

## Simultaneous Spectrophotometric Determination of Cu(II), Co(II) and Ni(II) using Ratio Spectra-Continuous Wavelet Transformation in some Food and Environmental Samples

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A razão entre o espectro contínuo e a transformada “wavelet” foi usada para a determinação simultânea de misturas ternárias de cobre, cobalto e níquel sem separação prévia. O método é baseado na reação de complexação destes cátions com 1-(2-piridilazo)-2-naftol (PAN) em meio micelar triton X-100, pH 8,0. Os resultados mostraram que Cu(II), Co(II) e Ni(II) foram determinados simultaneamente nos intervalos de concentração de 0,20-4,0, 0,20-4,0 e 0,50-7,0 mg L<sup>-1</sup>, respectivamente. Foram selecionadas diferentes wavelets-mãe, da família das transformadas wavelet no contínuo, e aplicadas sob condições ótimas nas determinações multi-componentes. O método foi testado pela análise de várias misturas ternárias sintéticas de íons Cu(II), Co(II) e Ni(II). Usando as condições otimizadas, o método proposto foi aplicado com sucesso na determinação simultânea destes metais em algumas amostras reais incluindo comprimidos multivitamínicos, chá, cevada, espinafre, leite em pó, solo, água do mar e amostras de água de torneira.

Ratio spectra-continuous wavelet transformation was used for the simultaneous determination of ternary mixtures of copper, cobalt and nickel without prior separation steps. The method is based on the complexation reaction of these cations with 1-(2-pyridylazo)-2-naphthol (PAN) in triton X-100 micellar media at pH 8.0. The results showed that Cu(II), Co(II) and Ni(II) could be determined simultaneously in the ranges 0.20-4.0, 0.20-4.0 and 0.50-7.0 mg L<sup>-1</sup>, respectively. Different mother wavelets from the family of continuous wavelet transforms were selected and applied under the optimal conditions for multi-component determinations. The method was tested by analyzing various synthetic ternary mixtures of Cu(II), Co(II) and Ni(II) ions. Under the working conditions, the proposed method was successfully applied for the simultaneous determination of these metals content evaluation in some real samples including multivitamin tablet, tea, barley, spinach, chocolate, milk powder, soil, sea water and tap water samples.

**Keywords:** Cu(II), Co(II), Ni(II), wavelet transformation, vegetables

### Introduction

Heavy metals are grouped within the category of environmental toxins; it is however a fact that many organisms need trace amounts of many metals to survive. They play significant roles in biological processes, in diseases, as well as in familial amyotrophic lateral sclerosis and others.<sup>1-4</sup>

Cobalt is beneficial for humans because it is a part of vitamin B<sub>12</sub> and is used to treat anemia with pregnant women.<sup>4</sup> Cobalt and nickel share right/left-sided cell receptors and are considered essential to human health,

too. While a cobalt and vitamin B<sub>12</sub> relationship is well documented, a similar, but less documented affiliation applies to nickel and vitamin B<sub>12</sub>. Nickel interacts with RNA and DNA. Copper and iron work together for optimal well-being. Copper helps to convert iron to the ferric form, the most useful type, and also helps transport iron to, and from, tissues. However, high concentrations of these metal ions may damage human health such as allergic reaction of the skin, irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhoea hair loss, bleeding, diarrhoea, coma and even death.<sup>5,6</sup>

In the literature, due to strong environment and biological impact caused by heavy metals, the determinations have

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been received particular attentions. Among analytical methods, flame atomic absorption spectrometry (FAAS) have been a technique widely used for quantification of metal species.<sup>7-9</sup>

Of the other reported methods in the literature on the determination of metal ions, we address to the ICP-MS,<sup>10,11</sup> ICP-OES,<sup>12</sup> spectrophotometry,<sup>13,14</sup> and electroanalytical techniques.<sup>15</sup>

Chemometric approaches such as multivariate calibration (partial least squares (PLS) and principal component regression (PCR)) have been used for the simultaneous determination.<sup>16-20</sup> PLS and PCR can be used for resolving overlapped spectral systems, but when the correlation of components increases, the error of predicted results will increase. Also these methods use an abstract mathematical content which it is not easy to understand and apply. For these reasons, we believe that simple new methods with easy to learn algorithms are necessary for quantitative and routine analysis of the mixtures. Few reports have been published on the application of wavelet transforms for simultaneous determination of chemical species. The combined use of continuous wavelet transformation (CWT) and zero-crossing was firstly formulated by Dinç and Baleanu,<sup>21-23</sup> for the quantitative resolution of two component mixtures. Also Dinç and co-workers,<sup>24-29</sup> used the ratio spectra-CWT with zero-crossing technique for the multicomponent spectral analysis of ternary mixtures of three active compounds with overlapping spectra. Recently, we applied CWT for simultaneous determination of metal ions in different mixtures,<sup>30</sup> determination of enantiomeric ratio,<sup>31</sup> simultaneous determination of binary mixture of surfactants and simultaneous kinetic determination of binary mixture.<sup>32,33</sup>

Recently, we successfully applied artificial neural networks (ANNs) for quaternary determination of Co<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> using a recently synthesized Schiff base. In general, design of ANNs architecture is very long.<sup>34</sup> These methods need several set of data as calibration, prediction and validation sets. Also like as multiplicative calibration methods, all of component should be presented in calibration step.

In the present study we use the main advantage of WT in extraction of characteristic information. Hence we report the applicability of CWT-zero crossing method as a new and easy method for analysis of the mixtures. Simultaneous spectrophotometric determination of Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> based on their complexes with 1-(2-pyridylazo)-2-naphthol (PAN), using CWT was performed. The method was validated by simultaneous determination of Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> in multivitamin tablet, tea, barley, spinach, chocolate, milk powder, soil, sea water and tap water samples.

## Theory of continuous wavelet transformation

Wavelet bases, like Fourier bases, reveal the signal regularity through the amplitude of coefficients, and their structure leads to a fast computational algorithm. However, wavelets are well localized and few coefficients are needed to represent local transient structures. As opposed to a Fourier basis, a wavelet basis defines a sparse representation of piecewise regular signals, which may include transients and singularities.<sup>35</sup> A wavelet transform is the representation of a function by wavelets. The wavelets are generated from a single basic wavelet  $\psi(t)$ , the so-called "mother wavelet", by scaling and translation. The subspace of scale  $a$ , or frequency band is generated by the functions,

$$\Psi_{(a,b)}(t) = \frac{1}{\sqrt{a}} \psi\left(\frac{t-b}{a}\right) \quad (18)$$

where  $a$  is positive and defines the scale and  $b$  is any real number and defines the shift. The original signal can be reconstructed by suitable integration over all the resulting frequency components after projection of a given signal on a continuous family of frequency bands. In this study Haar (haar) and Meyer (dmev) were used as mother wavelets.

## Experimental

### Reagent and standard solutions

All solutions were prepared using analytical grade reagents. Stock solutions of Cu<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> (1000 mg L<sup>-1</sup>) were prepared by dissolving Cu(NO<sub>3</sub>)<sub>2</sub>, CoCl<sub>2</sub> and NiCl<sub>2</sub>·6H<sub>2</sub>O (Fluka) in water. A 2.0 × 10<sup>-3</sup> mol L<sup>-1</sup> PAN solution was prepared by dissolving it in ethanol. Triton X-100 (TX-100) stock solution (10%, v/v) was prepared by dissolving appropriate amount of concentrated solution (Merck) in hot distilled water. A buffer solution of pH 8.0 was prepared from KH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>.

### Apparatus and data processing

A detection system consisting of analytic Jena SPECORD 250-222P169 UV/Vis double beam spectrophotometer with 1 cm path length quartz cell, was used. The slit length was 1 nm and scan speed of 100 nm s<sup>-1</sup> was selected. The spectra were recorded at 1 nm intervals. A Shimadzu 6700 atomic absorption spectrometer (Kyoto, Japan) was used. Hollow cathode lamps were employed as radiation source with a slit width of 2 nm and 8 mA lamp currents. A short program in MATLAB 7.1 was written for performing normalization of the data. Transformation of ratio spectra was performed in

MATLAB 7.1, then the WT ratio signals were transferred to EXCLE.

### Procedure

Suitable amounts of each metal, 1 mL of  $2.0 \times 10^{-3}$  mol L<sup>-1</sup> PAN solution, 1.0 mL TX-100 solution and 1.0 mL of buffer solution were added to a 10 mL volumetric flask.

To measure completeness of complex formation reaction, the absorbance values of metal-PAN complexes were monitored at different intervals of time. Shorter reaction time would minimize complex formation, while standing longer times, completed the complex formation. For Co<sup>2+</sup>, complex formation was completed during 20 min, but for Cu<sup>2+</sup> it was completed during 15 min and for Ni<sup>2+</sup> it was completed during 18 min. Hence further studies have been carried out at 20 min after mixing of reagents. The solution was diluted to the mark with water and allowed to stand for 20 min at room temperature. A portion of the solution was then transferred into a 1-cm glass cell to record the absorption spectra in the wavelength range 540-700 nm.

### Preparation of multivitamin tablet sample

Ten tablets were weighted and powdered in a mortar. A tablet amount and 2 mL concentrated HNO<sub>3</sub> was transferred to a 50 mL flask and diluted to the mark with doubly distilled water. The content of flask was mechanically shaken for a period of 30 min and filtered. After that the developed methods were applied to the final solution.

### Preparation of milk powder sample

A 0.5 g of sample was accurately weighted for determination and digested with HNO<sub>3</sub>-HClO<sub>4</sub> (9:1, v/v) to near dryness. Distilled water of 20 mL was added in the residue and evaporated to dry again for removing residual. The resulting solution was transferred into a 50.0 mL volumetric flask and diluted to the mark with water. After that the developed method was applied to the final solution.<sup>36</sup>

### Preparation of vegetables and foodstuff samples

Spinach, barely and tea leaves samples available on the local markets in Bushehr were purchased for investigation. First, the samples were cleaned with tap water and double distilled water. Then, the samples were dried at 110 °C. Each of the dried varieties of samples were ground to reduce particle size and then thoroughly mixed to ensure homogeneity samples individually. Masses of 300 mg

of cabbage, lettuce, spinach, and burley and soybean meal were transferred into separate 250 mL beakers and 5 mL of 0.5 mol L<sup>-1</sup> nitric acid was added to moisten the samples thoroughly. This was followed by adding 10 mL of concentrated nitric acid and heating on a hot plate (130 °C) for 3 h. After cooling to room temperature, 5 mL concentrated perchloric acid was added drop wise. The beaker was heated gently until completion of sample decomposition resulting in a clear solution. This was left to cool down and then was transferred into a 100 mL volumetric flask by rinsing the interior of the beaker with small portions of 0.1 mol L<sup>-1</sup> nitric acid and the solution was filled to the mark with the same acid.<sup>37</sup>

### Preparation of chocolate sample

The chocolate was taken for wet digestion with mixture of nitric acid (HNO<sub>3</sub>) and perchloric acid (HClO<sub>4</sub>) in the ratio 3:1 for decomposition. After gentle heating for 16 h, colorless solution was obtained, which was evaporated to near dryness. On completion of digestion and adequate cooling of residues, solutions were made up to 10 mL with 0.04 mol L<sup>-1</sup> nitric acid.<sup>38</sup>

### Preparation of soil sample

Soil was sampled from the surface layer (0-20 cm), air-dried and ground to pass 250 mm sieve prior to hydrolysis. The weighted soil samples were hydrolyzed with 12 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> (1 mL) in a closed hydrolysis flask at ambient temperature for 16 h followed by treatment with 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at 100 °C for 6 h. After hydrolysis, the mixture was filtered through a glass fiber filters (GF 6, Schleicher and Schuell, Germany).<sup>39</sup>

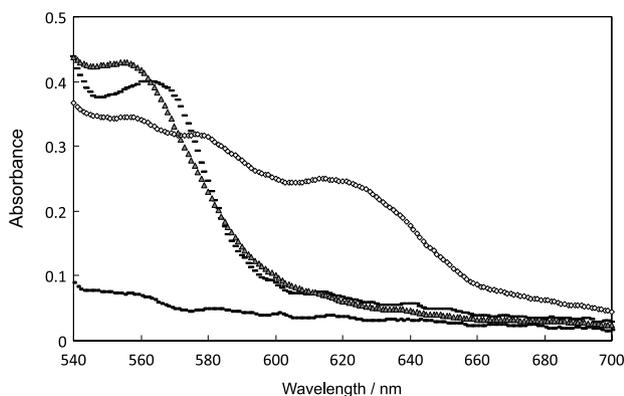
## Results and Discussion

### Spectral composition of complexes

Figure 1 shows the absorption spectra for Cu-PAN, Co-PAN and Ni-PAN complexes at pH 8.0 in wavelength range 540-700 nm against water blank. As Figure 1 shows, the absorption spectra of the complexes overlap, and therefore interfere in the spectrophotometric determination of each other.

### Optimization of the experimental conditions

The overall processes are influenced by pH of the solution, TX-100 concentration and concentration of PAN. Hence, these experimental parameters affecting



**Figure 1.** Spectra of PAN complexes with Ni<sup>2+</sup> (–) (0.80 mg L<sup>-1</sup>), Co<sup>2+</sup> (◇) (0.50 mg L<sup>-1</sup>), Cu<sup>2+</sup> (△) (0.80 mg L<sup>-1</sup>) and solid line 2 × 10<sup>-4</sup> mol L<sup>-1</sup> PAN at pH 8 in 1% (v/v) TX-100 micellar media.

the development of the colored complexes were carefully studied and optimized.

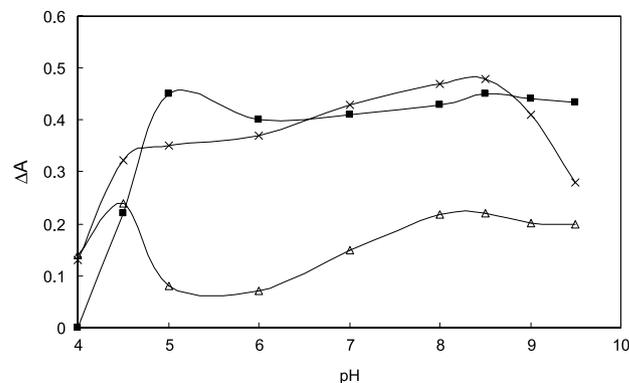
The complex formation reactions of Cu<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> with PAN are pH dependent. It was observed that the amounts of analytical signals increased by increasing pH values. In order to find the optimum pH, the effect of pH in the range 3-9.4 on the complex formation reactions of a constant concentration of each cation with PAN was investigated (Figure 2). The pH studies are carried out using sodium acetate-acetic acid (pH 3.0-4.5) and phosphate buffers (pH 5.0-9.4). Maximum colors of complexes were observed in the pH range 8.0-8.8 (Figure 2). Therefore, phosphate buffer solutions of pH 8.0 were used for further works.

The complexing agent concentration was also optimized and then 2.0 × 10<sup>-4</sup> mol L<sup>-1</sup> PAN was used as optimum concentration.

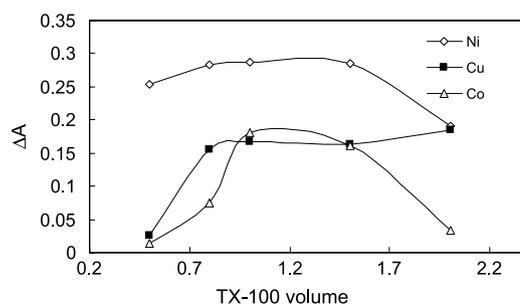
The concentration of TX-100 is another important factor. In order to obtain the optimum concentration of TX-100, the effect of surfactant concentration on the absorbance was investigated. Absorbance of the solutions increased by increasing TX-100 concentration up to 0.8% for Cu<sup>2+</sup> and 1% for Ni<sup>2+</sup> and Co<sup>2+</sup> ions. The absorbance for Ni<sup>2+</sup> and Co<sup>2+</sup> solutions remained nearly constant between 1.0-1.5% TX-100 and decreased at higher concentrations, but the absorbance remained nearly constant for Cu<sup>2+</sup> solutions at TX-100 concentrations higher than 0.8% (Figure 3). Therefore, 1% (v/v) TX-100 was used in proposed method.

Spectral characteristics and selection of appropriate mother wavelets

As Figure 1 shows, due to mutual interference of Cu-PAN, Co-PAN and Ni-PAN, applications of continuous wavelet transform and ratio spectra can provide successful determination of investigated elements without any separation steps. Absorption spectra in the linear concentration ranges



**Figure 2.** Effect of pH on  $\Delta A$  for Ni<sup>2+</sup> (x); Co<sup>2+</sup> (■) and Cu<sup>2+</sup> (△) complexes against blank solution (2 × 10<sup>-4</sup> mol L<sup>-1</sup> PAN).



**Figure 3.** Effect of TX-100 concentration on  $\Delta A$  for Cu<sup>2+</sup> (■); Ni<sup>2+</sup> (◇); Co<sup>2+</sup> (△) complexes against blank solution (2.0 × 10<sup>-4</sup> mol L<sup>-1</sup> PAN) at wavelengths 555, 565 and 620 nm for Cu<sup>2+</sup>, Cu<sup>2+</sup> and Co<sup>2+</sup>, respectively.

0.2-4 mg L<sup>-1</sup>, 0.2-4 mg L<sup>-1</sup> and 0.5-7 mg L<sup>-1</sup> were recorded for Co<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup>, respectively.

In order to analyze the ternary mixtures, one of the components should be considered as divisor. Recently, we examined the effect of normalized spectra of divisor in ternary mixtures analysis. Comparison of the results obtained using the spectra of standard solutions as divisors with those obtained using normalized spectra as divisor showed that the application of normalized spectra remove dependency of the results on the concentration of divisor, decreases the limit of detection (LOD), increases the amplitude of CWT graphs and improves the sensitivity and slope of CWT calibration graphs. So, in this paper we used normalized spectra of standard solution as divisor in further analysis. The ratio spectra were obtained with  $\Delta\lambda = 1$  nm. Various wavelet families were tested to find the optimal signal processing for obtaining desirable calibration graphs and reliable determination of the investigated elements. Haar (haar) and Meyer (dmey) were selected as optimal mother wavelets for transformation of absorption spectra.

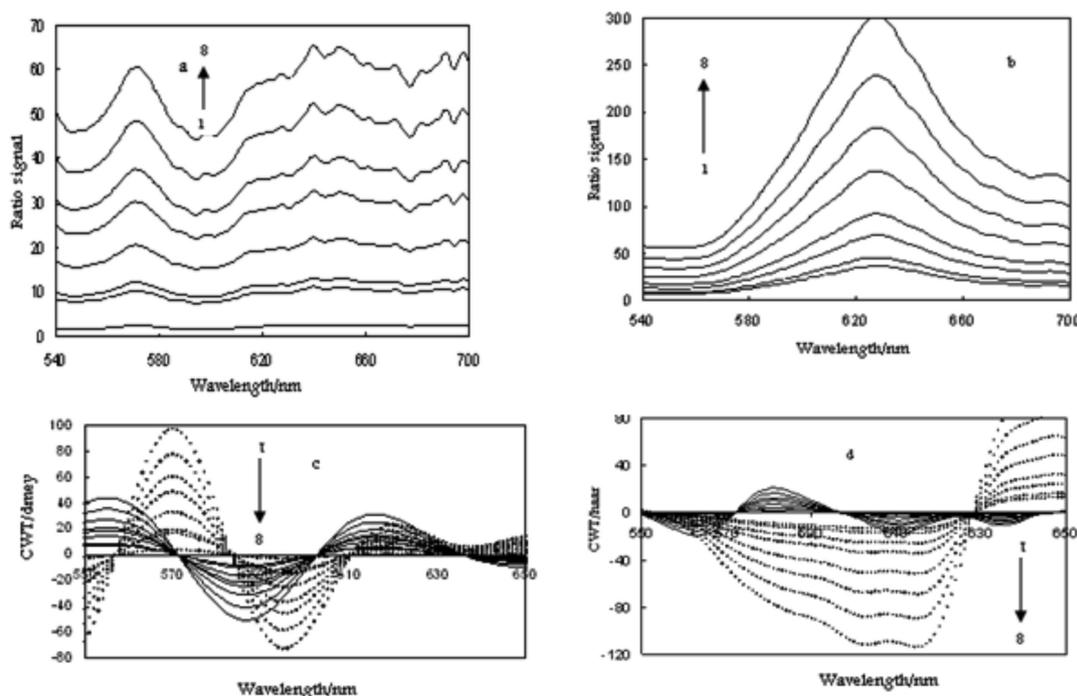
Analytical parameters

The absorption spectra of the standard solutions of Co<sup>2+</sup> and Ni<sup>2+</sup> with different concentrations were recorded

in the wavelength range 540-700 nm and divided by the normalized spectrum of the  $\text{Cu}^{2+}$  and the ratio spectra were obtained (Figures 4a and 4b). These ratio spectra were transferred from EXCLE to wavelet domain in MATLAB 7.1. Due to the higher amplitude of ratio spectra of normalized spectrum, the low value of scaling factor can improve the sensitivity of determination. The optimum value of scaling factor for determination of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  in their ternary mixture was found as  $a = 40$  with dmey. Figure 4c shows the graphs of CWT-dmey for calibration sets of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  and their ternary mixtures, which were obtained by dmey ( $a = 40$ ) on the ratio absorption spectra at the same wavelength range as ratio spectra. Calibration graphs for  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  were obtained by measuring the CWT signals at 558 or 588 for  $\text{Co}^{2+}$  corresponds to zero crosses of  $\text{Ni}^{2+}$  and 578 or 615 nm for  $\text{Ni}^{2+}$  corresponds to zero crosses of  $\text{Co}^{2+}$ . Linear regression analysis and its statistical results are shown in Table 1.

For the prediction of concentrations of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  in synthetic ternary mixtures, the same procedure was used except that the spectra of the mixture were used instead of the spectra of standard solution of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  and concentrations of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  in ternary mixtures were estimated by CWT-dmey calibration equations at zero crosses. The estimated recoveries of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ , which are obtained by proposed method are given in Table 2.

Also by haar (as a mother wavelet) the transformation of ratio spectra of standards of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  at ternary mixture solutions were performed. Normalized spectrum of  $\text{Cu}^{2+}$  was used as divisor. The optimum scaling value was found as  $a = 20$ . By measuring the amplitude of CWT signals at 572 or 598 nm for  $\text{Co}^{2+}$  (corresponding to zero crosses of  $\text{Ni}^{2+}$ ) and 628 nm for  $\text{Ni}^{2+}$  (corresponding to zero cross  $\text{Co}^{2+}$ ), the calibration graphs of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  were built (Figure 4d). Linear regression analysis and its statistical results are shown in Table 1. By using the



**Figure 4.** The ratio spectra for (a) Ni-PAN: (1) 0.065, (2) 1.0, (3) 1.3, (4) 1.5, (5) 2.0, (6) 3.0, (7) 5.0 and (8) 6.5  $\text{mg L}^{-1}$  and (b) Co-PAN: (1) 0.50, (2) 1.0, (3) 1.5, (4) 2.0, (5) 3.0, (6) 4.0, (7) 5.0 and (8) 6.5  $\text{mg L}^{-1}$ , created using normalized spectrum of  $\text{Cu}^{2+}$  as divisor; (c) CWT-dmey signal of Ni-PAN (–) and Co-PAN (•); (d) CWT-haar signal of Ni-PAN(–) and Co-PAN(•); concentrations are same as (a) and (b).

**Table 1.** Statistical results of calibration graphs obtained in zero cross points of Co-PAN and Ni-PAN using normalized spectrum of  $\text{Cu}^{2+}$  as divisor

Mother wavelet	Divisor	$\lambda$ / nm	Regression equation	$R^2$	LOD / ( $\text{mg L}^{-1}$ )	LOQ / ( $\text{mg L}^{-1}$ )
dmey	$\text{Cu}^{2+}$	558	$\Delta A = -6.948C_{\text{Co}} - 0.4956$	0.9969	0.013	0.043
		588	$\Delta A = 6.7311C_{\text{Co}} - 1.106$	0.9978	0.013	0.044
		578	$\Delta A = 8.494C_{\text{Ni}} + 1.378$	0.9992	0.010	0.035
		615	$\Delta A = -3.108C_{\text{Ni}} - 0.508$	0.9980	0.029	0.096
haar	$\text{Cu}^{2+}$	573	$\Delta A = -8.668C_{\text{Co}} - 0.618$	0.9969	0.010	0.034
		597	$\Delta A = -15.63C_{\text{Co}} + 1.11$	0.9969	0.006	0.020
		628	$\Delta A = -1.7846C_{\text{Ni}} - 0.124$	0.9979	0.050	0.168

calibration equations,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  were determined in ternary synthetic mixtures. Mean recovery results are presented in Table 2.

In the similar manner, simultaneous determination of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  in ternary mixtures by creating ratio spectra of standard solution of them by dividing to normalized spectrum of  $\text{Co}^{2+}$  was carried out. Transformation of these ratio spectra were performed by CWT-dmey ( $a = 40$ ) and CWT-haar ( $a = 20$ ). Amplitude of CWT-dmey graphs yield straight lines at 603 nm for  $\text{Ni}^{2+}$  (corresponding to zero cross of  $\text{Cu}^{2+}$ ) and 583 nm for  $\text{Cu}^{2+}$  (corresponding to zero cross of  $\text{Ni}^{2+}$ ). Also two straight lines from amplitudes of CWT-haar graphs were obtained at 552 and 566 nm for determination of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ , respectively. Its regression coefficients and statistical results at zero crosses are shown in Table 3. Mean recoveries and the relative standard deviations were calculated and the results were given in Table 2.

Simultaneous determination of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  using normalized spectrum of  $\text{Ni}^{2+}$  with dmey and haar was also performed. Standard and ternary mixtures spectra were divided by normalized spectrum of  $\text{Ni}^{2+}$ . The ratio spectra at optimum amount of scale values were transformed and CWT-dmey and CWT-haar coefficients were obtained. In similar way, the calibration equations were obtained at zero crosses and used for calculation of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  concentration in ternary mixtures (Table 3). Mean recoveries and the relative standard deviations were calculated and their results were given in Table 2.

The limit of detection (LOD) and limit of quantification (LOQ) of the method were calculated and are given in Tables 1 and 3.<sup>40</sup>

## Interference study

The interference study was performed by analyzing solutions containing  $2.0 \text{ mg L}^{-1}$  each of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  cations in the presence of different cations and anions. The tolerance limit was taken as the concentration of interfering ion caused less than 5% relative error in the determination of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ . The results showed that the ions  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{AsO}_4^{3-}$  did not interfere even when present in 1000-fold excess over the  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ . The ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{SCN}^-$  did not interfere up to 500-fold excess and interfered at higher concentrations. The ions  $\text{Si(IV)}$ ,  $\text{Pb}^{2+}$  and  $\text{Fe}^{2+}$  did not interfere up to 80-fold excess. Thiocyanate and thiourea did not interfere when present up to 50-fold excess but  $\text{Zn}^{2+}$  interfered at 4.5-fold excess over analytes. Interference effect of  $\text{Zn}^{2+}$  in vegetables and multivitamin tablet was removed after digestion of samples with  $\text{H}_2\text{S}$  in the presence of  $\text{NH}_3$  (white precipitate of  $\text{ZnS}$  was filtered from the solution).

The interference effect of organic matters could be eliminated by digestion procedures.

## Applications of the method to real samples

Results for the analysis of synthetic mixtures by the proposed method (Table 2) showed satisfactory results for the simultaneous determination of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ . To demonstrate the applicability of the optimized method to real samples, it was applied to the simultaneous determination of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  in barley, spinach, multivitamin tablet, chocolate and tea leaves, which contain the desired elements in different amounts.

**Table 2.** Mean recoveries and relative standard deviation for the simultaneous determination of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in various synthetic mixtures by the proposed method

	$\text{Cu}^{2+}$ as divisor		$\text{Co}^{2+}$ as divisor		$\text{Ni}^{2+}$ as divisor	
	$\text{Co}^{2+}$	$\text{Ni}^{2+}$	$\text{Cu}^{2+}$	$\text{Ni}^{2+}$	$\text{Co}^{2+}$	$\text{Cu}^{2+}$
dmey	$96.48 \pm 0.24$	$103.76 \pm 2.21$	$106.42 \pm 0.45$	$94.64 \pm 1.26$	$109.38 \pm 0.38$	$108.76 \pm 0.64$
haar	$100.95 \pm 0.46$	$107.03 \pm 0.45$	$95.74 \pm 0.38$	$105.12 \pm 0.26$	$107.03 \pm 0.04$	$92.46 \pm 2.26$

**Table 3.** Statistical results of calibration graphs obtained in zero cross points by proposed method

Mother wavelet	Divisor	$\lambda / \text{nm}$	Regression equation	$R^2$	LOD / ( $\text{mg L}^{-1}$ )	LOQ / ( $\text{mg L}^{-1}$ )
dmey	$\text{Co}^{2+}$	583	$\Delta A = -6.466C_{\text{Cu}} - 4.3741$	0.9818	0.014	0.046
		603	$\Delta A = -7.188C_{\text{Ni}} - 3.614$	0.9879	0.012	0.041
haar	$\text{Co}^{2+}$	566	$\Delta A = -15.31C_{\text{Cu}} - 10.360$	0.9989	0.005	0.020
		552	$\Delta A = 6.536C_{\text{Ni}} + 1.066$	0.9980	0.013	0.045
dmey	$\text{Ni}^{2+}$	619	$\Delta A = 21.38C_{\text{Cu}} + 1.526$	0.9969	0.004	0.014
		595	$\Delta A = -5.952C_{\text{Co}} - 0.2456$	0.9972	0.015	0.050
haar	$\text{Ni}^{2+}$	564	$\Delta A = 7.098C_{\text{Cu}} + 0.293$	0.9972	0.012	0.042
		572	$\Delta A = -14.96C_{\text{Co}} + 0.704$	0.9993	0.006	0.020
		597	$\Delta A = -33.29C_{\text{Co}} - 2.3749$	0.9969	0.002	0.010

**Table 4.** Simultaneous determination of Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> in different samples by proposed and FAAS (mg g<sup>-1</sup>) and student t-test at P = 0.05

Metal	Method	Sample <sup>a</sup>					t <sub>calculated</sub>				t <sub>critical</sub> <sup>c</sup>
		Chocolate	Tea	Spinach	Barley	Tablet	Tea	Spinach	Barley	Tablet	
Co <sup>2+</sup>	dmey	0.005 ± 0.0022	0.64 ± 0.060	0.03 ± 0.011	0.14 ± 0.012	-	2.3	1.5	1.7	-	2.53
	haar	0.005 ± 0.0013	0.62 ± 0.081	0.02 ± 0.014	0.14 ± 0.016	-	2.4	1.9	2.3	-	
	FAAS	0.005 ± 0.0020	0.72 ± 0.001	0.03 ± 0.001	0.15 ± 0.015	ND <sup>b</sup>	-	-	-	-	
Ni <sup>2+</sup>	dmey	0.001 ± 0.0001	0.124 ± 0.06	0.12 ± 0.010	0.13 ± 0.061	-	0.24	2.0	0.3	-	
	haar	0.001 ± 0.0001	0.14 ± 0.073	0.13 ± 0.012	0.13 ± 0.062	-	0.08	2.3	0.1	-	
	FAAS	0.002 ± 0.0010	0.13 ± 0.032	0.14 ± 0.044	0.14 ± 0.028	ND <sup>b</sup>	-	-	-	-	
Cu <sup>2+</sup>	dmey	0.003 ± 0.0012	0.04 ± 0.034	0.17 ± 0.050	0.01 ± 0.031	0.24 ± 0.041	-	1.0	-	0.74	
	haar	0.003 ± 0.0012	0.04 ± 0.031	0.17 ± 0.020	0.01 ± 0.032	0.25 ± 0.004	-	2.4	-	1.3	
	FAAS	0.003 ± 0.0011	ND <sup>b</sup>	0.19 ± 0.024	ND <sup>b</sup>	0.25 ± 0.012	-	-	-	-	

<sup>a</sup>Average of three determinations ± standard deviation; <sup>b</sup>ND: not detected; <sup>c</sup> for 2 degrees of freedom.

The concentrations of Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> were determined by the CWT-dmey and CWT-haar. The amounts of Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> in the samples were also determined by flame atomic absorption spectrometry (FAAS). The amounts of metal ions obtained by the proposed method were in good agreement with those obtained by FAAS as the statistically compared by student's t-test (P = 0.05). The results are shown in Table 4. As the results show, the calculated t values are less than that tabulated for 2 degrees of freedom and P = 0.50. This indicates that the values obtained by proposed method and standard method do not differ.

Reliability of proposed procedure was also checked by spiking experiments. The results are presented in Table 5 for milk powder, sea water and tap water. The analytical procedure of milk powder and soil samples was described in experimental section. It was added 0.50 mg L<sup>-1</sup> of stock solutions of cations for milk, sea water and tap water solutions, and 0.20 mg L<sup>-1</sup> for soil. This procedure was repeated three times for each cations.

The mean recoveries of the trace metal ions from a water samples, milk and soil samples were calculated.

**Table 5.** Simultaneous determination of Co<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> from spiked samples (for three spikes)

Ions	Added / (mg L <sup>-1</sup> )	Found / (mg L <sup>-1</sup> )	Recovery
Milk powder			
Co <sup>2+</sup>	0.50	0.525 ± 0.032	105
Ni <sup>2+</sup>	0.50	0.485 ± 0.028	97
Cu <sup>2+</sup>	0.50	0.520 ± 0.012	104
Sea water			
Co <sup>2+</sup>	0.50	0.515 ± 0.030	103
Ni <sup>2+</sup>	0.50	0.520 ± 0.042	104
Cu <sup>2+</sup>	0.50	0.480 ± 0.025	96
Tap water			
Co <sup>2+</sup>	0.50	0.520 ± 0.022	104
Ni <sup>2+</sup>	0.50	0.485 ± 0.018	97
Cu <sup>2+</sup>	0.50	0.523 ± 0.025	104.6
Soil			
Co <sup>2+</sup>	0.20	0.210 ± 0.018	105
Ni <sup>2+</sup>	0.20	0.204 ± 0.014	102
Cu <sup>2+</sup>	0.20	0.201 ± 0.017	100.5

The recoveries of the metal ions were in the order of 96-104%. The recovery of spiked samples is satisfactorily reasonable and indicates the capability of the method in the determination of Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> in real samples.

## Conclusions

The Cu<sup>2+</sup>, Ni<sup>2+</sup> and Co<sup>2+</sup> mixture based on their complexation with the common reagent PAN, due to the high spectral overlapping observed between the absorption spectra, is a complex system. For overcoming the drawback of spectral interferences, the ratio spectra-CWT zero crossing method is applied. The method, due to advantages such as simplicity, high reliability, reproducibility and sensitivity of ions, is a powerful tool for rapid and sensitive determination of these ions in various media. The method uses common reagent PAN and can decrease cost of analysis. The results are all satisfactory. An important advantage of the method is using normalized spectra. Hence, this removes the optimization step for divisor concentration and therefore reduces the analysis time.

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