

SYNTHESIS OF 6-(2-NAPHTHYL)-2,3-DIHYDRO-as-TRIAZINE-3-THIONE AS A SENSITIVE REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF Cu (II)

FAZEL SHAMSA, MALIHEH BARAZANDEH-TEHRANI

DEPARTMENT OF PHARMACEUTICAL CHEMISTRY, FACULTY OF PHARMACY, TEHRAN UNIVERSITY OF MEDICAL SCIENCES, TEHRAN, IRAN.

ABSTRACT

A Spectrophotometric method for determination of Cu (II) based on the complex formation with a new reagent 6-(2-naphthyl)-2,3-dihydro-as-triazine-3-thione (NDTT) is described. NDTT was synthesized based on the knowledge available for the preparation of 6-phenyl-2,3-dihydro-as-triazine-3-thione (PDTT). Reaction of 2-acetylnaphthalene 1 with amyl nitrite gave 2-naphthylglyoxal aldoxime 2, which upon reaction with thiosemicarbazide yielded 6-(2-naphthyl)-2,3-dihydro-as-triazine-3-thione (NDTT) 3. NDTT produces a red complex with copper which is easily extractable with chloroform at pH>8 while the reagent is not extracted under these conditions. The absorption of the complex in the UV region (313 nm) is about 7 times greater than in the visible region (508 nm). The mole ratio of the complex which is formed between Cu (II) and NDTT is 2:3, which was calculated by both the mole ratio and the continuous variation methods. The absorbance of the complex obeys Beer's law in the concentration range of 0.08-2 $\mu\text{g Cu(II)/ml}$ chloroform with $r = 0.998$ and detection limit of 13 ng/ml. This procedure can be carried out in the presence of many cations and anions in the presence or absence of the masking agents.

Keywords: 6-(2-naphthyl)-2, 3-dihydro-as-triazine-3-thione; Cu (II); Spectrophotometric analysis; Cu(II)-6-(2-naphthyl)-2, 3-dihydro-as-triazine-3-thione complex.

INTRODUCTION

Although modern analytical chemistry relies heavily on instrumentation and data processing, organic reagents play an important role across the whole range of the analytical procedures. Their uses vary from pH buffers to NMR shift reagents, and from organic reagents to enzyme substrates and chromatographic derivatization reagents. Determination of trace amounts of copper has received considerable attention and various methods have been developed. Many of these methods are either time-consuming or require complicated and expensive instruments. Therefore, development of methods that rapidly and conveniently determine low concentrations of copper in real samples seem desirable (1-7).

It has been reported that 6-Phenyl-2, 3-dihydro-as-triazine-3-thione (PDTT) forms a red complex with Cu^{2+} , which is easily extractable with chloroform over a wide range of pH. While the method is simple, it suffers from low sensitivity, in the way that the molar absorptivity of the complex is 5.0×10^3 (8). In this investigation the synthesis of 6-(2-naphthyl)-2, 3-dihydro-as-triazine-3-thione (NDTT) as a possible reagent for determination of Cu^{2+} is reported (Fig. 1). The purpose of this modification is to increase its

sensitivity relative to PDTT in the determination of Cu^{2+} . The preparation of NDTT was conducted based on the reported method for the preparation of PDTT (9), where the reacting moiety namely, triazine-3-thione, was left intact, and the chromophore group was changed.

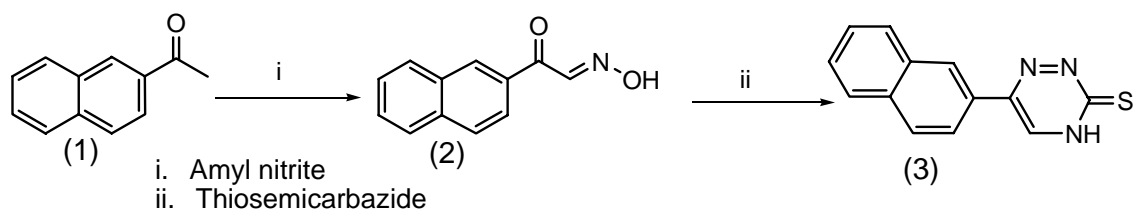
MATERIALS AND METHODS

Apparatus

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. The IR spectra were obtained using a Perkin-Elmer Model 781 spectrograph. The ^1H -NMR spectra were obtained on a Varian 400 Unity Plus and chemical shifts (δ) were determined in ppm relative to the internal tetramethylsilane. Mass spectra were obtained on a Finnigan MAT TSQ 70 spectrometer at 70 eV. Shimadzu 160A spectrophotometer was used for all absorption measurements.

Reagents and Chemicals

Anhydrous ethanol (Merck), sodium metal (Aldrich), amyl nitrite (Merck), 2-acetylnaphthalene (Merck), thiosemicarbazide (Merck), Chloroform (Merck), 2 N sodium hydroxide solution, 2 M tartaric acid solution (Fluka), and 0.0002 M solution of NDTT in 2 M NaOH



Scheme I. Synthesis of 6-(2-naphthyl)-2,3-dihydro-as-triazine-3-thione

(Merck) were used. NDTT solution in NaOH should be freshly prepared before use.

Copper nitrate solution

Pure elemental copper (exactly 0.5 g) was dissolved in hot concentrated HNO_3 , and after cooling, 50 ml HNO_3 (1:1) was added and the volume was adjusted to 500 ml by addition of the distilled water. Solutions with lower concentrations were prepared by proper dilution.

Solutions of Diverse ions

1% solutions of diverse ions were prepared by dissolving measured amounts of salts of the corresponding ions in distilled water. In some cases, acids were added to prevent hydrolysis. The following ions were studied: Fe^{2+} , Mg^{2+} , Co^{2+} , Bi^{3+} , Hg^{2+} , Ni^{2+} , Mn^{2+} , Pb^{2+} , Ba^{2+} , Ca^{2+} , Cd^{2+} , Sr^{2+} , Al^{3+} , CH_3COO^- , I^- , Br^- and $\text{Cr}_2\text{O}_7^{2-}$.

Synthesis of 2-naphthylglyoxaldoxime (2)

Sodium metal (1.2 g) was added to the cold anhydrous ethanol (30 ml) followed by dropwise addition of amyl nitrite (7 ml) under anhydrous conditions. To the resulting solution was gradually added 2-acetylnaphthalene (9.9 g) and the mixture stirred for 40 h at room temperature where a brown precipitate was produced. Water (40 ml) was added to the resulting mixture and then it was filtered. The filtrate was made acidic by addition of concentrated HCl and extracted with ether. The solvent was evaporated and the residue was crystallized from ethanol-water to give 2.3 g (20%) of the compound 2; m.p.: 90-93°C. IR (KBr ν): 3345(OH), 1690(C=O), 1619(C=N); $^1\text{H-NMR}$ (CDCl_3 , δ): 8.65 (s, 1H, H_1 naphthalene), 7.99(m, 5H, Ar—H and C=N), 7.60(m, 2H, Ar—H); MS (m/z , %), 199(M^+ , 42), 172(27), 155(88), 177(100), 77(8).

Synthesis of 6-(2-naphthyl)-2, 3-dihydro-as-triazine-3-thione (NDTT), (3)

Compound 2 (0.5g), thiosemicarbazide (0.6g), H_2O (15ml) and concentrated HCl (0.25ml) were refluxed for 3 h. The progress of the reaction was monitored by TLC using a mixture of chloroform and methanol (3:1) as a mobile phase. The reaction mixture was cooled, the precipitate was filtered and crystallized from DMSO- H_2O to give

72 mg (10%) of the compound 3; m.p.:248-251°C. IR (KBr ν): 3390 Cm^{-1} (NH); $^1\text{H-NMR}$ (CDCl_3 , δ): 8.60 (bs, 1H, NH), 8.45(s, 1H, H_1 naphthalene), 7.8 (m, 5H, Ar—H and HC_5 triazine), 7.58(m, 2H, Ar—H); MS (m/z , %), 239(M^+ , 23), 222(9), 172(8), 166(15), 152(100), 139(17), 126(24), 76(16).

General procedure for determination of Cu^{2+}

A mixture of 1-20 μg Cu^{2+} , 0.0002 M (5 ml) of NDTT and 2 M tartaric acid (1 ml) in a 100 ml separatory funnel was shaken thoroughly and the resulting complex was extracted with 4, 3 and 2 ml of chloroform. The extracts were collected in a 10 ml volumetric flask and adjusted to the volume with chloroform. The absorbance of the extracts was measured at 313 nm versus the blank.

RESULTS AND DISCUSSION

Absorption Curves

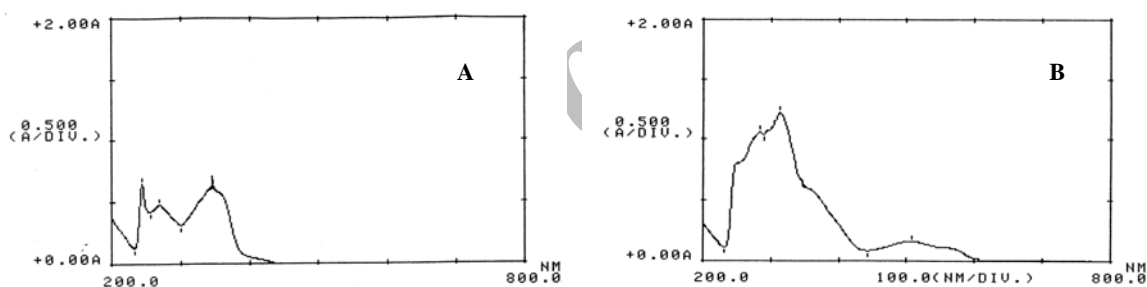
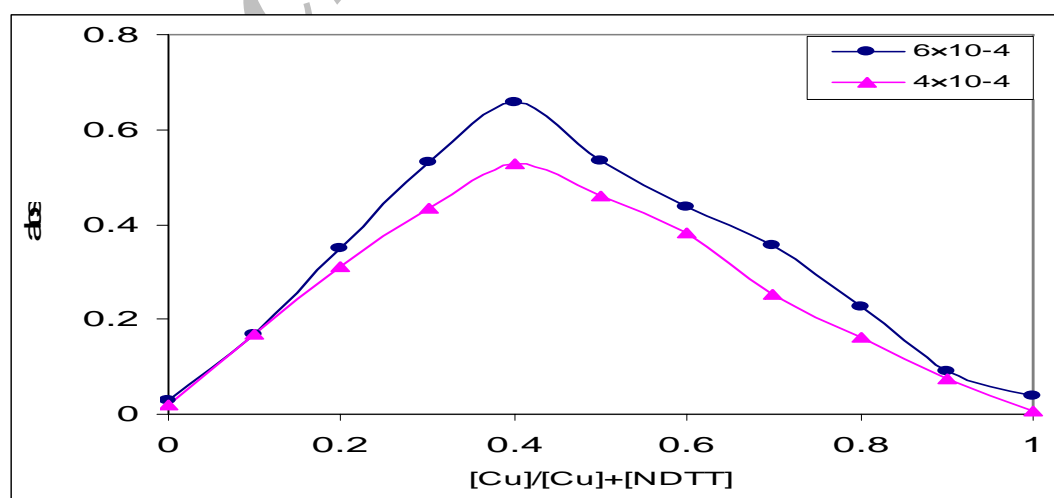
Absorption curves of Cu (II)-NDTT complex corresponding to about 2 μg Cu (II)/ml chloroform or NDTT alone in chloroform are shown in Fig.1. The absorption measurements were made in the wavelength range of 250-800 nm. The complex in chloroform showed maximum absorptions at 313 and 508 nm, where NDTT alone obtained by extraction with chloroform in acidic pH showed maximum absorptions at 248, 270 and 346 nm (Fig.1). Briefly, a bathochromic shift with hyperchromic effect is produced due to the reaction between Cu^{2+} and NDTT in alkaline pH. All spectrophotometric measurements were made at 313 nm, since the absorption of Cu (II)-NDTT complex at 313nm was almost 7 times stronger than the absorption at 508 nm. NDTT alone is not extractable by chloroform in alkaline pH; therefore, no interference is exerted by NDTT on the complex absorption. The molar absorptivity of the complex is 3.31×10^4 ; the absorbance of 0.365 corresponds to Cu^{2+} concentration of 0.7 $\mu\text{g}/\text{ml}$ chloroform.

Effect of pH

The pH of the aqueous layer was changed between 7-14 using borate buffers. The results showed maximum extraction of the complex and

Table 1. Absorbance and concentration of identical samples used for calculation of precision and accuracy

Sampled Cu ($\mu\text{g/ml}$)	Abs	Measured Cu ($\mu\text{g/ml}$)	Sampled Cu ($\mu\text{g/ml}$)	Abs	Measured Cu ($\mu\text{g/ml}$)
14	0.731	13.993	4	0.221	4.234
14	0.715	13.687	4	0.214	4.100
14	0.732	14.012	4	0.210	4.023
14	0.737	14.108	4	0.206	3.946
14	0.737	14.108	4	0.217	4.157
14	0.731	13.993	4	0.210	4.023
14	0.742	14.203	4	0.212	4.061
14	0.728	13.935	4	0.209	4.003
14	0.735	14.069	4	0.217	4.157
14	0.738	14.126	4	0.212	4.061
S.D.		0.014			0.086
C.V.		1.0			2.1
%Accuracy		0.1			1.88
Mean \pm S.D.		14.023 \pm 0.014			4.0765 \pm 0.086

**Figure1.** Absorption spectra of NDTT in chloroform (A) and Cu (II)-NDTT complex in chloroform (B); NDTT was extracted in acidic medium (tartaric acid) but the complex was extracted according to the general procedure..**Figure 2.** Composition of Cu (II)-NDTT complex at 313 nm by continuous variation method $[\text{Cu}^{+2}] + [\text{NDTT}]$: 4×10^{-4} M; 6×10^{-4} M

minimum extraction of NDTT at pH > 13. So the optimum pH for the Cu-NDTT complex extraction is pH > 13.

Stability of Complex

The Cu (II)-NDTT complex was very stable and began to fade slowly after 2 days. The complex was also stable toward buffers having pH > 6. It was decomposed at pH < 4. In the absence of tartaric acid during the analysis, copper ion was precipitated.

Conformity to Beer's law

The absorbance of Cu (II)-NDTT complex corresponding to different quantities of Cu^{2+} was plotted versus the amounts of Cu^{2+} . The complex follows Beer's law at 313 nm over the concentration range of 0.08-2 μg Cu^{2+}/ml chloroform with $r = 0.998$ ($C = 18.229\text{ABS} - 0.0286$).

Nature of the complex

The composition of the complex was determined by the continuous variation method (10, 11, 12) as follows: The total molar concentration of the mixture ($\text{Cu}^{2+} + \text{NDTT}$) was kept constant at two different concentrations; 0.4 and 0.6 mM. Following the general procedure, spectrophotometric measurements were carried out at 313 nm and the absorbance of the solutions was plotted versus the mole fraction of Cu (II). The maxima happened at 0.4 mole fraction of Cu (II) indicating the presence of 2:3 ratio of Cu (II) to NDTT in the complex (Fig. 2). The recommended structure of Cu-NDTT complex is proposed in Fig.3. (13)

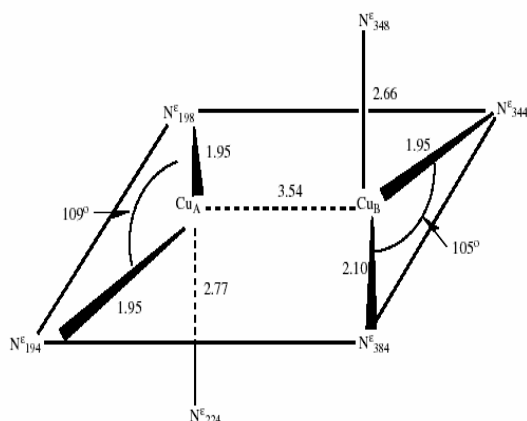


Figure 3. Recommended structure of the 2:3 Cu-NDTT complex

Determination of the optimum amount of NDTT

For this purpose the mole ratio method was employed (14). The concentration of Cu (II) was kept constant at 2×10^{-4} M, while the NDTT concentration was varied between 1×10^{-4} to $6 \times$

10^{-4} M. Spectrophotometric measurements were carried out according to the general procedure. The absorbance was plotted against the reagent to metal mole ratio. A continuous increase in absorbance occurred as the concentration of NDTT increased up to 3×10^{-4} M, the NDTT to Cu^{2+} ratio of 1.5. At higher NDTT concentrations, the absorbance of the complex did not change (Fig. 4). Therefore, in all determinations of Cu^{2+} a little more than this ratio was employed.

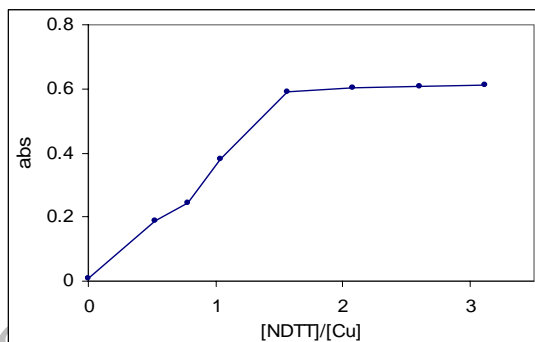


Figure 4. Variation of the absorbance at 313 nm. $[\text{Cu}^{2+}] = 2 \times 10^{-4}$ M

Effect of Diverse Ions

To determine the effect of diverse ions, a standard Cu (NO_3)₂ solution containing 10 μg of Cu^{2+} and the ion in question were transferred to a separatory funnel, followed by an excess of NDTT solution. The method was completed as mentioned under the general procedure.

The following three groups were examined in the case of determination of 10 μg Cu^{2+} :

1) Mn^{2+} , Bi^{3+} , $\text{Cr}_2\text{O}_7^{2-}$, Br^- , CH_3COO^- and I^-

These ions do not interfere with the formation and extraction of Cu^{2+} -NDTT complex, because they do not produce interfering products with NDTT, NaOH or tartaric acid.

2) Fe^{2+} , Ba^{2+} , Mg^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} and Sr^{2+} do not give interfering complexes with NDTT. However, they are precipitated by addition of sodium hydroxide, and the precipitates had physical interferences. This precipitation could be prevented by the addition of an excess of tartaric acid. Al^{3+} and Pb^{2+} form white precipitates with NaOH which are soluble in excess NaOH solution; therefore no interference was observed.

3) Nickel and mercury ions form complexes with NDTT which have absorption at 313 nm. To analyze Cu^{2+} in the presence of Hg^{2+} and Ni^{2+} , no suitable masking agent was found.

Precision and Accuracy

A set of ten identical samples, each with a final Cu^{2+} content of 4 μg were treated according to the recommended procedure, and their absorbances

were measured. This was repeated with a final Cu^{2+} content of 14 μg for another set of ten samples. The accuracy varied from 0.1% at 14 μg to 1.88% at 4 μg . The percentage of the relative standard deviation (coefficient of variation) varied from 1.0% at 14 μg to 2.1% at 4 μg of Cu^{2+} (Table 1).

CONCLUSION

The following conclusions may be drawn from this investigation.

- NDTT is specific for Cu^{2+} , since it produces a red complex only with Cu^{2+} .
- Since the cations such as Hg^{2+} , Ni^{2+} in microgram levels interfere with Cu^{2+} analysis by this method, they could be analyzed by similar procedure.
- The proposed method is more sensitive than the recently published spectrophotometric methods for Cu^{2+} (15).

- This method is very simple and the extraction of complex by CHCl_3 is easily established at alkaline pH.
- Since the reagent contains naphthyl fluorophore moiety it might has fluorogenic property and could be used as a fluorogenic reagent for the cations with which it forms complex. Some experiments have been carried out for this purpose and the results will be presented in future works.
- This reagent may be employed for the analysis of Cu^{2+} , Hg^{2+} or Ni^{2+} by HPLC which was confirmed by some primary experiments.

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