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Development of Extractive Spectrophotometric Method for the Determination of Copper (II) with Schiff Base 2-{(*E*)-[(2, 4-dichlorophenyl) imino] methyl } -6-methoxyphenol

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Abstract: ***Using 2-(E)-[(2,4-dichlorophenyl)imino]methyl-6-methoxyphenol [DCPIMMP], a robust spectrophotometric technique has been devised to measure copper (II). DCPIMMP extracts quantifiable amounts of Cu(II) into chloroform from an aqueous solution with a pH between 3.9 and 5.9. The chloroform extracts show maximum absorption at 590 nm(λ_{max}). Beer's Law is obeyed over the Cu (II) concentration range of 0.5 to 20.0 µg/ml. The Molar absorptivity and Sandell's sensitivity for Cu–DCPIMMP system is 3559 L mol $^{-1}$ cm^{-1} and 0.018µg cm^{-2}respectively. The composition of extracted species is found to be 1: 2 [Cu-DCPIMMP] by Job's continuous variation and Mole-ratio method. Interference by various ions has been studied. The proposed method is rapid, sensitive, reproducible and accurate and it has been satisfactory applied for the determination of Copper in Pharmaceutical Samples.***

Keywords: Solvent Extraction, Extractive Spectrophotometry, Copper (II), Schiff base, 2-{(*E*)-[(2,4-dichlorophenyl)imino]methyl}-6-methoxyphenol [DCPIMMP], Pharmaceutical sample.

1. Introduction

Various reagents [1-10] are available for the spectrophotometric determination of Copper (II) of which Oximes, Schiff bases and its derivatives constitute an important class. Synthesis and application of Schiff base 2-{(E)-[(2,4-dichlorophenyl)imino]methyl}-6-methoxyphenol [DCPIMMP] have not been reported. In the present communication, we describe the extractive spectrophotometric determination of Cu (II) with 2-{(E)-[(2,4-dichlorophenyl)imino]methyl}-6-methoxyphenol [DCPIMMP].

2. Materials and methods

For measuring absorbance, an ELICO-SL 159 spectrophotometer with optically matched quartz or glass cells with a 1 cm path length was employed. For measuring pH, an ELICO-LI 127 pH metre was used. According to a reported technique, 2,4-dichloro aniline and 2-hydroxy-3-methoxybenzaldehyde (o-vanillin) were condensed to synthesize the reagent DCPIMMP [11]. Using ethanol recrystallization is done, the end product was identified using elemental and spectral analyses. With ethanol, a 0.5% solution of it was Prepared. Copper acetate was dissolved in double-distilled water that also contained a few diluted drops of glacial acetic acid to prepared a stock solution of Cu (II). Diethyl-dithiocarbamate technique was used to standardize it [11]. Copper (II) working solutions were created using the proper dilution.All other reagents used were of the AR grade, and doubly distilled water was utilised to prepare all solutions.

Preparation Of Schiff's Base

2-Hydroxy-3-methoxybenzaldehyde (0.002 mole) and 2,4-Dichloroaniline (0.002 mole) were dissolved in absolute alcohol. It was attached to water condenser and refluxed for 3-4 hours. After that mixture was poured to a beaker and kept in the fridge overnight. The product was filtered dried & crystallized [12-13]. Orange colour crystals of Schiff's base, 2-{(*E*)-[(2,4-dichlorophenyl)imino]methyl}-6-methoxyphenol [DCPIMMP] obtained.

Extraction and separation of Cu (II)

A 25 ml beaker was filled with an aliquot of an aqueous solution containing 500 µg of Cu (II) and 2 ml of a 0.5% solution of DCPIMMP made in ethanol. The pH of the solution was adjusted to the required value using a dilute solution of HCl/NaOH, with the total volume remaining at 10 ml of distilled water. After that, the finished solution was poured into a 125 ml separatory funnel. A separatory funnel was used to add each of the two 5 ml portions of organic solvent that were used to wash the beaker to the solution.

The two phases were equilibrated for one minute and allowed to separate. After the separation of two phases, pH of the equilibrated aqueous phase was measured and Copper content in each phase was determined by Diethyl-dithiocarbamate method[11]. The extraction was carried out with different solvents to find out the best extracting solvent. On the basis of copper content in aqueous and an organic phase, extraction coefficient and percent extraction were calculated.

Extractive spectrophotometric determination of Cu (II)

2 ml of a potassium hydrogen phthalate (KHP) and HCl buffer solution with a pH of 5 and 1 ml of a 0.5% solution of DCPIMMP prepared in ethanol were added to an aliquot of an aqueous solution containing 5-200 µg of Cu (II). With the help of distilled water, the solution's volume was increased to 10 ml. The phases were allowed to separate after the solution was equilibrated for one minute with 10 ml of chloroform. The 10 ml measuring flask in which the chloroform extract was taken was filled to the prescribed level with chloroform. At 590 nm, the absorbance of a reagent blank prepared under the same conditions was compared to that of the chloroform extract. The calibration curve was used to calculate the Cu (II) content of the sample solution. Prior to extraction and pH adjustment, the appropriate foreign ions were added to the aqueous phase to evaluate the effects of other ions.

Determination of Copper in pharmaceutical sample

10 ml of aquaregia were used to dissolve 2 mg of pharmaceutical sample in boiling water. The resultant solution was evaporated until it was completely dry, and the residue was then dissolved in 10 ml of 1 M HCl, filtered if necessary, and then diluted to 100 ml with double-distilled water. The previously stated method was used to analyse an aliquot of this solution (1 ml) for the presence of iron.

3. Results and Discussion

DCPIMMP was able to quantitatively extract (99.95%) copper (II) from an aqueous solution with a pH range of 3.0-6.0 into chloroform. (fig. 1). Organic solvents used for extraction of Cu (II) can be arranged on the basis of their extraction coefficient values as chloroform> carbon tetrachloride>xylene>toluene>benzene>Nitro benzene>ethyl acetate>n-butanol>Iso amyl alcohol>benzyl alcohol (fig. 2).

As chloroform proved to be the most effective extracting solvent, it was used for extraction throughout the entire work.

Cu-DCPIMMP complex chloroform extract showed a significant peak at 590 nm. Since the reagent's absorbance at this wavelength is quite small, the absorption measurements were performed at this wavelength (fig. 3). The outcome demonstrates that the system verified Beer's law over a Cu (II) concentration range of 0.5 to 20 µg /ml at this wavelength (Fig-4). According to calculations based on Cu (II) concentration, the extracted species' molar absorptivity and Sandell's sensitivity were determined to be 3559 L mol $^{-1}$ cm^{-1} and 0.018 µg cm^{-2}, respectively [13]. It was discovered that 200 µg of Cu (II) could be extracted from 1 ml of a DCPIMMP 0.5% solution prepared in ethanol. It was discovered that the chloroform extract's colour was stable.

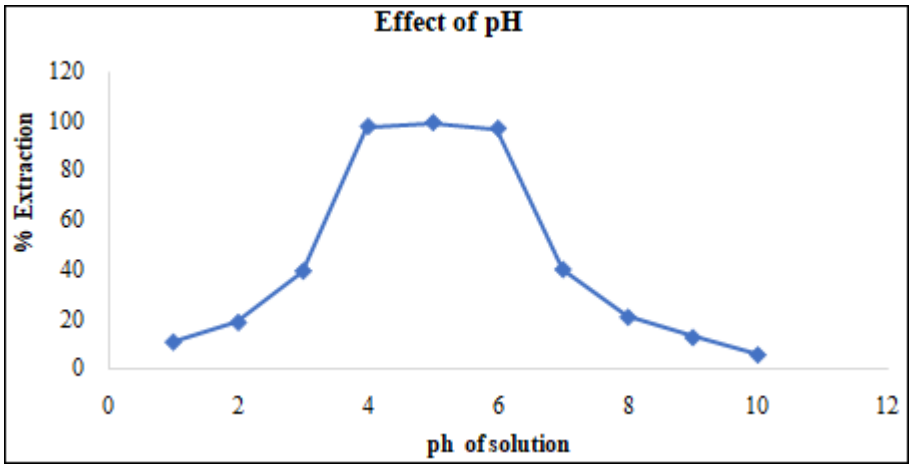

Figure 1: Effect of pH

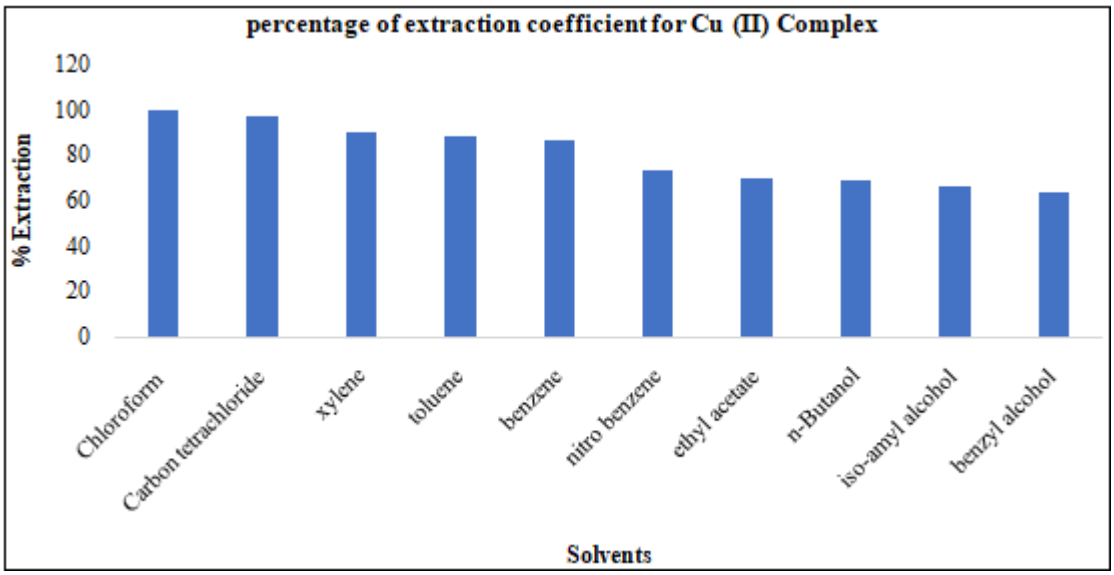

Figure 2: Percentage of extraction coefficient for Cu complex in different solvent

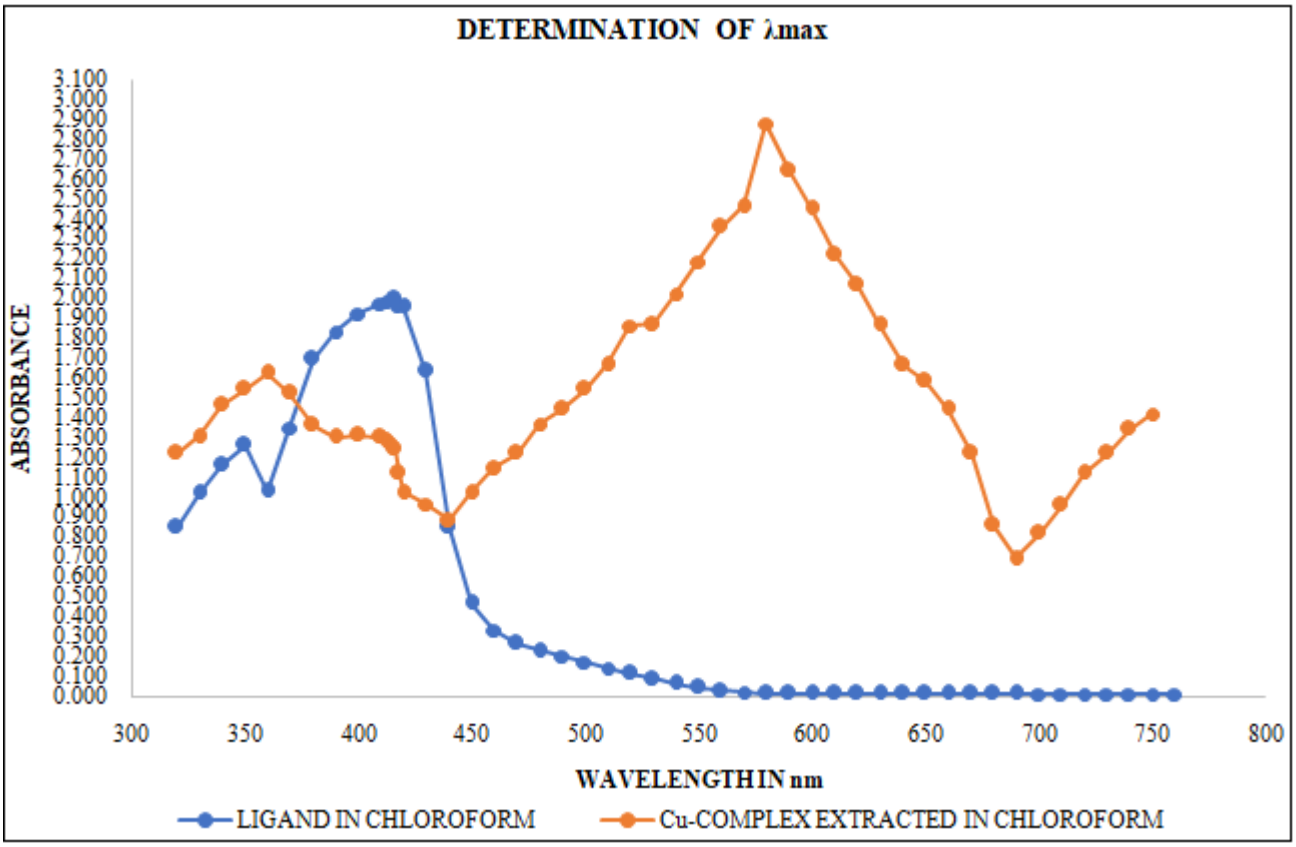

Figure 3: Determination of λmax

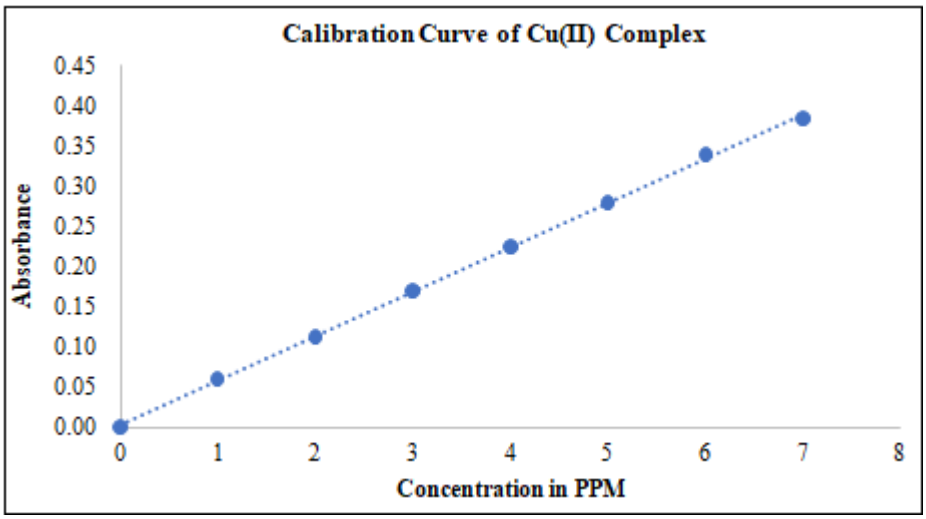

Figure 4: Calibration curve of Cu Complex

Effect of other ions

Copper (II) (100 µg) was measured with different ions present. The spectrophotometric determination of Cu (II) (100 µg) was not affected by the presence of the following ions in the amounts indicated:10 mg each of Li (I), Be (II), Ba (II), Ca (II), Sr (II), Al (III), Ti (III), V (V), Mo (VI)& Ni (II). 100 ppm of each Os (IV), Pd (II), Pt (IV), Rh (III) and Ru (III). And 20 mg each of chloride, bromide, iodide, fluoride, chlorate, bromate, iodate, sulphide, phosphates, tartrate, acetate, citrate and thiosulphate, triethanolamine, ascorbic acid. The use of a suitable masking agent removed interference caused by various ions. (table 1).

Table 1: Effect of other ion

Sr No	Interfering ion	Amount added in mg	Masking agent added 1 ml of 0.5 M solution
1	Mn(II)	10	Potassium tartarrate
2	Ag(I) & Pd (II)	10	Potassium thiocyanante
3	Mn (II)	10	thiocyanante
4	Fe(III) , Cr(III) & V(II)	10	Triethanol amine
5	Ni(II)	10	5-sulphosalicylic acid

Composition of the extracted complex

The composition of the extracted complex was found to be 1:2 (Cu:DCPIMMP) by Job's continuous variation and Mole ratio methods (fig.5 & fig. 6).

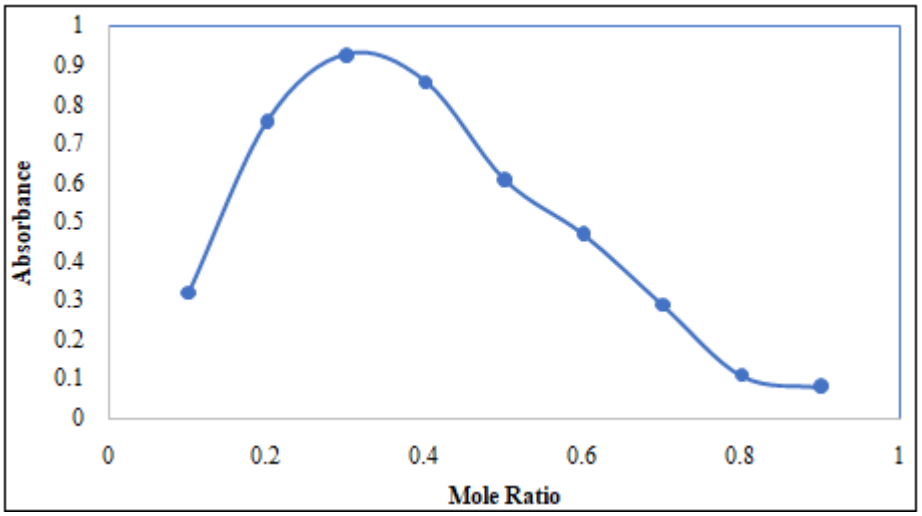

Figure 5: Graph of Job's continuous variation

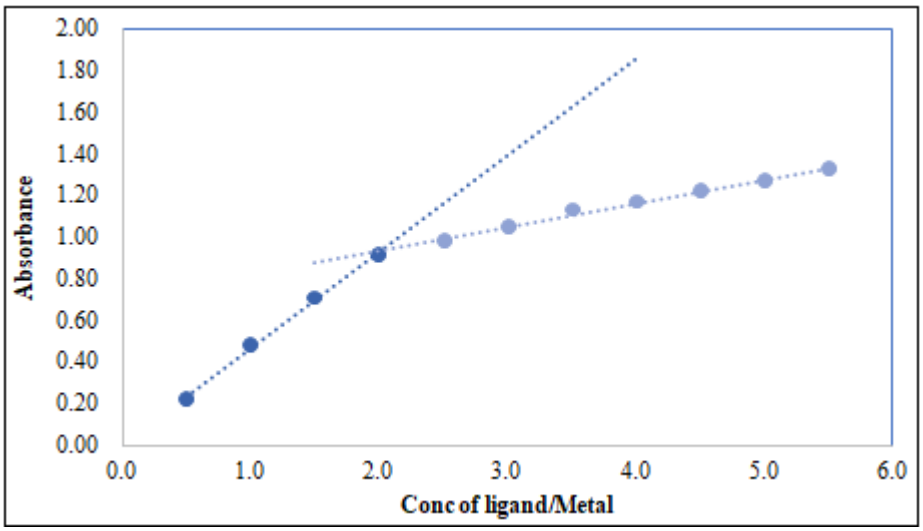

Figure 6: Graph of Mole ratio methods

Precision, accuracy, sensitivity and application of method

The method's precision and accuracy were evaluated by analysing a solution containing a known amount of Cu (II) using the recommended procedure. The average of ten determinations of 5 µg Cu (II) in 10 cm3 solutions was 4.98 µg, ranging between 4.95 and 5.01 at the 95% confidence limit, with a standard deviation of ±0.0487. The proposed method was used to determine copper amounts in pharmaceutical samples. The sample analysis results were comparable to those obtained by the Diethyl-dithiocarbamate method [11]. (table 2).

Table 2: The results of the analysis

Percentage of Cu (II)	Diethyl-dithiocarbamate method	Proposed method
Alloy Sample Cu-Al alloy	80.10 %	79.60 %
Pharmaceutical sample Zincovit	0.493 mg	0.480 mg

4. Conclusion

From the above discussions, it is found that Schiff base, Copper (II), Schiff base, 2-{(*E*)-[(2,4-dichlorophenyl)imino]methyl}-6-methoxyphenol [DCPIMMP] is a goodsensitive reagent for the development of rapid and sensitiveextractive spectrophotometric method for the determination of Cu (II) and it has been satisfactory applied for the determination ofCopper in Pharmaceuticals Samples.

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References

[1] R. E. Peterson and M. E. Boiler, Anal, Chem., 27, 1195-1197 (1955).
[2] R. B. Singh, B. S. Garg and R. P. Singh, Talanta, 26, 525-526 (1979).
[3] H. A. Mahajan and M. R. Patil, Chim Anal., 37, 239-242 (1992).
[4] B. Maria and E. Świcicka, Talanta, 43(3), 471-478 (1996).
[5] M. Khambekar and A. D. Sawant, J. Indian Chem. Soc., 36A (5), 459-460 (1997).
[6] K. Pala and M. SahedurRahmand, Spectrophotometric Study of Ruthenium (III) using 2-Pyridyl Thioquanaldemide (PTQA), Talanta, 48(5), 1075-1084 (1999).
[7] K. N. Vidhate, M. K. Lande, B. R. Arbad, Extractive Spectrophotometric Simultaneous Determination of Ru (III), J. Indian Chem. Soc., 86(1), 109-112 (2009).
[8] R. M. Makhijani And V. D. Barhate, Int. J. Chem. Sci.: 11(1), 2013, 605-613 ISSN 0972-768X
[9] R. S. Lokhande, Santosh Kulkarni, Shirish Pitale, S.K.Patil , S. P. Janwadkar, International Journal of Pharma Sciences and Research (IJPSR) Vol.2(9), 2011,184-188.
[10] B. K. Reddy, J. R. Kumar, K. J. Reddy, L. S. Sarma, A. V. Reddy, Analytical Sciences March 2003, Vol. 19 2003.
[11] Noll, C. A., & Betz, L. D. (1952). Determination of Copper Ion by Modified Sodium Diethyldithiocarbamate Procedure. Analytical Chemistry, 24(12), 1894–1895
[12] Vogel AI, Practical Organic Chemistry: 5th Ed., London; Longman group limited: 1989
[13] AI. Vogel, Text Book of Quantitative Inorganic Analysis, Longman Green and Co. Ltd., London (1978).
[14] E. B. Sandell, Colorimetric Determination of Traces of Metals; 3rd Edn. Interscience, N.Y. (1965) p. 414.

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