Simultaneous Determination of Copper and Manganese as their Ternary Complexes with Alizarin Complexone and Fluoride using First derivative Spectrophotometry

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Abstract

A sensitive and selective spectrophotometric method for rapid simultaneous determination of copper and manganese is proposed. The method is based on the ternary metal complexes with alizarin complexone (alizarin-3-methylamine-N,N-diacetic acid , AC) and fluoride, and the use of zero-crossing and derivative ratio spectra techniques. The range $2.54 – 12.7$ · µg ml^{-1} copper could be determined in the presence of $2.19 – 10.9$ µg ml^{-1} manganese and vice versa. The developed methods were applied for the simultaneous determination of copper and manganese in their binary mixtures and were found to give satisfactory results.

Keywords : Copper(II) , Manganese(II) , Alizarin complexone , Fluoride , Derivative spectrophotometry.

1. Introduction

Copper is an important trace element in animal metabolism. The major concentration of copper in human body is in liver and bones. Blood contains number of copper proteins and it is necessary for the synthesis of hemoglobin. Though copper is essential for human metabolism, it becomes hazardous when present in excess. Higher levels of copper(II) are toxic and severe oral intoxication will affect mainly the blood and kidneys.

Although numerous organic reagents[1-6] have been proposed for spectrophotometric determination of copper(II), none of these methods are completely satisfactory.

The most widely used methods for the spectrophotometric determination of manganese are based on the oxidation of an organic reagent by hydrogen peroxide, catalyzed by manganese(II)[7-11]. Use of selective reagents for direct spectrophotometric determination of manganese is particularly difficult and several methods have the draw-back of interferences from many cations and anions. Much work has been discussed for overcoming these interferences[11] .

Derivative spectrophotometry has been shown to be more versatile than classical spectrophotometry for solving analytical problems. The zero-crossing method developed by O'Haver[12] and the derivative ratio spectra developed by Salinas et al. [13] have been widely used for the simultaneous determination of metal ions in their binary mixtures through the formation of complexes with the same organic ligands [13,14].

Alizarin complexone (alizarin-3-methylamine-N,N- diacetic acid, AC) is one of the most commonly reagents used for spectrophotometric determination of metal ions[15-20]. Fluoride ion is a unique ligand in that it shows almost pure electrostatic interactions with metal ions in solutions. The formation constants of a series of the mixed ligand complexes MLF were determined[15,18,21]. Therefore, a rapid, sensitive and inexpensive method for the simultaneous determination of manganese and copper in mixtures by first derivative spectrophotometry using zero-crossing and derivative ratio spectra techniques has been reported. The methods are based on the coloured ternary complexes that both manganese and copper form with alizarin complexone and fluoride in 40% ethanol - water medium. The proposed methods have been applied for the simultaneous determination of manganese and copper in some synthetic mixtures.

2. Experimental
2.1. Instruments

Ordinary absorption and first derivative spectral measurements were made on a T80+ (England) double beam UV-Vis spectrophotometer using 10-mm matched quartz cells. The first derivative spectra were recorded at a scan speed of 240 nm min^{-1}, $\Delta\lambda=5$ nm and a slit width of 2 nm. The smoothing and differentiation calculation are based on a least-squares polynomial convulation function using 17 data points.

The pH values of solutions were measured using AD 1030 pH/mV pH meter equipped with a Radiometer combined glass electrode. The pH meter was calibrated regularly before use with standard buffer solutions and the pH values in water- ethanol medium were corrected as described elsewhere[22].

2.2. Chemicals and Solutions

All chemicals were of analytical reagent grade and doubly distilled water or absolute ethanol was used for preparation of solutions .

A 2×10^{-3} mol L^{-1} stock standard solution of alizarin complexone was prepared by dissolving an accurately weighted amount of sigma pure grade reagent in absolute ethanol.

Solution of concentration 2×10^{-3} mol L^{-1} sodium fluoride (Merck) was daily prepared.

A 2×10^{-3} mol L^{-1} stock standard solutions of copper(II) sulphate and manganese(II) chloride were prepared by dissolving the requist amounts of the analytical pure reagents in bidistilled water.Copper and manganese solutions were standardized volumetrically[23].

Other solutions included, sodium perchlorate (1 mol L^{-1}), standard solutions of sodium hydroxide and perchloric acid. Solutions of diverse ions used for interference studies were prepared from AnalaR products of nitrates, acetates or chlorides of the metal ions and potassium or sodium salts of the anions to be tested. The ionic strength of solutions was maintained at a

constant value of $I = 0.1$ mol L^{-1} (NaClO$_4$). All measurements were made in 40% (v/v) ethanol at 25°C.

2.3. procedures.

2.3.1 Zero-order spectrophotometric determination of copper and manganese.

Transfer an aliquot of a sample solution containing copper(II) (up to 300· μg) or manganese(II) (up to 275 · μg) into a 25 ml calibrated flasks. Add 5 ml of 2×10^{-3} mol L^{-1} Alizarin complexone solution and 5 ml 2×10^{-3} mol L^{-1} fluoride solution. Add 5 ml of absolute ethanol to ensure a final ethanol content of 40% (v/v). Adjust the pH to 5.0 using 1×10^{-2} mol L^{-1} HClO$_4$ while keeping the ionic strength constant at 0.1 mol L^{-1} (NaClO$_4$). Dilute to volume with doubly distilled water and record the normal spectra from 400 - 700 nm against a reagent blank as the reference. Measure the absorbance of the solutions at 507 or 520 nm to determine copper(II) or manganese(II) respectively.

2.3.2 Simultaneous determination of copper(II) and manganese(II) in their binary mixture.

2.3.2.1 Zero- crossing method .

For the normal spectra of Cu-AC-F and Mn-AC-F systems containing different concentrations of the analyte, stored previously in a computer, record the first derivative spectra to detect the zero-crossing points of each analyte. By the same way record the first derivative spectra of Cu-AC-F and Mn-AC-F in their binary mixtures. The concentrations of copper and manganese can be determined by measuring the first derivative signal D^1 at 520 nm (zero-crossing point of manganese complex) and at 507 nm (zero-crossing point of copper complex) respectively.

2.3.2.2 Derivative ratio spectra methods:

Record the ratio spectrum of a binary mixture containing copper and manganese-AC-F complexes, using Mn-complex as a divisor, for the obtained ratio spectrum, record the first

derivative spectrum, copper can be determined using the absolute value of the first derivative divided spectrum ([1]DD) at 545 nm. By the same way but with the use of Cu-complex as a divisor, manganese can be determined the absolute value of the first derivative divided spectrum ([1]DD) at 610 and 638 nm.

3. Results and discussion.

3.1. Acid-base properties of AC.

In ethanol water mixtures containing 40% (v/v) ethanol and at pH 3.2 - 10.5, AC exists in five different forms, (LH_4, LH_3^-, LH_2^{-2}, LH^{-3} and L^{-4}), exhibiting the absorbance maxima at 270, 335, 423, 525 and 580 nm, respectively. The mean pK_a values of the reagent are pK_{a1} (LH_4/LH_3^-) = 4.5, pK_{a2} (LH_3^-/LH_2^{-2}) = 5.0, pK_{a3} (LH_2^{-2}/LH^{-3}) = 5.4 and pK_{a4} (LH^{-3}/L^{-4}) = 8.5 (I = 0.1 , 25 °C)[19]

3.2. Absorption spectra and optimum pH.

The visible spectra of alizarin complexone (AC, 2×10^{-4} mol L^{-1}) show an absorption band at 423 nm within the pH range 4.8 - 5.2 The spectrum of fluoride ion (2×10^{-4} mol L^{-1}) exhibits no measurable absorbance in the visible region and there are no significant changes in colour or absorbance in the presence of Cu(II) or Mn(II) ions. However, the solution containing AC and F^- undergoes an observable change in colour from yellowish brown to violet when mixed with Cu(II) or Mn(II) ions. The spectrum of the reaction mixture against a blank solution containing the same concentration of the two ligands exhibits a new band at 507 and 520 nm for solutions containing Cu(II) or Mn(II) respectively. The latter bands are unambiguously due to the formation of mixed-ligand complexes of Cu(II) and Mn(II) with AC and fluoride ion, with maximum colour development at pH= 5.0 (Fig. 1.).

3.3. Spectrophotometric determination of Cu(II) and Mn(II).

A standard solution of copper(II) or manganese(II) containing 30 - 300 □µg of copper (or 30 – 375 .µg of manganese)

was introduced into a 25-ml calibrated flask, then 6.25 ml of (2×10^{-3} mol L^{-1}) AC and 5 ml of F^{-} ion (2.5×10^{-3} mol L^{-1}) were added . Dilute perchloric acid was added to adjust the pH at 5.0 , 2.5 ml of 0.1 mol L^{-1} $NaClO_4$ were added and the solution was diluted to volume with doubly distilled water and the request amount of ethanol (40% v/v). After thoroughly mixing the reaction mixture, the absorbance was measured at 507 nm or 520 nm to determine Cu(II) or Mn(II) respectively , against a reagent blank similarly prepared but containing no metal ions.

3.4. Calibration graphs and reproducibility.

Under the optimum conditions cited above, a linear calibration graph for Cu(II)-AC-F system was obtained up to a concentration of 15.8 · μg ml^{-1} copper with a molar absorptivity of 3.2×10^{4} L mol^{-1} cm^{-1} at 507 nm. Also a calibration graph for Mn(II)-AC-F system was obtained up to a concentration of 13.7 · μg ml^{-1} manganese with a molar absorptivity of 2.5×10^{4} L mol^{-1} cm^{-1} at 520 nm. Ring boom plots showed that the optimum working range for the determination of copper was 2.54 - 12.7 · μg mL^{-1}, while that of manganese was 2.19 - 10.9 · μg mL^{-1}. The calculated relative standard deviation (RSD) for ten determinations each having 5.08 · μg ml^{-1} copper or 4.39 · μg ml^{-1} manganese was found to be 0.75 for copper and 0.85% for manganese.

3.5. Stoichiometry of the complexes

Job's method of continuous variation [24] was applied to establish the composition of the ternary Cu(II)-AC-F and Mn(II)-AC-F complexes. The molar fractions of two of the components were varied continuously, keeping their combined concentration constant, and keeping the third component in a large excess for all solutions in the series. Under these conditions, the ternary system was modified to a quasi-binary system. The results shown graphically in (Fig.2 a,b) indicate that the over-all Cu(II)-AC-F and Mn(II)-AC-F composition is 1:1:1 at the pH used. Taking into account the pK_a values of alizarin complexon and

the stoichiometric composition of the mixed ligand complexes , the complexation equlibria will proceed according to the following reaction:

$$M^{2+}+H_2L^{2-}+F^- = MLF^{3-}+2H^+$$
$$(M^{2+} = Cu^{2+} or\ Mn^{2+})$$
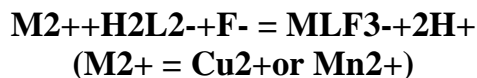
The stoichiometry of the ternary systems were also determined by applying the molar ratio method[25] .

3.6. Simultaneous determination of copper and manganese in mixtures.

3.6.1. Absorption spectra:

The absorption spectra of Cu(II)-AC-F and Mn(II)-AC-F complexes are shown in **Fig.3.** The total absorption spectra of a mixture of copper and manganese complexes is given. Due to the fact that absorption spectra of copper and manganese complexes overlap, the determination of copper and manganese in their mixtures by zero-order spectrophotometry is frequently difficult. The procedure for the simultaneous analysis, which involves the measuring of the total absorbance of the mixture at the two wavelengths of maximum absorption followed by simultaneous equations, was investigated. However, results of poor accuracy and reproducibility are obtained. This disadvantage has been overcome by use of derivative spectrophotometry**.**

3.6.2. Derivative spectra.

Appropriate parameters were selected to record the first-derivative spectra using the zerocrossing method and the derivative ratio method to select suitable wavelengths for obtaining linear analytical calibration graphs.

3.6.2.1 Zero- crossing method

Zero-crossing method developed by O'Haver[12] is based on the measurements of the absolute value of the total derivative spectrum of the mixture at an abscissa value (wavelength) where the intensity of one component of the mixture goes to zero. At this wavelength the intensity is directly proportional to the other component.

The reproducibility of zero-crossing wavelengths of derivative spectra was checked by recording the first derivative spectra of Cu(II)-AC-F and Mn(II)-AC-F systems (pH=5.0) at different concentrations of the analytes (Fig.4. a,b). The zero-crossing wavelengths of copper and manganese are obtained at 507 and 520 nm , respectively.

(Fig.5.) shows the first derivative spectra of two series containing increasing amounts of copper or manganese ions. Copper and manganese can be determined using the absolute value of the total derivative spectrum at a wavelength corresponding to the zero-crossing points of the other components. The heights h_1 (Fig.5a) and h_2 (Fig.5b) corresponding to values taken at 520 nm (zero-crossing points of Mn complex) and at 507 nm (zero-crossing points of Cu complex) are proportional to copper and manganese concentrations , respectively.

3.6.2.2. Derivative ratio method

Derivative ratio method developed by Salinas et al [13] is based on the use of the first derivative of the ratios of the spectra. The absorption spectrum of the mixture is obtained and divided (amplitude by amplitude at appropriate wavelengths) by the absorption spectrum of a standard solution of one of the components (previously stored in a computer), and the first derivative of the ratio spectrum is obtained. The concentration of the other component is then determined from a calibration graph. (Fig. 6) shows the derivative ratio spectra of two a series of binary mixtures, the first one containing increasing amounts of copper, using Mn-complex as a divisor. Copper can be determined using the absolute value of the total first derivative divided spectrum (^{1}DD) at proper wavelengths. The height h_3 (Fig. 6a) , corresponding to the values taken at 545 nm is proportional to copper concentration.

By the same way, the derivative ratio spectra of a second series of binary mixtures but containing increasing amounts of manganese, and using Cu- complex as a divisor, are recorded . Manganese can be determined using the absolute value of the

total first derivative divided spectrum (^{1}DD) at suitable wavelengths. The heights h_4 and h_5 (Fig.6b), corresponding to the values taken at 610 and 638 nm are proportional to manganese concentration.

3.7. Calibration graphs and statistical analysis of the results.

The calibration graphs, prepared by plotting the first derivative value (^{1}D) or the first derivative divided value (^{1}DD) versus copper or manganese concentration, gave a straight lines passing through the origin, confirming the mutual independence of the derivative signals of the two complexes ,the calibration graph obtained by the recommended methods were linear over a range of 2.54 – 12.7· μg ml^{-1} of copper in the presence of 2.19 – 10.9 · μg ml^{-1} of manganese, and vice versa. A critical evaluation of the proposed methods as obtained by statistical analysis of the experimental results are giving in (Table 1).

In order to test the accuracy and precision of the methods, five successive measurements were carried out with standard solution containing 6.35 · μ g ml^{-1} of Cu(II) and 5.49 · μg ml^{-1} of Mn(II) . Relative standard deviations for zero-crossing and derivative ratio spectra methods of Cu(II) were 1.5 and 1.1 respectively and those for Mn(II) were 1.3 and 0.85% , respectively. The detection limits (at the 95% confidence level) of the proposed methods for the mean of four analysis (N_1) were calculated. The minimum detectable amount, Δx_{min} , is given by[26].

$$\Delta x_{min} = \overline{X}_l - \overline{X}_b > ts_b \sqrt{\frac{N_1 + N_b}{N_1 \, N_b}}$$

Where the subscript b refers to the blank determination. The statistical parameter t= 2.36 for seven degrees of freedom and 95% confidence. The calculated detection limits are 75 ng ml-for Cu(II) and 64 ng ml-1 for Mn(II) using zero-crossing technique and 92 ng ml-1 for Cu(II) and 81 ng ml-1 for Mn (II) using derivative ratio spectra technique.

3.8. Effect of diverse ions

Effect of the presence of diverse ions in the simultaneous determination of copper and manganese as their ternary complexes with alizarine complexone and fluoride was studied under optimum conditions. Absorbance measurements in zero-crossing and derivative ratio spectra techniques proved useful in overcoming interferences in a number of cases where the use of a masking agent could not help. The tolerance of the method to foreign ions was investigated with solutions containing 0.20 mg of Cu and 0.15 mg of Mn per 25 ml and various amounts of foreign ions.

The simultaneous determination of Cu and Mn was possible in the presence of Li^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , Cd^{2+} , Ba^{2+} , SO_4^{2-} , SO_3^{-2} , NO_3^- , Cl^- , Br^- , I^- and $B_4O_7^{--}$ (25 mg) , Co^{2+} , Ni^{2+} , Hg^{2+} , pb^{2+} , and Ag^+ (10 mg) , Ca^{2+} , Mg^{2+} and Sr^{2+} (5mg) Fe^{3+} , Zr^{4+} , Mo^{6+} and Al^{3+} (2.5 mg) Cr^{3+} , Y^{3+} and CN^- (0.5 mg) , Zn^{2+} . EDTA and HPO_4^{2-} interfered seriously even when present in amount of 0.25 mg. The interference of Zn^{2+} can be eliminated by the simultaneous use of zero-crossing and derivative ratio spectra techniques.

3.9 Applications

To confirm the usefulness of the proposed methods, copper and manganese have been determined simultaneously in some synthetic samples. The results obtained (Table 2) are in a good agreement with the certified amounts. Simplicity, sensitivity, large range of linearity besides accuracy and precision are the main advantages of the proposed methods.

4. Conclusion

The proposed method allows the simultaneous determination of Cu (II) (2.54 - 12.7 · $\mu g\ ml^{-1}$) and Mn(II) (2.19 – 10.9· $\mu g\ ml^{-1}$) in their binary mixtures using zero-crossing and derivative ratio spectra techniques. This work illustrates the potential of derivative spectrophotometry as a simple , rapid and accurate tool for simultaneous determination of Cu(II) and

Mn(II) in synthetic mixtures relative to zero order spectrophotometric technique [6 , 27 , 28] .

Table 1 :- Statistical analysis of the determination of copper and manganese in mixtures as their (Cu - and Mn-AC–F) ternary complexes using zero-crossing and derivative ratio spectra methods.

Metal ion	Method	λnm	Regression equationb	Correlation coefficient
Cu	Zero- crossing	520a	$\frac{1}{D} = 0.021\ C_{cu} + 0.002$	0.9995
	Derivative ratio spectra	545a	$\frac{1}{DD} = 0.094\ C_{cu} + 0.04$	0.9991
Mn	Zero- crossing	507a	$\frac{1}{D} = 0.022\ C_{Mn} + 0.04$	0.9998
	Derivative ratio spectra	610 a	$\frac{1}{DD} = 3.72\ C_{Mn} + 5.42$	0.9855
		638	$\frac{1}{DD} = 3.43\ C_{Mn} + 12.3$	0.7823

a: recommended procedures .
b: (C) concentration (µg ml^{-1}).

Table 2 Application of the proposed methods to simultaneous determination of copper and manganese in some synthetic mixtures.

| Composition of mixture(µg ml⁻¹)		Zero-crossing				Derivative ratio method					
						5.45 µg ml⁻¹ Mn as advisor		6.35 µg ml⁻¹ Cu as advisor				
Cu	Mn	1 D at 520 nm		1 D at 507 nm		1 DD at 545 nm		1 DD at 610 nm		1 DD at 635 nm	
		Cu found	recovery %	Mn found	recovery %	Cu found	recovery %	Mn found	recovery %	Mn found	recovery %
3.17	2.75	3.16	99.68	2.76	100.36	3.17	100	2.74	99.64	2.74	99.64
3.17	5.49	3.18	100.32	5.51	100.36	3.16	99.68	5.50	100.18	5.51	100.36
3.17	8.23	3.15	99.37	8.20	99.64	3.18	100.32	8.21	99.76	8.22	99.88
6.35	2.75	6.33	99.69	2.76	100.36	6.34	99.84	2.76	100.36	2.77	100.73
6.35	5.49	6.35	100	5.50	100. 18	6.33	99.69	5.51	100.36	5.52	100.55
6.35	8.23	6.36	100.16	8.19	99.51	6.32	99.53	8.21	99.76	8.20	99.64
9.50	2.75	9.47	99.68	2.74	99.64	9.49	99.89	2.74	99..64	2.74	99.64
9.50	5.49	9.44	99.37	5.48	99.82	9.45	99.47	5.48	99.82	5.47	99.64
9.50	8.23	9.41	99.05	8.18	99.39	9.40	98.95	8.18	99.39	8.19	99.51
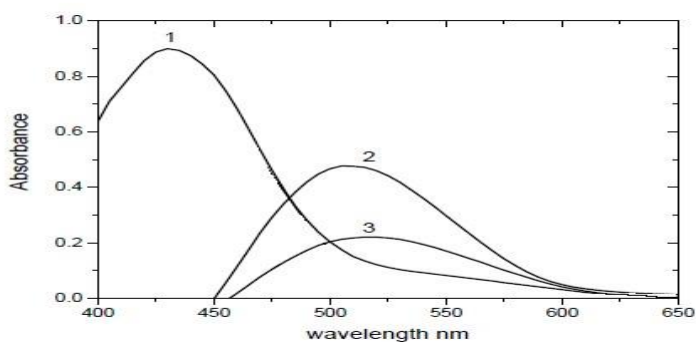
Figure 1. Absorption spectra of Cu(II) – and Mn(II)-AC-F ternary complexes in 40% ethanol [Cu(II)] =[Mn(II)]= 2×10^{-4} mol L^{-1} , 1) AC spectrum or AC-F spectrum both give the same spectrum , 2) 1:1:1 Cu(II)-AC–F , 3) 1:1:1 Mn(II)-AC-F (versus reagent blank) -1 40% ethanol , 0.1 mol L (NaClO₄) , pH=5.0.
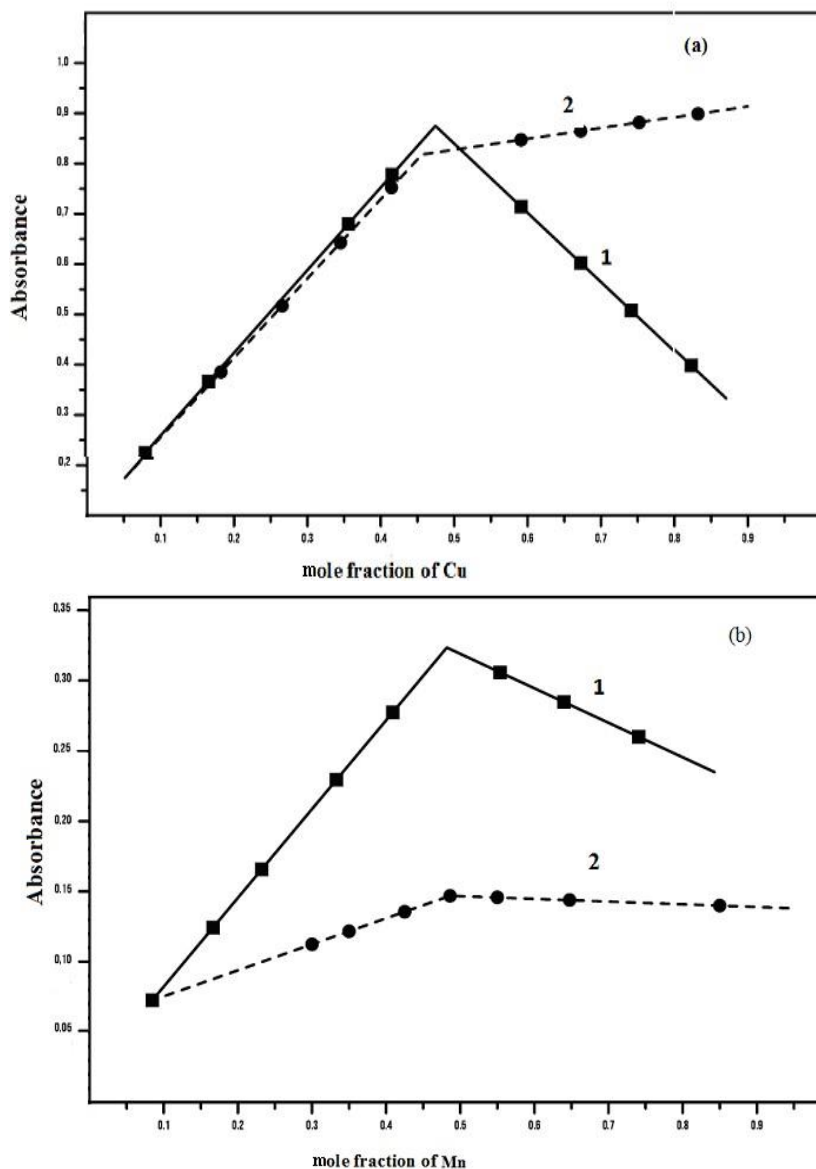
Figure 2. Jop plots of a) Cu-AC-F ternary complex 1) Cu(II)-AC (in the presence of excess fluoride), 2) Cu(II)-F (in the presence of excess AC) and b) Mn-AC-F ternary complexes 1) Mn(II)-AC (in the presence of excess fluoride), and 2) Mn(II)-F (in the presence of excess AC) 40% ethanol , 0.1 mol L^{-1} (NaClO$_4$) , pH=5.0.
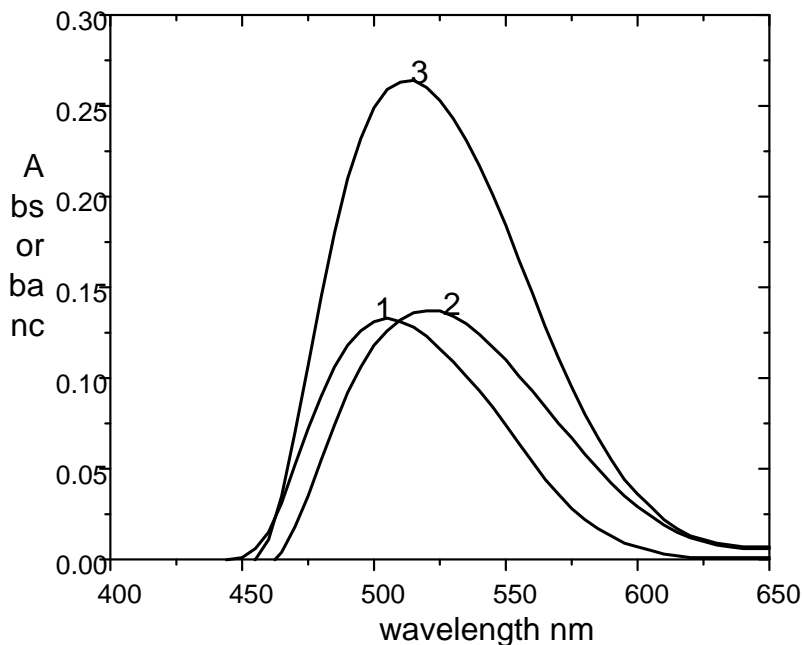
Figure 3. Absorption spectra of 1) Cu(II)-AC-F ternary complex, 2) Mn(II)-AC-F ternary complex and 3) mixture of Cu(II)- and Mn(II)-AC-F ternary complexes. [Cu(II)]= 2.54 μg ml^{-1}, [Mn(II)]= 2.19 μg ml^{-1}, [AC]=[F^{-}]= 5×10^{-4} mol L^{-1}, 40% ethanol , 0.1 mol L^{-1} (NaClO$_4$) , pH=5.0 .
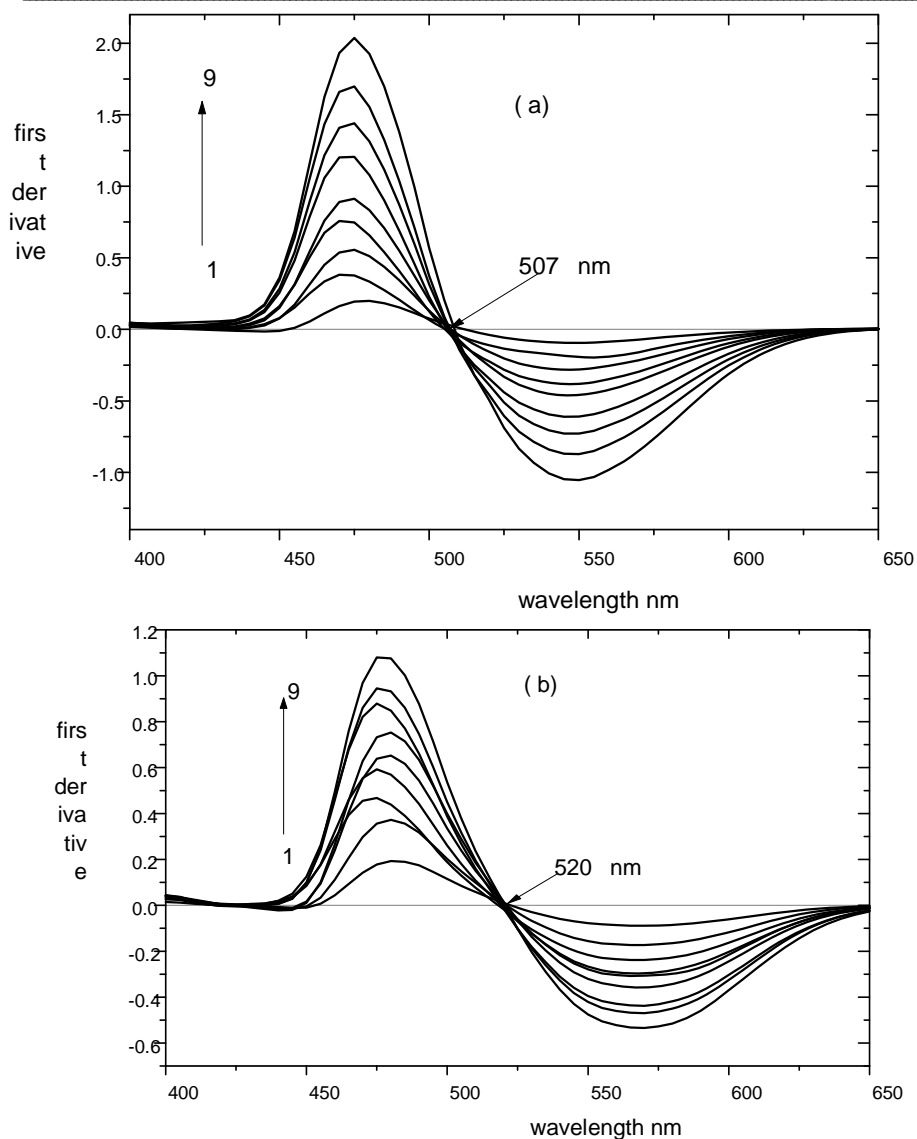
Figure 4. First-derivative spectra of a) Cu(II)-AC-F and b) Mn(II)-AC-F ternary complexes [Cu(II)]= 1) 1.27, 2) 2.54, 3) 3.81, 4) 5.08, 5) 6.35, 6) 8.25, 7) 10.16, 8) 12.7 9) 15.8 μg ml^{-1} , [Mn(II)]= 1) 1.09, 2) 2.19, 3) 3.3, 4) 4.39, 5) 5.49, 6) 7.13, 7) 8.78, 8) 10.9, 9) 13.7 μg ml^{-1}, [AC]= [F]= 5×10^{-4} mol L^{-1}, 40% ethanol , 0.1 mol L^{-1} (NaClO$_4$) , pH=5.0 .
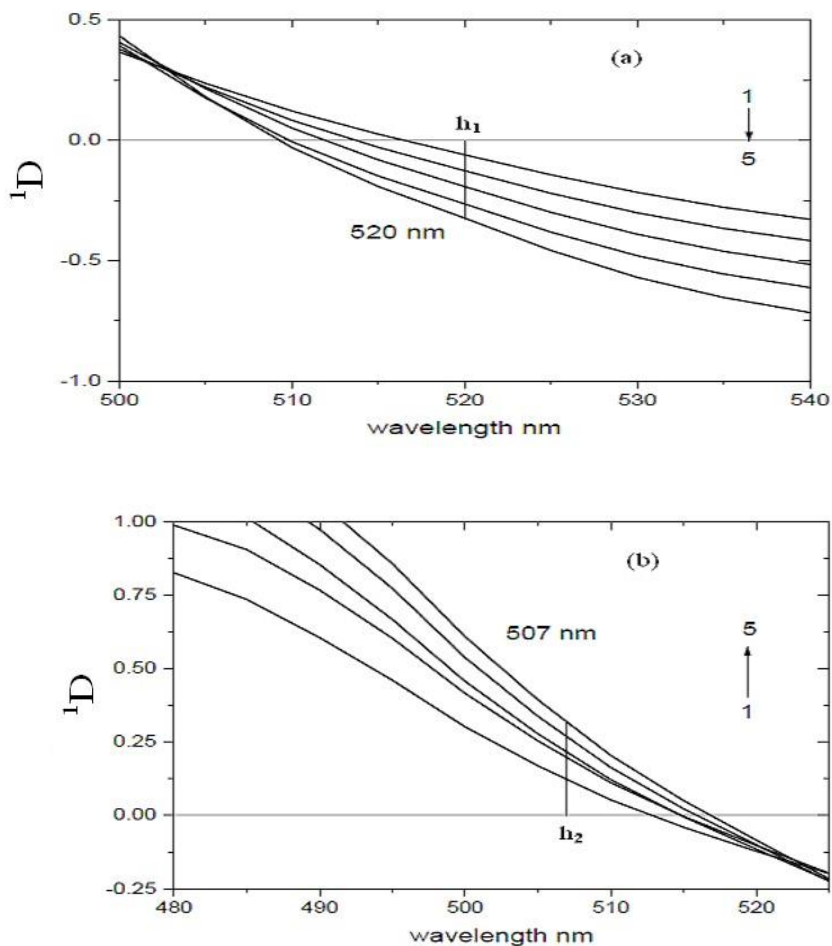
Figure 5. **First-derivative spectra of (a) mixture of Mn(II)-AC-F complex and an increasing concentrations of Cu(II)-AC-F complex (a) [Mn(II)]=5.49 μg ml^{-1}, [Cu(II)]= 1) 3.175, 2) 6.35, 3) 9.5, 4) 12.7, 5) 15.8 μg ml^{-1} and (b) a mixture of Cu(II)-AC-F complex and an increasing concentrations of Mn(II)-AC-F complex [Cu(II)]= 6.35 μg ml^{-1} , [Mn(II)]= 1) 2.75 2) 5.49, 3) 8.23, 4) 10.9, 5) 13.7 μg ml^{-1} , [AC]= [F^{-}]= 5×10^{-4} mol L^{-1}, 40% ethanol , 0.1 mol L^{-1} (NaClO$_4$) , pH=5.0**
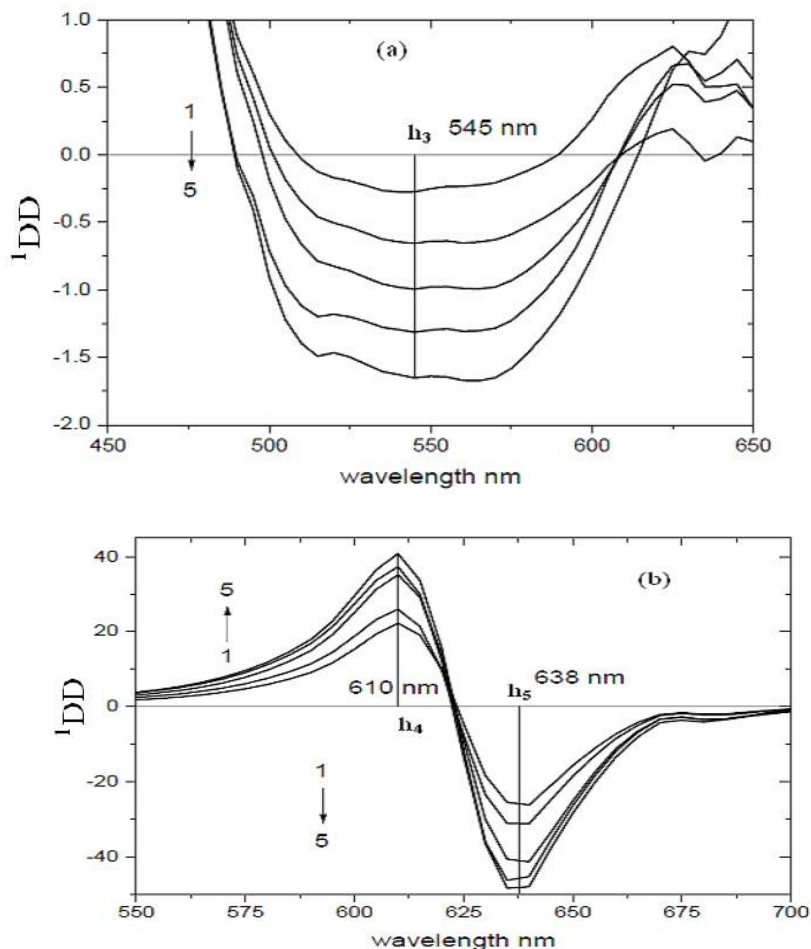
Figure 6. First-derivative of ratio spectra of binary mixtures of Cu(II)- and Mn(II)-AC-F complexes a) a series containing increment amounts of Cu(II) , [Cu(II)]= 1) 3.175, 2) 6.35, 3) 9.5, 4) 12.7, 5) 15.8 µg mL^{-1} , [Mn(II)]= 5.49 µg mL^{-1}, [Mn(II)]= 3.29 µg mL^{-1} as a divisor b) a series containing increment amounts of Mn(II) , [Mn(II)] = 1) 2.75 2) 5.49, 3) 8.23, 4) 10.9, 5) 13.7 µg mL-1, [Cu(II)]= 6.35 µg mL-1, [Cu(II)]= 3.81 µg mL-1 as a divisor, [AC]= [F-]= 5×10-4 mol L-1, 40% ethanol , 0.1 mol L-1 (NaClO4) , pH=5.0 .

References

1. **Thakur M`. , Deb.M.K .** " The use of 1-[pyridyl-(2)-azo]-naphthol-(2) in the presence of TX-100 and N,N'-diphenylbenzamidine for the spectrophotometric determination of copper in real samples ". Talanta , 49(3) , 561-569 , **(1999).**

2. **Arauja A.N. , Costa R.C.C.** . " Colorimetric determination of copper in aqueous samples using a flow injection system with a pre-concentration poly(ethylenimine) column ". Talanta, 50(2) , 337-343 , **(1999).**

3. **Blanco T. , Maniasso N. , Gine M.F** . " Liquid–liquid extraction in flow injection analysis using an open-phase separator for the spectrophotometric determination of copper in plant digests ". Analyst, 123 , 191-193 , **(1998)**.

4. **Nejati M. , Yazdinejad**."Spectrophotometric determination of trace amount of copper(II) ion based on complexation with an an thraquinone derivative ". Analytical aciences (Japan) , 22(4) , 617-619 , **(2006).**

5. **Ramanjaneyulu G. , Reddy P. Raveendra , Reddy V.Krishna , Reddy Sreenivasulu** ." Direct and Derivative Spectrophotometric Determination of Copper(II) with 5-Bromosalicylaldehyde Thiose micarbazone ". The Open Analytical Chemistry Journal , 2 , 78-82 , **(2008)**.

6. **Hashem E.Y. , Seleim M.M. , El-Zohry A.M.** ." Spectrophotometric

7. determination of copper(II) in pharmaceutical, biological and water samples by 4-(2′benzothiazolylazo)-salicylic acid ". Journal of applied spectroscopy, 78(4) , 586-593 , **(2011)**.

8. **Perez-Bendito D. , Valcarcel M. , Ternero M. , Pino F.** ." Kinetic determination of traces of manganese(II) by its catalytic effect on the autoxidation of 1,4dihydroxy phthalimide dithiosemicarbazone ". Anal. Chim. Acta , 94(2) , 405-414 , **(1977)**.

9. **Saro Raya T. , Perez-Bendito D. .** " Semi-automatic catalytic titration of aminopolycarboxylic acids and metal ions with the 4,4′-dihydroxybenzophenone thiosemicarbazone - hydrogen peroxide - copper(II) system ". Analyst 108 , 857-863 , **(1983)**.

10. **Moreno A. , Silva M. , Perez-Bendito D. , Valcarcel M,** ." Kinetic fluorimetric determination of nanogram amounts of manganese, based on its catalysis of the oxidation of 2-hydroxybenzaldehyde thiosemicarbazone with hydrogen peroxide ". Talanta 30(2) , 107-110 , (**1983**).

11. **Rubio S. , Gomez A. , Valcarcel M.** . " Fluorimetric determination of manganese at the nanogram level by catalytic oxidation of pyridoxal 2-pyridylhydrazone by hydrogen peroxide ". Analyst , 109 , 717-722 , (**1984**).

12. **Chiswell B. , Rauchile G. , Pascoe M.** . " Spectrophotometric methods for the determination of manganese ". Talanta 37(2) , 237-259 , (**1990)**.

13. **O'Haver T.C.** . "Derivative and wavelength modulation spectrometry " . Anal. Chem. 51(1) , 91A-99A , **(1979)**.

13. **Salinas F. , Berezas J.J. , Espinoza-Mansilla A.** ." A new ethod for quantitative multicomponent analysis resolution of mixtures of salicylic and salicyluric acids " . Talanta 37(3) , 347-351 , (**1990**).

14. **Sedaira H.** " Simultaneous determination of manganese and zinc in mixtures using first- and second-derivative spectrophotometry". Talanta 51(1) , 39-48 , (**2000)**.

15. **Wada H. , Mori H. , Nakagawa G.** ." Spectrophotometric

determination   of fluoride with lanthanum/alizarin complexone by flow injection analysis " . Anal. Chim. Acta 172 , 297-302 , **(1985)**.

16. **Gao H.W. , Braz J.** ." Spectrophotometric Determination of a Trace Amounts of Calcium Using the Calcium Complex with Alizarin". Chem. Soc. 13(1) , 78-81 , **(2002).**

17. **Fain V.Y. , Avakyan V.G. , Zaitsev B.E. , Ryabov M.A.** ." Metal complexes with alizarin and alizarin red S: Electronic absorption spectra and structure of ligands ". Russ. J. Coord. Chem. 30(5) , 365-370 , **(2004)**.

18. **Shimada K. , Shimoda T. , Kokusen H. , Nakano S.** ." Automatic micro distillation flow-injection system for the spectrophotometric determination of fluoride ". Talanta 66(1) , 80-85 , **(2005)**.

19. **Idriss K.A. , Sedaira H. , Ahmed S.S.** ." Determination of strontium and simultaneous determination of strontium oxide, magnesium oxide and calcium oxide content of Portland cement by derivative ratio spectrophotometry ".Talanta 78(1) , 81-87 , **(2009)**.

20. **Idriss K.A. , Sedaira H. , Hashem E.Y. , Selim A.F.** ." Determination of iron (III) , aluminum (III) and titanium (IV) oxide in portland cement using UV/Vis spectroscopy ". Assiut University Journal of Chemistry (AUJC) 49 , 12-25 , **(2020)**.

21. **Yuchi A. , Hotta H. , Wada H. , Nakagawa G.** ." Mixed Ligand Complexes of Trivalent Metal Ions with an Amine-N-polycarboxylate and Fluoride ". Bull. Chem. Soc. Jpn 60(4) , 1379-1382 , **(1987)**.

22. **Idriss K.A. , Hassan M.K. , Abu-Bakr M.S. , Sedaira H. .** " Spectrophotometric study of the complexation equilibria of yttrium(III) with quinizarin green ". Analyst 109 , 1389-1392 , **(1984)**.

23. **Vogel A.I.** ." A text book of quantitative inorganic analysis "4th Edn. ELBS and Longman ". **(1978**).

24. **Seleim M.M. , Idriss K.A. , Saleh M.S. , Hashem E.Y.** ." Ternary complexes in solution: complex formation between the 1 : 1 thorium(IV)-alizarin maroon complex and thiosalicylic acid ". Analyst 111 , 677-680 , **(1986)**.

25. **Yoe. G.H. , Jones A.L.** ." Colorimetric Determination of Iron with Disodium-1,2dihydroxybenzene-3,5-disulfonate". Ind.Eng. Chem., Anal. Ed. 16(2) , 111-118 , **(1944**).

26. **Skoog D.A. , West D.M. , Holler F.J.** ." Fundamentals of Analytical chemistry ". 6, Saunders Coll. Publishing, Florida, (**1996)**.

27. **Khan S. P. , Reddy P. R. , Reddy V.K. .** " Spectrophotometric determination of manganese(II) with 2-hydroxy-1-Naphthaldehyde Isonicotinoylhydrazone ". International journal of chemical and analytical science 2(10) , 1215-1218 , **(2011**).

28. **Chauhan J. S. , Pandya A. V.** . "Spectrophotometric determination of Mn(II) ion by pyridine 2,6-dicarboxylic acid ". International journal of engineering science invention 2(2) , 36-43 , **(2013**).

الملخص العربي

التقدير المتزامن للنحاس و المنجنيز على هيئة متركباتهما الثلاثية مع الاليزارين كومبلكسون و الفلوريد وذلك باستخدام القياسات الطيفية المشتقة.

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في هذا البحث تم اجراء طريقة طيفية للتقدير المتزامن لكل من ايون النحاس الثنائى و ايون المنجنيز الثنائى فى مخاليط ثنائية منهما. تعتمد هذه الطريقة على تكوين متراكبات فلزية ثلاثية مع آل من الاليزارين آومبلكسون وايون الفلوريد . وقد تم استخدام طريقتى التقاطع الصفرى ومشتقة الاطياف النسبية حيث تم تقدير النحاس (7. $µg\ ml12^{-1}$ – 54.2) فى وجود المنجنيز (9. $µg\ ml10^{-1}$ – 19.2) والعكس صحيح. وعندما تكون النتائج محققة لقانون بير (Beer's law) نجد ان طريقة التقاطع الصفرى تعتمد على ان المشتقة الطيفية الاولى D1 للاطياف العادية (Normal spectra) تساوى صفرعند λmax (الطول الموجى الذى يقابل اقصى امتصاص) وعليه فان D1 للمخلوط الثنائى تتناسب طرديا مع ترآيز احد المكونات بشرط قياسها عند λmax (والتى تقابل نقطة الصفر) للمكون الاخر. عند استخدام هذه الطريقة تم تقدير النحاس عند 520 nm (λmax او نقطة الصفر للمنجنيز) آذلك تم تقدير المنجنيز عند 507 nm (λmax او نقطة الصفر للنحاس) . اما طريقة المشتقة الاولى للاطياف النسبيه (DD^1) تعتمد على ان DD^1 للمكون الذى تم استخدامه آمقسوم عليه " divisor " تساوى صفر وعليه تكون قيمة DD^1 للمخلوط الثنائى تتناسب طرديا مع ترآيز المكون الاخر . عند استخدام هذه الطريقة تم تقدير النحاس عند 545 nm بينما تم تقدير المنجنيز عن 610 nm , 638 nm . تتميز هذه الطريقة بانتقائية و حساسية عالية جدا و قد تم تطبيق الدراسة لتحليل عدة مخاليط ثنائية من النحاس الثنائى و المنجنيز الثنائى وآانت النتائج مرضية تماما .