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H-point standard addition method for simultaneous determination of Fe(II), Co(II) and Cu(II) in micellar media with simultaneous addition of three analytes

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Abstract

H-point standard addition method, HPSAM, with simultaneous addition of three analytes is proposed for the resolution of ternary mixtures. It is a modification of the previously described H-point standard addition method that permits the resolution of three species from a unique calibration set by making the simultaneous addition of the three analytes. The method calculates the analyte concentration from spectral data at two wavelengths where the two species selected as interferents present the same absorbance relationship. These wavelength pairs are easily found, and can be selected to give the most precise results. Diethyldithiocarbomate (DDC) in a cationic micellar solution of cetyltrimethylammonium bromide (CTAB) was used for determination of Fe(II), Co(II) and Cu(II) at pH 5.50. The results showed that simultaneous determination of Fe(II), Co(II) and Cu(II) could be preformed in the range of 0.0–6.0, 0.0–8.0 and 0.0–12.0 μg ml^{-1}, respectively. The proposed method was successfully applied to the simultaneous determination of Fe(II), Co(II) and Cu(II) in several synthetic mixtures containing different concentration of Fe(II), Co(II) and Cu(II).

Keywords: H-point standard addition method (HPSAM); Ternary mixtures; Fe(II); Co(II); Cu(II)

1. Introduction

Iron, cobalt and copper have some similar chemical behavior and appear together in many samples, especially alloys. Due to the industrial facilities, heavy metal contents in environmental samples increase unfavorably. So accurate and reliable analytical methods possessing high sensitivity and selectivity coupled with convenience and economy for the determination of heavy metals are required. Several analytical techniques such as X-ray fluorescence (XRF) [1,2], neutron activation analysis (NAA) [3], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [4,5], atomic absorption spectrometry using either flame (FAAS) [6,7], or electrothermal atomization (ETAAS) [8,9], chromatography [10–12], electroanalytical techniques [13–15], UV–vis spectrophotometry [16–20] have been used for the multielement analysis in different matrices. Some of these methods are not convenient for routine analysis of large sets of samples because of their high cost and in some cases low sensitivity and selectivity. So demands for more sensitive and less expensive methods have been made in analytical chemistry especially where rapid analysis is needed. Despite of the success of AAS and ICP-MS techniques there is still great interest in the application of spectrophotometric methods in determination of metal ions, due to both the rapidity and simplicity of the technique. However, the simultaneous determination of multielements by the use of traditional UV–vis spectrophotometric techniques is difficult without any separation processes because of overlapped absorption spectra. H-point standard addition method (HPSAM), which is a modification of the standard addition method, permits both proportional and constant errors produced by the matrix of the sample to be corrected directly. The fundamentals of HPSAM were outlined by Bosch Reig and Campins Falco in 1988 [21]. It permits the determination of two species with extensively or even completely overlapping spectra [22]. Absorbance increments were used where only the analyte concentration was required [23]. This variant allows the elimination of the blank bias error due to the use of absorbent blank [24,25]. In addition, it has been

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applied to HPLC [26,27] and to the analysis of kinetic data [28], with an additional variant, time. The basis of the method has also been developed for the use of spectroflourimetry and synchronous spectroflourimetry [29]. The method is also of use when the interferents are not known [30]. In this way, the generalised H-point standard additions methods (GHPSAM) have been proposed [31]. HPSAM is also used in electroanalytical techniques [32] and in the studies of chemical equilibria systems [33]. It is also developed for resolution of binary mixtures with simultaneous addition of both analytes [34].

The basis of the HPSAM for spectrophotometric determination of ternary mixtures was established in 1995 [35]. The method calculates the analyte concentration from spectral data at two wavelengths where the two species selected as interferents present the same absorbance relationship. In this variant of HPSAM, in order to obtain the concentration of all three analytes, the standard addition method should be done individually for every analyte and a calibration line for each analyte should be plotted. However, this methodology can be simplified by using a single calibration graph with simultaneous standard additions of three analytes.

The ability of micellar systems to solubilize a wide variety of compounds, which are insoluble or springly soluble in water, is one of their main properties. As a consequence of incorporation in a micellar structure, the chemical equilibria, the reactivity as well as spectral and electrochemical responses of the substrates can be drastically altered. These properties have proved to be very useful in many areas of analytical chemistry, such as separation techniques or determination based on spectral methods [36,37]. Many of the analytical applications using micellar solutions involve determination of metal ions via their complexation with suitable ligands [37]. In the case of uncharged metal complexes, solubilization in micellar solutions can be described in terms of distribution equilibria between the micelles and aqueous phase, in which the micellar phase plays the same role as the organic solvent in liquid–liquid extraction [38–40]. Micelles can enhance the sensitivity of spectrophotometric procedure, and analytical use can also be made of other effects such as variations of equilibrium constants, micellar analysis, spectral shifts, and co-solubilization of samples, reagents, and products [41–44]. To determine several metal ions using their colored complexes by UV–vis spectrophotometry cationic surfactants [45–47] are used rather than anionic or non-ionic surfactants. Since the electrostatic attractive interaction between metal ion and cationic surfactants is not present, and the process, which metal ion combines with chelating agent to form a complex, is not affected.

The increasing important of the use of iron, cobalt and copper in widely different fields, particularly in metallurgy has made it necessary to develop simple, inexpensive and sensitive methods for the determination of traces of these ions in different samples. Diethyldithiocarbomate (DDC) combines with iron, cobalt and copper ions to form metal complexes [48]. These complexes do not dissolve in aqueous solutions, so it is necessary to do a solvent extraction. Micellar systems are convenient to use because they are optically transparent, readily available and stable [48].

In this work, the HPSAM is developed in order to make simultaneous standard addition of three analytes to obtain their concentration from a unique calibration set. To the best of our knowledge this is the first report on the simultaneous standard addition of three species for using ternary version of HPSAM. Iron, cobalt and copper are determined simultaneously using DDC as complexing agent in micellar medium of cetyltrimethylammonium bromide (CTAB) with simultaneous addition of three species without any pretreatement processes.

2. Theoretical background

Consider S as a ternary mixture consisting of the compounds X, Y and Z. Absorbance of the sample at each wavelength will be the sum of the individual absorbances of the species X, Y and Z at this wavelength:

$$A_{S,j} = \varepsilon_{X,j} C_X^0 + \varepsilon_{Y,j} C_Y^0 + \varepsilon_{Z,j} C_Z^0 = A_{X,j}^0 + A_{Y,j}^0 + A_{Z,j}^0 \tag{1}$$

where $\varepsilon_{X,j}$, $\varepsilon_{Y,j}$ and $\varepsilon_{Z,j}$ are the molar absorption coefficients for the species X, Y and Z at λ_j; C_X^0, C_Y^0 and C_Z^0 are the concentration of the species X, Y and Z in the sample; $A_{X,j}^0$, $A_{Y,j}^0$ and $A_{Z,j}^0$ are the individual absorbances of the species X, Y and Z in the sample.

For ternary mixtures, the method can calculate the concentration of an analyte, for example the species X, in the presence of the other two species Y and Z, from spectral data at two wavelengths $\lambda_{X(1)}$ and $\lambda_{X(2)}$, where the two other species selected as interferents present the same absorbance relationship [35]:

$$\frac{A_{Y,X(1)}}{A_{Y,X(2)}} = \frac{A_{Z,X(1)}}{A_{Z,X(2)}} = r_{Y,Z} \tag{2}$$

The factor $r_{Y,Z}$ allows the transformation of the analytical signals for Y and Z at $\lambda_{X(1)}$ and $\lambda_{X(2)}$ into a null slope line. These wavelength pairs allow the determination of any analyte X in the presence of the two interferences simultaneously. The H-point can be obtained by intersecting the line measured at wavelength $\lambda_{X(1)}$ and the line obtained by multiplying the graph at wavelength $\lambda_{X(2)}$ and the compensating factor $r_{Y,Z}$. The calculation of the unbiased analyte concentration can be made from the abscissa of the H-point:

$$-C_{\mathrm{H}(X)} = \frac{A_{X,X(1)}^0 - r_{Y,Z} \times A_{X,X(2)}^0}{r_{Y,Z} \times M_{X,X(2)} - M_{X,X(1)}} \tag{3}$$

where the superscript zero denotes the sample solution.

In this work, we used the benefit of the simultaneous standard addition of the three species X, Y and Z, in order to obtain their concentration in the sample from a unique calibration set. The required data to apply the method are the absorbance of sample and the absorbance of the sample spiked with known amount of X, Y and Z species at previously selected wavelengths.

Suppose that $\lambda_{X(1)}$ and $\lambda_{X(2)}$ are selected according to Eq. (2). The relation of the added concentrations between species X, Y and Z, C_Y^i/C_X^i and C_Z^i/C_X^i is the same in all the solutions prepared to apply the method (because the additions are made from a standard mixture of three analytes). Then, the equations of the lines that describe the absorbance of the successive standard additions by application of the HPSAM versus the added concentration of analyte X at two previously selected wavelengths will be:

For $\lambda_{X(1)}$:

$$\begin{aligned} A_{X(1)} &= A^0_{X,X(1)} + A^0_{Y,X(1)} + A^0_{Z,X(1)} + M_{X,X(1)}C^i_X \\ &\quad + M_{Y,X(1)}C^i_Y + M_{Z,X(1)}C^i_Z \\ &= A^0_{X,X(1)} + A^0_{Y,X(1)} + A^0_{Z,X(1)} + M_{X,X(1)}C^i_X \\ &\quad + M_{Y,X(1)}\frac{C^i_Y}{C^i_X}C^i_X + M_{Z,X(1)}\frac{C^i_Z}{C^i_X}C^i_X \\ &= A^0_{X,X(1)} + A^0_{Y,X(1)} + A^0_{Z,X(1)} \\ &\quad + \left[M_{X,X(1)} + \frac{C^i_Y}{C^i_X}M_{Y,X(1)} + \frac{C^i_Z}{C^i_X}M_{Z,X(1)}\right]C^i_X \\ i &= 0, 1, \ldots, n \end{aligned} \tag{4}$$

For $\lambda_{X(2)}$:

$$\begin{aligned} A_{X(2)} &= A^0_{X,X(2)} + A^0_{Y,X(2)} + A^0_{Z,X(2)} + M_{X,X(2)}C^i_X \\ &\quad + M_{Y,X(2)}C^i_Y + M_{Z,X(2)}C^i_Z \\ &= A^0_{X,X(2)} + A^0_{Y,X(2)} + A^0_{Z,X(2)} + M_{X,X(2)}C^i_X \\ &\quad + M_{Y,X(2)}\frac{C^i_Y}{C^i_X}C^i_X + M_{Z,X(2)}\frac{C^i_Z}{C^i_X}C^i_X \\ &= A^0_{X,X(2)} + A^0_{Y,X(2)} + A^0_{Z,X(2)} \\ &\quad + \left[M_{X,X(2)} + \frac{C^i_Y}{C^i_X}M_{Y,X(2)} + \frac{C^i_Z}{C^i_X}M_{Z,X(2)}\right]C^i_X \\ i &= 0, 1, \ldots, n \end{aligned} \tag{5}$$

where $A_{X(1)}$ and $A_{X(2)}$ are the measured absorbance at the two previously selected wavelengths; $M_{X,X(1)}$, $M_{Y,X(1)}$ and $M_{Z,X(1)}$ and $M_{X,X(2)}$, $M_{Y,X(2)}$ and $M_{Z,X(2)}$ are the slopes due to the addition of species of X, Y and Z in the lines obtained at $\lambda_{X(1)}$ and $\lambda_{X(2)}$; C^i_X, C^i_Y and C^i_Z are the concentration of species X, Y and Z added in the i solutions; n is the number of additions. When $i = 0$ corresponds with the solution where only exists sample. If we multiply Eq. (5) by the value for $r_{Y,Z}$ obtained in expression (2), the following equation will be obtained:

$$\begin{aligned} r_{Y,Z}A_{X(2)} &= r_{Y,Z}A^0_{X,X(2)} + r_{Y,Z}A^0_{Y,X(2)} + r_{Y,Z}A^0_{Z,X(2)} \\ &\quad + \left[M_{X,X(2)} + \frac{C^i_Y}{C^i_X}M_{Y,X(2)} + \frac{C^i_Z}{C^i_X}M_{Z,X(2)}\right]C^i_X r_{Y,Z} \\ &= r_{Y,Z}A^0_{X,X(2)} + A^0_{Y,X(1)} + A^0_{Z,X(1)} \\ &\quad + \left[r_{Y,Z}M_{X,X(2)} + \frac{C^i_Y}{C^i_X}M_{Y,X(1)} + \frac{C^i_Z}{C^i_X}M_{Z,X(1)}\right]C^i_X \end{aligned} \tag{6}$$

If we represent the analytical signal, absorbance at the two previously selected wavelengths $\lambda_{X(1)}$ and $\lambda_{X(2)}$ versus the concentration added of species X, we will obtain two lines, with intercepts $A^0_{X,X(1)} + A^0_{Y,X(1)} + A^0_{Z,X(1)}$ and $r_{Y,Z}A^0_{X,X(2)} + r_{Y,Z}A^0_{Y,X(2)} + r_{Y,Z}A^0_{Z,X(2)}$ $(= r_{Y,Z}A^0_{X,X(2)} + A^0_{Y,X(1)} + A^0_{Z,X(1)})$ and slopes:

$$M_{X,X(1)} + \frac{C^i_Y}{C^i_X}M_{Y,X(1)} + \frac{C^i_Z}{C^i_X}M_{Z,X(1)}$$

and

$$M_{X,X(2)} + \frac{C^i_Y}{C^i_X}M_{Y,X(2)}r_{Y,Z} + \frac{C^i_Z}{C^i_X}M_{Z,X(2)}r_{Y,Z}$$

The slopes obtained are the ones obtained if the addition was made of analyte X alone, with the addition of a constant, which depends on the relative concentration of each species in the standard and the absorbance of the species Y and Z at the selected wavelengths. Both lines intersect at the H-point, with the coordinates $(-C_{\mathrm{H}(X)}, A_{\mathrm{H}(Y,Z)})$ where $C_{\mathrm{H}(X)}$ is the unbiased analyte X concentration. If we operate in Eqs. (4) and (6), and taking into account that $A^0_{Y,X(1)} = r_{Y,Z}A^0_{Y,X(2)}$ and $A^0_{Z,X(1)} = r_{Y,Z}A^0_{Z,X(2)}$ and then $M_{Y,X(1)} = r_{Y,Z}M_{Y,X(2)}$ and $M_{Z,X(1)} = r_{Y,Z}M_{Z,X(2)}$:

$$\begin{aligned} & A^0_{X,X(1)} + A^0_{Y,X(1)} + A^0_{Z,X(1)} \\ &\quad + \left[M_{X,X(1)} + \frac{C^i_Y}{C^i_X}M_{Y,X(1)} + \frac{C^i_Z}{C^i_X}M_{Z,X(1)}\right](-C_{\mathrm{H}(X)}) \\ &= r_{Y,Z}A^0_{X,X(2)} + r_{Y,Z}A^0_{Y,X(2)} + r_{Y,Z}A^0_{Z,X(2)} \\ &\quad + \left[M_{X,X(2)}r_{Y,Z} + \frac{C^i_Y}{C^i_X}M_{Y,X(2)}r_{Y,Z} + \frac{C^i_Z}{C^i_X}M_{Z,X(2)}r_{Y,Z}\right] \\ &\quad \times (-C_{\mathrm{H}(X)}) \end{aligned} \tag{7}$$

from where:

$$C_{\mathrm{H}(X)} = \frac{(A^0_{X,X(1)} - r_{Y,Z}A^0_{X,X(2)}) + (A^0_{Y,X(1)} - r_{Y,Z}A^0_{Y,X(2)}) + (A^0_{Z,X(1)} - r_{Y,Z}A^0_{Z,X(2)})}{(r_{Y,Z}M_{X,X(2)} - M_{X,X(1)}) + \frac{C^i_Y}{C^i_X}(r_{Y,Z}M_{Y,X(2)} - M_{Y,X(1)}) + \frac{C^i_Z}{C^i_X}(r_{Y,Z}M_{Z,X(2)} - M_{Z,X(1)})} = \frac{A^0_{X,X(1)} - r_{Y,Z}A^0_{X,X(2)}}{r_{Y,Z}M_{X,X(2)} - M_{X,X(1)}} \tag{8}$$

where $C_{\mathrm{H}(X)} = C^0_X$ is the unbiased analyte concentration in the sample, because Eq. (8) depends only on variables related with the analyte, it is equivalent to:

$$-C_{\mathrm{H}(X)} = \frac{A^0_{X,X(1)} - r_{Y,Z}A^0_{X,X(2)}}{r_{Y,Z}M_{X,X(2)} - M_{X,X(1)}} = \frac{-A^0_{X,X(1)}}{M_{X,X(1)}} = \frac{-A^0_{X,X(2)}}{M_{X,X(2)}} \tag{9}$$

The incorrigible error due to the present of two interferents, in spite of their concentration are not constant, has been transformed into a constant systematic error, which is easily valuable, as the HPSAM basis predicts. In effect, if Eq. (9) is substituted in Eq. (4) or (6), we can prove that $A_{\mathrm{H}(Y)}$ is equivalent to:

$$\begin{aligned} A_{H(Y)} &= A^0_{Y,X(1)} + A^0_{Z,X(1)} - \left[\frac{C^i_Y}{C^i_X} M_{Y,X(1)} + \frac{C^i_Z}{C^i_X} M_{Z,X(1)}\right] C_{H(X)} \\ &= r_{Y,Z} A^0_{Y,X(2)} + r_{Y,Z} A^0_{Z,X(2)} - \left[\frac{C^i_Y}{C^i_X} r_{Y,Z} M_{Y,X(2)} + \frac{C^i_Z}{C^i_X} r_{Y,Z} M_{Z,X(2)}\right] C_{H(X)} \end{aligned} \tag{10}$$

The two wavelengths at which Eq. (2) is fulfilled are easily found, as it is derived from this equation, rewritten in the following form:

$$\frac{A_{Y,X(1)}}{A_{Z,X(1)}} = \frac{r_{Y,Z} \times A_{Y,X(2)}}{r_{Y,Z} \times A_{Z,X(2)}} = \frac{A_{Y,X(2)}}{A_{Z,X(2)}} \tag{11}$$

because in this case $r_{Y,Z}$ will be the same for the compounds Y and Z.

For analysis of a special analyte, i.e., X, only spectra of the species Y and Z are needed. The quotient between both spectra is then applied and the wavelength pairs that show the same value for this quotient are sought. Although this relationship depends on the concentration of Y and Z, it will be equal at the two selected wavelengths, independently of the concentration chosen from all possible wavelength pairs, it will be demonstrated that for every analyte there are some pairs that provide the best sensitivity. As the wavelength pairs, which obey Eq. (2), are known the optimization is easily performed for each analyte.

3. Experimental

3.1. Apparatus

UV–vis absorbance digitized spectra were collected on a Perkin-Elmer Lambda 45 spectrophotometer, using a 1 cm quartz cell, a scan rate of 480 nm min^{-1} and a slit width of 2 nm. The spectra were recorded between 320 and 700 nm, each 0.2 nm. Measurements of pH were made with a Metrohm 744 pH-meter using a combined glass electrode. The computations were made with a Pentium III computer.

3.2. Reagents

All reagents were of analytical reagent grade and used without further purification. Triply distilled water was used throughout the study. A stock solution (1000 μg ml^{-1}) of iron(II), cobalt(II) and copper(II) were prepared by dissolving $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Merck), $Co(NO_3)_2 \cdot 6H_2O$ (Merck) and $Cu(NO_3)_2 \cdot 3H_2O$ (Merck), respectively. A stock solution of diethyldithiocarbomate (0.025 M) was prepared by dissolving sodium diethyldithiocarbomate (Merck) in ethanol (Merck). A stock solution of cationic micellar (0.26 M) was prepared from *N*-cetyl-*N*,*N*-tri-methylammonium bromide (Merck). All of the solutions were prepared fresh daily. A buffer of (pH 5.5) was prepared by using tris(hydroxymethyl)aminomethane (Merck) and appropriate concentration of hydrochloric acid [49].

3.3. Procedures

Two milliliters buffer solution pH 5.5, 5 ml of stock CTAB solution (0.26), 1.6 ml of stock DDC solution (0.025 M) and appropriate volume of Fe(II), Co(II) and Cu(II) were added to 10-ml volumetric flask and made up to the mark with water. For each measurement, 2.5 ml of the above solution was transferred to a spectrophotometric cell and absorbances were measured at appropriate wavelengths. Synthetic samples containing different concentration ratio of Fe(II), Co(II) and Cu(II) were prepared, and standard additions of Fe(II) (up to 6 μg ml^{-1}), Co(II) (up to 10 μg ml^{-1}) and Cu(II) (up to 23 μg ml^{-1}) were made. Simultaneous determination of Fe(II), Co(II) and Cu(II) with HPSAM was performed by measuring the absorbances at 340, 409, 353, 406, 505 and 595 nm for each sample solution. The concentration range of Fe(II), Co(II) and Cu(II) for construction of HPSAM calibration graph were 0.0–6.0, 0.0–8.0 and 0.0–12 μg ml^{-1}, respectively.

4. Results and discussion

Diethyldithiocarbomate is frequently used as a photometric reagent for Fe(II), Co(II) and Cu(II). The photometry in the visible range is quite easy because the free DDC dose not absorb in the visible range. Interest in DDC is related to its chelating ability towards metal ions and to the analytical applications based on the micelle enhanced absorption of its metal chelates. The absorption spectra of DDC and its complexes with iron, cobalt, copper and their ternary synthetic mixture under certain experimental conditions are shown in Fig. 1. As can be seen, the spectra of the three complexes overlap severely throughout the wavelength range. Investigation was carried out to obtain the

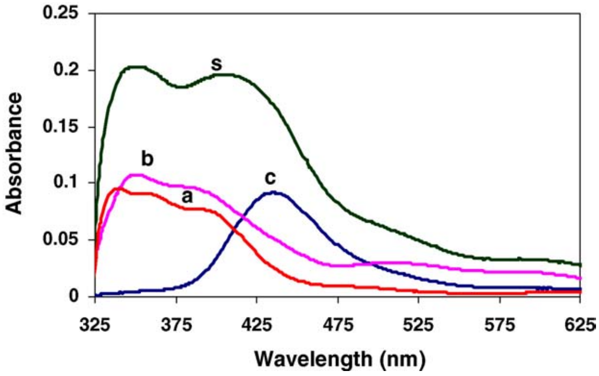

Fig. 1. Absorption spectra of (a) 0.41 μg ml^{-1} Co(II), (b) 0.28 μg ml^{-1} Fe(II) and (c) 0.53 μg ml^{-1} Cu(II), and (s) mixture of them at pH 5.5.

most favorable conditions for the simultaneous determination of iron, cobalt and copper ions.

4.1. Optimization

The experimental variables were optimized by the univarite method for each element separately. In preliminary experiments, it was found that the complex formation kinetics of Cu(II) and Co(II) with DDC in micellar medium of CTAB is quite fast but the measured absorbance for the iron complex formation is a function of time and depends on the concentration of CTAB. Therefore, the effect of amounts of micelle on absorbance was investigated. The concentration of the micelle was varied from 0.09 to 0.175 M and it was found that a stable absorbance was obtained in 0.13 M of CTAB. At higher concentration of CTAB the absorbance values decreased. So, for achieving the best sensitivity and stability the 0.13 M of CTAB was chosen as optimum concentration.

The influence of the pH values on the spectrum of each complex at a constant concentration was investigated separately. There were no significant changes in the spectrum of Co(II) complex in the pH range of 3–8, but the spectrum of Fe(II) and Cu(II) complexes showed change in absorbances at all wavelengths. The effect of pH range on Fe(II) and Cu(II) complexes at the λ_{max} of each complexes is shown in Fig. 2. For achieving the appropriate condition for applying HPSAM, pH 5.5 was selected as an optimum pH. Several types of buffers were used for adjusting the pH and tris buffer (0.05 M) was found to be the most suitable.

Absorbance of DDC-metal ion-CTAB has been found to increase with increase in the concentration of ligand. An excess concentration of ligand has been chosen to ensure quantitative subsequent formation of complexes in the whole the calibration region for three metal ions. The maximal and stable absorbance was gained with 0.004 M DDC.

4.2. Individual calibration

After optimization of parameters, absorption of the solutions containing increasing amount of each ions (i.e., iron, cobalt and copper) and a fixed (but excess) amount of the ligand in the optimum condition at appropriate wavelength for each complexes was plotted separately against the metal ion concentration in order to obtain the linear range over which the absorbance was proportional to metal ion concentration. There exist a linear correlation between the absorbances at the λ_{max} of each complexes and concentration of ions. Linearity observed was up to 0.0–6.0, 0.0–10.0 and 0.0–23.0 μg ml^{-1} for iron, cobalt and copper ions, respectively.

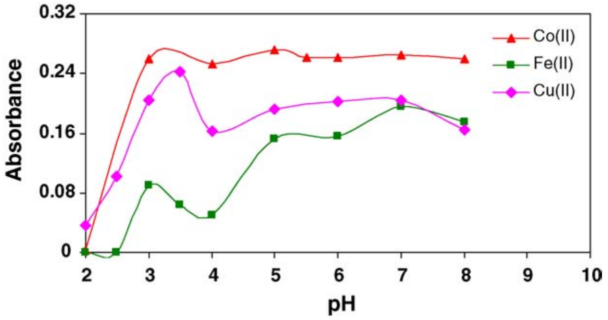

Fig. 2. Effect of pH on the change in absorbance of the complexes of Fe(II), Co(II) and Cu(II) with DDC.

4.3. Wavelength selection

In order to resolve the mixtures of Fe(II), Co(II) and Cu(II), the quotients between the spectra of Fe(II), Co(II) and Cu(II) must be obtained, according to Eq. (3). Fig. 3 shows these quotients. It must be noted that if the spectral behavior of the two interferents is similar, then the quotients are obtained with

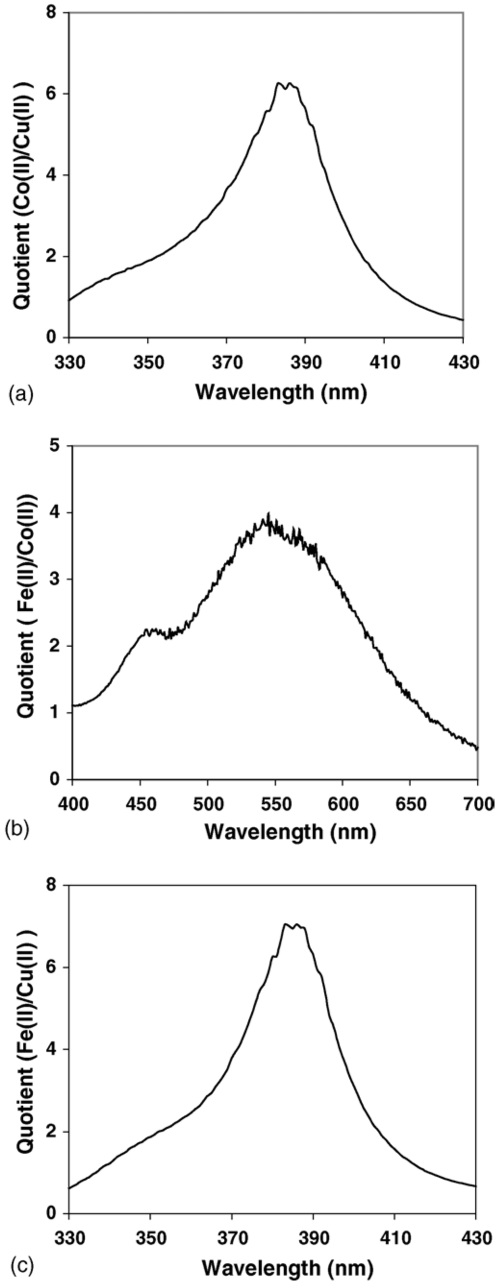

Fig. 3. Quotient between the spectra of Fe(II), Co(II) and Cu(II) with DDC.

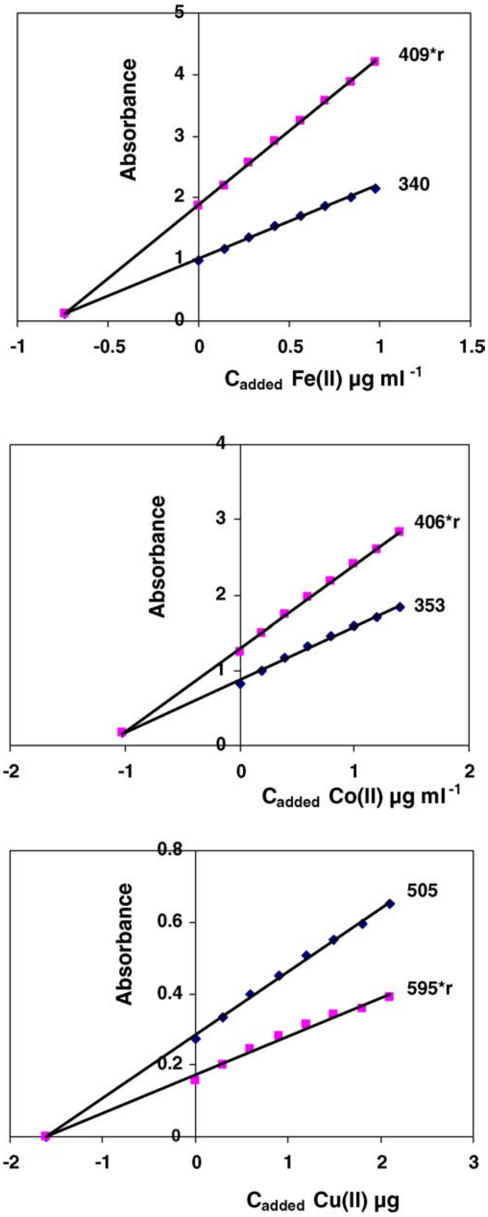

Fig. 4. H-point standard addition plots for calculation of the Fe(II) (0.7 μg ml^{-1}), Co(II) (1.0 μg ml^{-1}) and Cu(II) (1.5 μg ml^{-1}) concentrations from one calibration set.

some noise (Fig. 3b). However, where the spectral behavior of the interferents is more different (Fig. 3a and c), the quotients obtained are smoother. From these results, the wavelength pairs that show the same ratio of absorbance value in order to calculate the analyte concentration can be obtained. This method can be employed to determine any analyte in the presence of a selected pair of interferents. The three best wavelength pairs (those that give the greatest value for the denominator in Eq. (3)) were selected. The three wavelength pairs, 340–409, 353–406 and 505–595 nm were applied for calculation of Fe(II), Co(II) and Cu(II) concentrations, respectively. Fig. 4 shows the H-point standard addition plots for calculation of the Fe(II), Co(II) and Cu(II) concentrations from one calibration set.

Table 1
Results of four replicate experiments for the analysis of Fe(II)–Cu(II)–Co(II) mixtures (Fe(II) = 1.0 μg ml^{-1}, Cu(II) = 2.0 μg ml^{-1} and Co(II) = 1.5 μg ml^{-1})

Replicate	Found (μg ml^{-1})		
	Fe(II)	Cu(II)	Co(II)
1	0.91	2.05	1.41
2	1.02	2.20	1.50
3	0.93	1.96	1.51
4	1.00	2.20	1.46
Mean	0.96	2.10	1.47
S_{CH}	0.05	0.12	0.04

4.4. Reproducibility of the method

To check the reproducibility of the proposed method four replicate experiments on a ternary mixture of Fe(II), Co(II) and Cu(II) were done (Table 1). A good standard deviation was obtained for Fe(II), Co(II) and Cu(II).

4.5. Accuracy

Several synthetic mixed samples with different concentration ratio of Fe(II), Co(II) and Cu(II) were analyzed using HPSAM with simultaneous addition of three analytes. As can be seen from Table 2, the accuracy of the method is satisfactory.

4.6. Limit of detection

Limit of detection was calculated as LOD = $C_H + 3S_{CH}$, where C_H and S_{CH} are the mean and standard deviation of several ($n = 4$) replicated measurements of a blank sample using HPSAM with simultaneous addition of three analytes. The corresponding values obtained for Fe(II), Co(II) and Cu(II) were 0.01, 0.04 and 0.1 μg ml^{-1}, respectively.

4.7. Interferents

The effect of different ions at different concentration on the absorbance of a solution mixture containing 1 μg ml^{-1} of each metal ion was studied. An ion was considered as interference, which its presence produced a variation in the absorbance of

Table 2
Result of several experiments for the analysis of Fe(II)–Co(II)–Cu(II) mixtures in different concentration ratios

Sample (μg ml^{-1})			Found (μg ml^{-1})			Relative error (%)		
Fe(II)	Cu(II)	Co(II)	Fe(II)	Cu(II)	Co(II)	Fe(II)	Cu(II)	Co(II)
0.70	1.50	1.00	0.74	1.61	1.02	5.7	7.3	2
0.20	2.00	2.00	0.20	1.96	1.95	0	−2	−2.5
1.00	1.00	1.00	1.04	0.93	1.00	4	−7	0
2.80	1.40	0.70	2.70	1.47	0.68	−3.6	5	−2.8
0.22	2.20	2.20	0.23	2.18	2.20	4.5	−0.9	0
1.26	2.70	1.80	1.31	2.58	1.83	3.9	−4.4	1.7
2.00	0.20	2.80	1.97	0.22	2.98	−1.5	10	6.4
0.98	2.10	1.40	1.03	2.05	1.39	5.1	−2.4	−0.7
0.24	2.40	2.40	0.25	2.45	2.42	4.2	2.1	0.8
1.12	2.40	1.60	1.17	2.22	1.61	4.4	−7.5	0.6

Table 3
Tolerance ratio for foreign ions in the determination of 1.0 μg ml^{-1} of Fe(II), Co(II) and Cu(II)

Ion	Tolerated ratio
CHCOO$^-$, phthalate, tartrate, citrate, ClO^{4-}, SO$_4{}^{2-}$, CO$_3{}^{2-}$, NO$_3{}^-$, Cl$^-$, I$^-$, Br$^-$	100
F$^-$, P$_2$O$_7{}^{4-}$	60
Ca^{2+}, Ba^{2+}, Na$^+$, K$^+$, Sr^{2+}	100
Mn^{2+}, Cd^{2+}	50
Zn^{2+}, Al^{3+}, Be^{2+}	30
Th^{4+}, Cr^{3+}	4
Ag$^+$, Bi^{3+}	1

Table 4
Results of analysis of Fe(II)–Co(II)–Cu(II) in synthetic alloys and spiked water samples

Sample	Fe(II) (μg ml^{-1})		Co(II) (μg ml^{-1})		Cu(II) (μg ml^{-1})	
	Present	Found	Present	Found	Present	Found
Copper alloy	1.70	1.80	0.70	0.74	86.5	83.0
Beryllium copper alloy	0.10	0.10	2.70	2.60	96.8	96.2
Tap water	1.50	1.47	1.00	0.92	2.00	2.02
Mineral water	2.00	2.04	0.50	0.55	1.00	1.04

the sample (at considered wavelengths) greater than ±5%. The tolerance limits are depicted in Table 3. The ions, which interfere most strongly, were Ni^{2+}, Fe^{3+} and Pb^{2+} because they form colored complex with DDC.

4.8. Application of the method

The proposed method was successfully applied to the simultaneous determination of Fe(II), Co(II) and Cu(II) in sipked water samples and two synthetic samples that had composition prepared according to some alloys [50]. The results are shown in Table 4. The spiked real environmental sample and synthetic samples with complex composition according to real alloys were considered as real samples. The good agreement between these results and known values indicate the successful applicability of the proposed method for simultaneous determination of Fe(II), Co(II) and Cu(II) in complex samples.

5. Conclusion

Based on the results obtained, it has been shown that proposed HPSAM for resolving ternary mixtures calculate the analyte concentration free from the abscissa of the H-point. The principal advantages of the method are: (1) absorbance data, and not first derivative data, are used; hence the signal-to-noise ratio is not diminished. In addition, the method takes into account the matrix effect. (2) The wavelength pairs for measuring the analyte are easily obtained from the spectral behavior of the interferents. (3) A few points are necessary to obtain good results. (4) The method works well even if the interferents overlap the analyte band(s) completely. (5) With simultaneous standard addition of the three species X, Y and Z, we can obtain their concentration from a unique calibration set.

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