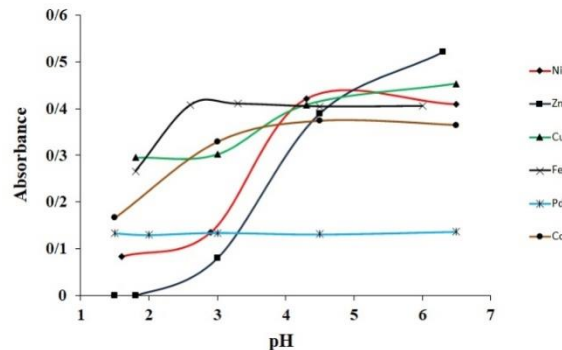


Fig. 3. Effect of pH on absorbance of Co-PAN, Zn-PAN, Fe-PAN, Cu-PAN, Ni-PAN and Pd-PAN complexes. Conditions: PAN, 0.005% (w/v); Triton X100, 1% (v/v); Concentration of cations is 1.0 $\mu\text{g/mL}$

Although in the proposed method utilizing maximum absorption wavelengths of the complexes is the first recommendation, however in the cases which maximum wavelengths are close together using another two wavelengths which are far from will be suitable selection.

4.2. Effect of the experimental variables

A number of parameters may influence the

Metal ion	Wavelengths (nm)	Linear Range ($\mu\text{g/mL}$)	Divisor ($\mu\text{g/mL}$)	RSD (%)
Co	581	0.1-3	-	1.83
Cu	556	0.1-3	-	1.56
Ni	569	0.1-3	-	1.91
Pd	617	0.1-4	-	1.32
Fe	550	0.1-3.5	-	2.07
Zn	555	0.1-3	-	1.78
Co-Pd	581-617	0.1-3	Pd(3)	3.67
Pd-Co	617-581	0.5-5	Co(0.5)	2.99
Co-Zn	581-555	0.1-3	Zn(0.5)	3.45
Zn-Co	555-581	0.5-3	Co(1)	2.60
Co - Cu	581-556	0.1-3	Cu(1)	3.22
Cu-Co	556-581	0.1-3	Co(0.1)	3.53
Cu-Ni	556-569	0.1-3	Ni(0.5)	3.65
Ni-Cu	569-556	0.5-3	Cu(0.5)	3.98
Fe-Ni	610-569	0.5-3	Ni(0.5)	3.30
Ni-Fe	569-550	0.5-3	Fe(0.1)	3.19
Zn-Ni	555-569	0.5-3	Ni(0.5)	3.02
Ni-Zn	569-555	0.5-3	Zn(2)	3.84
Cu-Zn	556-580	0.1-3	Zn(0.5)	3.61
Zn-Cu	580-556	0.5-3	Cu(1)	4.01
Zn-Fe	600-555	0.5-3	Fe(2)	3.73
Fe-Zn	555-600	0.5-3	Zn(1)	3.61
Cu-Fe	556-600	0.1-3	Fe(2)	4.12
Fe-Cu	600-556	0.5-3	Cu(0.5)	4.03
Co-Fe	581-550	0.1-3	Fe(1)	3.95
Fe-Co	550-581	0.5-3	Co(1)	3.74
Co-Ni	581-569	0.1-3	Ni(1)	3.29
Ni-Co	569-581	0.5-3	Co(1)	3.52
Co-Pd-Ni	581-617-569	0.5-3	Pd(3)-Ni(0.5)	4.12
Co-Pd-Cu	581-617-556	0.5-3	Pd(3)-Cu(1)	3.88
Co-Pd-Fe	581-617-550	0.5-3	Pd(3)-Fe(1)	3.93
Co-Pd-Zn	581-617-555	0.5-3	Pd(3)-Zn(0.5)	3.76
Ni-Co-Zn	569-621-555	0.5-2.5	Co(1)-Zn(1)	4.09
Ni-Co-Cu	569-621-556	0.5-2.5	Co(1)-Cu(0.5)	4.21

determination of metal ions based on the formation of metal-PAN complex in Triton X-100 micellar media.

To gain the highest sensitivity and precision it was necessary to optimize these parameters. The optimization was done using "one at a time" approach.

The results of our experiments showed that the stability of complexes in nonionic micellizing agents is high in comparison with anionic surfactants. Triton X-100 was used as micelling agent in this work.

Table 2. Statistical data for the spectrophotometric analysis of binary and ternary mixtures of Co, Pd, Ni, Fe, Cu and Zn cations using the proposed method.

The effect of Triton X-100 was studied in the concentration range of 0.05–2% (v/v). Results showed that sensitivity increases up to 0.50% and remains constant until 2% and then decreases slightly in determination of all metal ions. Unfortunately, Pd-PAN complex has not enough stability under 1.5% of Triton X100. Thus, 1.5% of Triton X100 was selected as working concentration.

To obtain the optimum concentration of the PAN, the effect of its concentration was studied in the range of 0.0001-0.0100% (w/v) and the absorbance of complexes were measured at the appropriate wavelengths. It was concluded that PAN concentrations higher than 0.01% in is not suitable for satisfactory complexation. As shown in Fig. 4, the absorbance of the complexes remains constant in the range taken 0.0025-0.01%.

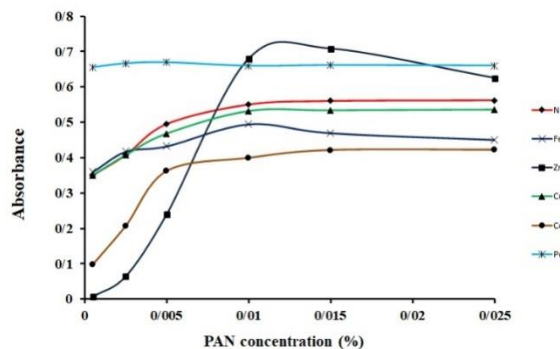


Fig. 4. Effect of PAN concentration on the sensitivity. Conditions: pH 4.5, Triton X100 concentration of 1.5% (v/v); Concentration of cations is 1.0 $\mu\text{g/mL}$ except Pd that is 2 $\mu\text{g/mL}$

For assurance of the completion of complex formation, 0.0075% was taken as an optimum concentration of PAN. Since the concentration of buffer solution did not affect the absorbance of the analyte, a normal ionic strength (1.5 mL of prepared buffer solution in 10 mL, 0.015 M) used throughout.

According to the theoretical background, the absorbance of binary and ternary mixtures should be

divided by the absorbance of one or two standard samples (divisor), respectively. Different concentrations of the divisor were tested and the optimum value for determination of each ion was selected (Table 2).

4.3. Analytical parameters

Quantitative characteristics of the proposed method were studied under the optimized analysis conditions to evaluate the method performance and summarized in Table 2. According to the proposed method, individual ions can be analyzed by measuring the signal in a single wavelength, and binary and ternary mixtures can be analyzed by measuring the signal in two or three wavelengths, respectively. The obtained results revealed that very good regression coefficients were reached for all mixtures within the tested concentration ranges. The proposed method benefits sufficient linear ranges (0.1-5 $\mu\text{g/L}$) and good linearity ($R^2 > 0.99$). Repeatability of the method was also assessed and the relative standard deviations (RSDs) were obtained $\leq 4.21\%$ by its application on

the seven similar standard solutions of cations.. The proposed method offers some advantages over other similar spectrophotometric methods, such as being fast, simple, and cost effective (Table 3).

4. 4. Determination of metal ions in tap water mixtures

To evaluate the applicability of the proposed method for real samples it was applied for determination of cations in synthetic binary and ternary mixtures of tap water. A tap water sample was collected from our laboratory (Tabriz, Iran), filtered through a 0.45 μm pore size filters and stored in clean polyethylene bottles. Due to the very low levels of the above mentioned cations in water samples, the accuracy of the method was evaluated performing recovery experiments for spiked sample solutions. Recoveries ranged from 95 to 105% which reveal sufficient accuracy (Table 4).

Table 3 Comparison of analytical performances of the proposed method with some other colorimetric multicomponent analysis methods reported in the literature for the determination of metal ions

Parameter	Proposed method	[26]	[27]	[28]	[29]
Method	Ratio spectra	Microfluidic paper-based analysis	Carboxylic Cation-Exchangers	second-derivative spectrophotometry	partial leastsquare(PLS)
Sample volume (mL)	10	0.3	25	5	10
Matrix	Tap water	Tap water	Tap water	environmental, food and a traditional medicine samples	Tap water
² Procedure time (min)	≥ 30	≥ 120	≥ 30	≥ 60	≥ 60
³ LR (mg/L)	Cu(II) 0.1–3.0 Co(II) 0.1–3.0 Ni(II) 0.–3.0 Fe(II) 0.1–3.5 Pd(II) 0.1–4.0 Zn(II) 0.1-3.0	Cu(II) 0.32–63.55 Co(II) 0.59–4.71 Ni(II) 5.87–352.16 Hg(II) 0.20–12.04 Mn(II) 0.11–0.55	Cu(II) 0.09–3.18 Co(II) 0.09–2.91 Mn(II) 0.03–0.82	Cu(II) 0–0.60 Zn(II) 0–0.60 Cd(II) 0–0.40 Hg(II) 0–0.82 Pb(II) 0–0.48	Cu(II) 1.0–3.0 Fe(II) 0.20–1.0 Al(III) 0.06–0.60
RSD %	≤ 4.21	≤ 8.2 Cu(II) 0.32 Co(II) 0.59	≤ 11 Cu(II) 0.016 Co(II) 0.045 Mn(II) 0.003	≤ 4.71	NA
LOD (mg/L)	NA	Ni(II) 5.87 Hg(II) 0.20 Mn(II) 0.11		NA	NA

Table 4. Determination of cations in tap water samples spiked with different amounts of Cu, Co, Ni, Fe, Zn, and Pd ions.

sample	Added ($\mu\text{g/mL}$)						Found($\mu\text{g/mL}$)						Recovery($\mu\text{g/mL}$)					
	Pd	Co	Ni	Fe	Cu	Zn	Pd	Co	Ni	Fe	Cu	Zn	Pd	Co	Ni	Fe	Cu	Zn
1	0.50	0.50	-	-	-	-	0.52	0.51	-	-	-	-	104	102	-	-	-	-
2	2.00	0.50	-	-	-	-	1.98	0.52	-	-	-	-	99	105	-	-	-	-
3	0.50	1.50	-	-	-	-	0.53	1.48	-	-	-	-	105	99	-	-	-	-
4	-	0.50	-	-	0.50	-	-	0.52	-	-	0.52	-	-	104	-	-	104	-
5	-	0.50	-	-	1.50	-	-	0.50	-	-	1.51	-	-	100	-	-	101	-
6	-	1.50	-	-	0.50	-	-	1.50	-	-	0.52	-	-	100	-	-	104	-
7	-	-	0.50	-	0.50	-	-	-	0.52	-	0.49	-	-	-	104	-	98	-
8	-	-	0.50	-	1.50	-	-	-	0.53	-	1.46	-	-	-	105	-	97	-
9	-	-	1.20	-	0.50	-	-	-	1.14	-	0.47	-	-	-	95	-	95	-
10	-	-	0.50	-	-	0.50	-	-	0.52	-	-	0.49	-	-	104	-	-	98
11	-	-	1.00	-	-	0.50	-	-	1.00	-	-	0.47	-	-	100	-	-	95
12	-	-	0.50	-	-	1.50	-	-	0.53	-	-	1.47	-	-	98	-	-	98
13	-	-	0.50	0.50	-	-	-	-	0.51	0.49	-	-	-	-	102	98	-	-
14	-	-	1.00	0.50	-	-	-	-	0.98	0.47	-	-	-	-	98	94	-	-
15	-	-	0.50	1.50	-	-	-	-	0.53	1.52	-	-	-	-	105	101	-	-
16	-	-	-	-	0.50	0.50	-	-	-	-	0.51	0.48	-	-	-	-	102	96
17	-	-	-	-	0.50	1.50	-	-	-	-	0.53	1.48	-	-	-	-	105	99
18	-	-	-	-	1.50	0.50	-	-	-	-	1.46	0.47	-	-	-	-	97	95
19	-	-	-	0.50	-	0.50	-	-	-	0.52	-	0.48	-	-	-	104	-	96
20	-	-	-	0.50	-	1.50	-	-	-	0.51	-	1.47	-	-	-	102	-	98
21	-	-	-	1.50	-	0.50	-	-	-	1.53	-	0.48	-	-	-	102	-	96
22	-	-	-	0.50	0.50	-	-	-	-	0.52	0.53	-	-	-	-	104	105	-
23	-	-	-	0.50	1.50	-	-	-	-	0.51	1.52	-	-	-	-	102	101	-
24	-	-	-	1.50	0.50	-	-	-	-	1.48	0.53	-	-	-	-	99	105	-
25	-	0.50	-	0.50	-	-	-	0.51	-	0.49	-	-	-	102	-	98	-	-
26	-	1.50	-	0.50	-	-	-	1.44	-	0.48	-	-	-	96	-	96	-	-
27	-	0.50	-	1.50	-	-	-	0.50	-	1.47	-	-	-	100	-	98	-	-
28	-	0.50	0.50	-	-	-	-	0.51	0.52	-	-	-	-	102	104	-	-	-
29	-	1.50	0.50	-	-	-	-	1.46	0.53	-	-	-	-	97	105	-	-	-
30	-	0.50	1.00	-	-	-	-	0.53	1.03	-	-	-	-	105	103	-	-	-
31	-	0.50	-	-	-	0.50	-	0.50	-	-	-	0.49	-	100	-	-	-	98
32	-	1.50	-	-	-	0.50	-	1.51	-	-	-	0.47	-	100	-	-	-	95
33	1.00	0.50	0.50	-	-	-	1.02	0.49	-	-	-	-	102	98	-	-	-	-
34	1.00	0.50	-	0.50	-	-	1.01	0.48	-	0.52	-	-	101	96	-	104	-	-
35	0.50	1.00	-	-	0.50	-	-	0.98	-	-	0.51	-	-	98	-	-	102	-
36	1.00	0.50	-	-	-	0.50	-	0.50	-	-	-	0.48	-	100	-	-	-	95
37	0.50	0.50	1.00	-	-	-	-	0.51	1.03	-	-	-	-	102	103	-	-	-
38	0.80	0.60	-	-	1.00	-	-	0.61	-	-	1.04	-	-	102	-	-	104	-
39	-	0.90	1.00	-	0.50	-	-	0.93	1.04	-	0.49	-	-	103	104	-	98	-
40	-	1.50	0.50	-	-	0.50	-	1.54	0.51	-	-	0.52	-	103	102	-	-	104
41	-	0.50	1.00	-	-	0.80	-	0.48	1.05	-	-	0.84	-	96	105	-	-	105
42	-	0.80	1.00	-	1.00	-	-	0.82	0.99	-	1.01	-	-	103	99	-	101	-

Conflict of interest

The author declares no conflict of interest.

5. Conclusions

In the present work, we proposed a simple approach for simultaneous determination of binary and ternary mixtures. In this method, there is no need for considering the whole range of the mixture spectra and hence it seems to be a good alternative for simultaneous determination of binary or ternary mixtures. The method is very simple and easy to

operate needing only the spectrophotometric data in two or three wavelengths without any additional operations, and is more robust than mean centering method in the relatively high level of noise. The proposed method was applied for the simultaneous determination of copper, cobalt, zinc, palladium, iron, and nickel in synthetic mixtures of tap water. The results obtained show a very good level of accuracy and precision

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