Simultaneous Determination Of Iron And Copper In Amixture Using First And Second Derivatives Spectrophotometry

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Abstract:-

Amethod for the simultaneous determination of iron (III) and copper (II) in a mixture by derivative spec trophotometry is described .The method is based on the complexes formed by both metal ions with 6-(5-chloro-2- hydroxy-3-sulfophenylazo)-5-hydroxy-1-naphthalene sulfonic acid (Mordant blue-9) in acidic medium. The range of determination is between 5- 30µg/25ml and 5-35µg/25ml for iron and copper respectivel

Introduction

Many organic reagents have been employed for quantitative spec trophotometric determination of iron (III) and copper (II)[1], but these required separation, pH control, and masking agents to enhance selectivity. Normally, when a component in a mixture is to be determined, interferences from other components often cause errors. Several methods are proposed for these determinations ,they including two wavelength methods ,curve fitting method and derivative method [2,3] Derivative technique has been used for simultaneous determination of inorganic ions through the formation of their complexes with the same organic ligand. For example, determination of cobalt and nickel with 1-hydroxy-2- carboxy anthraquinone[4] , beryllium and magnesium [5] ,iron and copper[6,7] , and the determination of nickel ,zinc and copper by pyridylazonaphthol (PAN)reagent.[8,9] Derivative spectrophotometry is used for resolution of ions, removal of turbidity ,and enhancement of spectral signals [10,11]

Aim:

The determination of iron and copper in mixture is difficult as these two elements interfere owing to a considerable overlap of the spectra. This problem had been solved by the application of the first and second derivative as established in this paper .

Experimental

Reagents

All reagents used were of analytical grade**.**

Iron(III) stock solution, 1g/L prepared from $FeCl_3.6H_2O$ (Merck)in distilled water.

Copper (II) stock solution , 1 g/L prepared from $CuSO_4.5H_2O$ (Merck) in distilled water .

Mordant blue-9 (MB9) reagent : 0.001 M ,prepared by dissolving 0.0251 g of this reagent (Hopkins and William, Ltd.) in 50 ml distilled water . the reagent is stable at least for one week.

Buffer solution pH 3.75

prepared by mixing 1.0211 g of potassium hydrogen phthalate and 6.2 ml of 0.1 M hydrochloric acid ,then dilution to 100 ml with distilled water [12].

Apparatus

A Shimadzu UV-Visible recording spec trophotometer (model UV-160) and 1cm ε

quartz cells were used for the normal and derivative spectrophotometry

Recommended procedure

optimum conditions [13] for iron and copper were listed in Table(I)which are the same condition for iron(III)and copper(II)simultaneously .

Table 1:Optimum conditions for iron(III)and copper(II) with Mordant blue -9 reagent.

Parameters	Values
pH	3.75
$\varepsilon max .(l.mol^{-1}.cm^{-1})$	4100
Sandell index $(ng.cm^{-2})$	13
Order of addition	no effect
Linearity (ppm)	0.1 − 2
R.S.D, %	2±
ml of 0.001 M reagent	2.0
λmax Fe (III) complex	650 nm
λmax Cu (II) complex	542 nm
λmax for both in the mixture	586 nm

To an aliquot of the sample solution ,containing 5-30 µg of iron and 5-35 µg of copper in 25 ml calibrated flasks, were added 4 ml of potassium hydrogen phthalate buffer pH 3.75, 3 ml of 0.001 M (MB9) reagent and diluted to the mark with distilled water .The normal and first derivative signals for the height of iron at zero-crossing point for copper 542nm we determined and recorded the value with calibration graph ,then copper height at the zero –crossing point of iron (650nm)was determined, see Figures 1 ,2 and 3, and compared with graph shown in Figure 5.
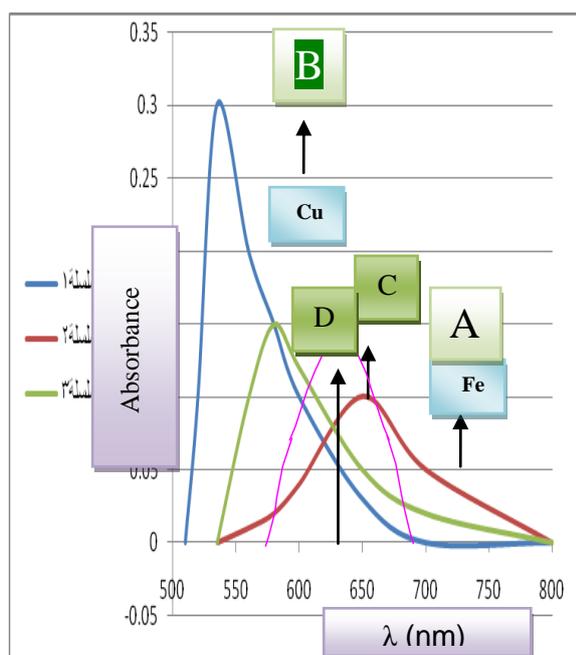
Fig.(1):Absorption spectra zero order of (**A**)iron complex ,(**B**)copper complex and (**C**) mixture of iron and copper at Fe= 30 μg/25 ml and Cu = 35 μg/25 ml vs   reagent blank (**D**)mixture against distilled water at 560 nm .
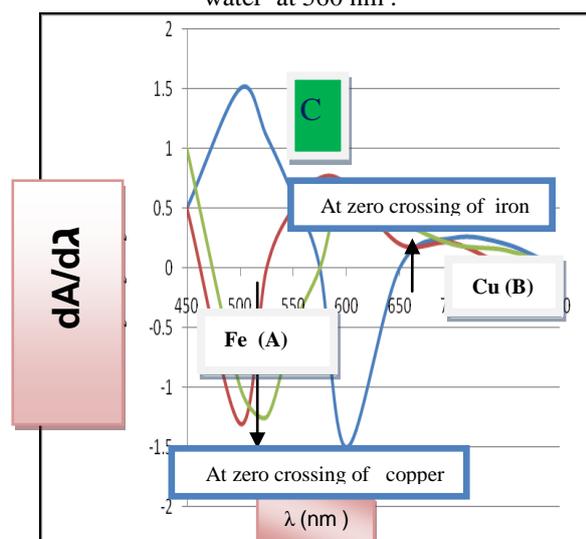

Fig.(2) :First –derivative spectra of (A)iron complex ;(B)copper complex ,and (C)mixture of iron and copper complex ; Fe= 30μg/25 ml and Cu=35μg/25 ml.
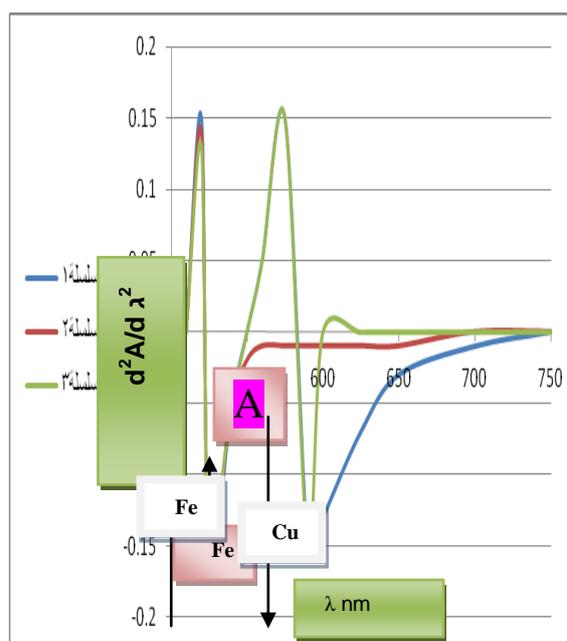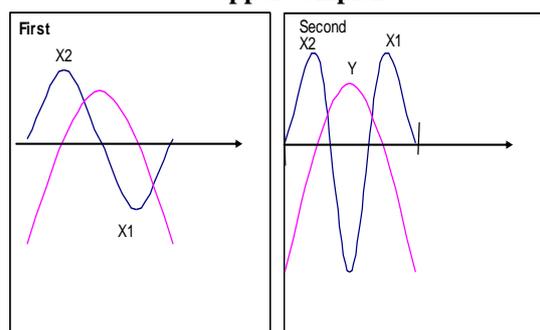

Fig.(3): Second derivative spectra of (A) iron ;(B) copper complex and (C) mixture of iron and copper complex

Spec trophotometric measurements ,Fig.1,show the absorption spectrum of iron complex which has an absorption maximum at 650 nm , copper at 542 nm, and the spectrum of the mixture at 586 nm .,which is located between them ,which indicating a large overlap between the two spectra. .Fig .2 shows the first derivative absorption spectra of the complexes of Fe(III) and Cu (II) with MB9 reagent and a mixture of both complexes ,i.e the hight of iron(III) on complex curve at zero crossing of copper(II) in 524 nm **.**The zero –crossing method which involves the measurement of the absolute value of the total derivative   spectrum ,the graphical method can not be used ,because of poor resolution of the spectrum of the mixture .In first derivative ,the amplitude of the derivative signal of one of the two components passes through zero. Measurement of the value of the mixture gave the value of the other component ,hence the height Fe(III) and Cu(II) in the first derivative spectrum of the mixture [Fig. 2. curve C]corresponding to the value taken at 542 and 650 nm are proportional to iron and copper concentration, respectively.

Results And Discussion
Principle of the method:
The points on derivatives are : [10]

a . The first derivative crosses the zero axis at the same wavelength value as the maximum of the original peak (Y), (zero-order). This is true for any peak shape and is often as a way to determine the position of the peak.

b. The second derivative spectrum has a negative peak (Y) corresponding to the position of original peak maximum. The second derivative spectrum has two 'satellite ' peaks (X1 and X2) one on each side of the main negative peak. The central , negative peak of the second- order spectrum is narrower than the original peak. These facts may be generalized for higher order spectra. The central zero-crossing position remains in live with the main peak position for all odd order spectra, this peak will alternate in sign from negative to positive as each higher order spectrum is calculated .The number of satellites will increase with each even-order spectrum , there being four in the fourth derivative at the same time the peak will become narrower and narrower. See Figure(4).

Fig . 4   dealised representation of 1st / 4th derivative on Gaussian peak.
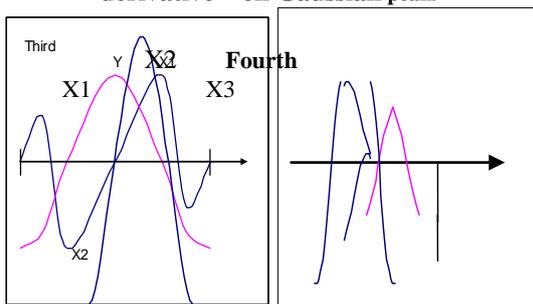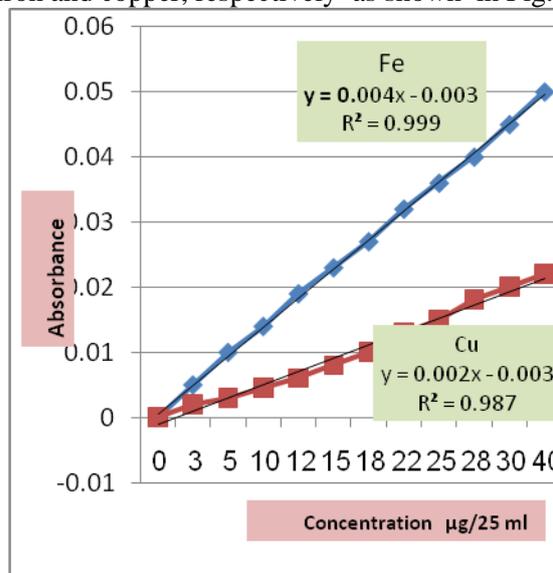

Table 2 :Results of the simultaneous determination copper and iron in a mixture with MB9 using a *first de*rivative spect.

Sample No.	µg added		µg found			
	Cu	Fe	Cu	Cu R.E%	Fe	Fe R.E%
1	40	10	37.7	5.75	9.4	6.0
2	70	30	76.1	8.70	29.4	2.0
3	10	40	10.6	6.00	38.4	4.0
4	30	10	30	---	10.0	---
5	10	30	10.0	____	31.2	4.0
6	70	10	67.2	4.00	9.4	6.0
7	30	50	28.0	6.60	53.3	6.6

The second derivative spectra of the complex are shown in Fig .3 ,it can be seen that the higher peak of the derivative are more significant (higher signals).The intensity of the signals at 525 ,575 nm. are directly prortional to the amount of copper and iron respectively .The calibration graph obtained showed a linear relationship between the distance measurement and the concentration of the metal ions in the range of 5- 30 µg/25 ml and 5 - 35 µg/25 ml for iron and copper, respectively as shown in Fig.5.

Fig.(5) : Calibration curves of iron III and copper II in mixture using first derivative spectrophotmetric technique. From Table 3. Showed the results of

simultaneous determination of Cu   Fe carried out as described under recommended procedure.

Table 3 : Result of the simultaneous determination of iron and copper in their mixture with MB9 using 2nd derivative spectrophotometry

Sample No.	µg added		µg found			
	Cu	Fe	Cu	Cu R.E%	Fe	Fe R.E%
1	40	10	39.9	0.25	9.9	1.0
2	30	10	29.8	0.66	9.8	2.0
3	10	30	9.9	1.00	28.3	9.0
4	50	20	47.7	4.66	18.5	7.5
5	70	10	68.2	2.57	9.2	8.0

Therefore Table 2 and 3 have shown that the second derivative is more sensitive ,the later have low relative error and offered significant values than first derivative .

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تقدير الحديد الثلاثي والنحاس الثنائي في مزيج باستخدام طيف المشتقة الاولى والثانية

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الملخص

يتضمن البحث طريقة طيفية آنية لتقدير الحديد (III) والنحاس (II) في المزيج بالاعتماد على طيف المشتقة الأولى والثانية ،وتعتمد الطريقة على تكوين معقدين لكلا الايونين مع كاشف6− (5−كلورو−2−هيدروكسي−3−سلفوفنيل ازو)−5−هيدروكسي−1−نفثا لين حامض السلفونيك في الوسط ألحامضي ، حيث كان مدى القيا س 5−30 مايكرو غرام لكل ٢٥ مل من الحديد(III) و 5−35 مايكرو غرام لكل ٢٥ مل من النحاس (II)على التوالي