

Derivative Spectrophotometric Method for Simultaneous Determination of Nickel(II) and Copper(II) Using 6-(Anthracen-2-yl)-2,3-dihydro-1,2,4-triazine-3-thione

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Derivative spectrophotometric method using newly synthesized reagent, 6-(anthracen-2-yl)-2,3-dihydro-1,2,4-triazine-3-thione (ADTT), has been developed for the simultaneous determination of copper and nickel. The reagent was synthesized by the acylation of anthracene and then reaction of the resulted product with amyl nitrite to produce (anthracen-2-yl)-glyoxal aldoxime. After addition of thiosemicarbazone the reagent was prepared. Copper and nickel were determined by using zero-crossing method in the second, third and fourth order derivative spectra after derivatization in basic medium. Beers's law was obeyed in the range of 5-35 $\mu\text{g/mL}$ for copper at 387 nm (second order) and 554 nm (third order) and 5-35 $\mu\text{g/mL}$ nickel at 447 nm (first order), 400 nm (third order) and 385 nm (fourth order). The limit of quantification was 5 $\mu\text{g/mL}$ for both cations. The within-day and between-day variations in three concentrations were less than 3.36 and 4.73 % in all measurements, respectively. The proposed method is simple and accurate for determination of binary mixtures.

Key Words: Derivative spectrophotometry, Copper, Nickel, 6-(anthracen-2-yl)-2,3-dihydro-1,2,4-triazine-3-thione.

INTRODUCTION

Copper is a transition metal and is one of the essential micronutrients. Copper is found in environmental, biological and alloy samples. There are also a large number of enzymes contains copper which act as redox catalysts¹⁻³. Nickel is also an important element not only for industry, but also for biological system. Nickel compounds are widely used in industry, nickel-cadmium batteries, nickel alloys and electronic equipments^{4,5}. Due to the importance of copper(II) and nickel(II), it is necessary to develop simple and sensitive techniques for the simultaneous determination of these cations in a wide variety of samples such as environmental, industrial, geometrical or pharmaceutical samples. A survey of literature reveals that few works have been reported before for simultaneous determination of these ions. Derivative spectrophotometric determination has been performed based on the complexation reaction with different reagents, 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone, methylthymol blue or zincon⁶⁻¹⁰. By using appropriate chromogenic reagents, low concentrations of these cations should be determined by spectrophotometric methods. When the zero order spectrophotometric method could not be used because of the overlapping of the spectra, derivative spectrophotometry could be utilized for increasing selectivity without the need for prior separation and

masking agents. In continuation of our recent studies on some sensitive complexing reagents¹¹⁻¹³ for determination of selected cations in trace amount, a new reagent has been synthesized. This reagents, 6-(anthracen-2-yl)-2,3-dihydro-1,2,4-triazine-3-thione (I) (Fig. 1), was employed as complexing reagent for simultaneous determination of nickel (II) and copper(II) in synthetic mixtures. Due to overlapping spectra of the resulted chromogenic complexes, derivative spectrophotometric method based on zero-crossing technique was used for simultaneous determination of these cations.

EXPERIMENTAL

Anthracene, aluminium chloride, acetyl chloride, amyl nitrite, thiosemicarbazide, chloroform, sodium hydroxide, tartaric acid and other chemicals were of analytical grade and purchased from Merck (Darmstadt, Germany).

Synthesis of 6-(anthracen-2-yl)-2,3-dihydro-1,2,4-triazine-3-thione: The reagent, 6-(anthracen-2-yl)-2,3-dihydro-1,2,4-triazine-3-thione (ADTT), was synthesized from 2-acetylanthracene in the lab based on a method reported before¹¹. 2-Acetylanthracene was prepared by addition of AlCl_3 in nitrobenzene to anthracene followed by dropwise addition of acetylchloride under anhydrous condition and stirred for 3 h at 25 °C. 2-Acetylanthracene was produced in a good yield (75 %). By the reaction of 2-acetylanthracene with amyl nitrite

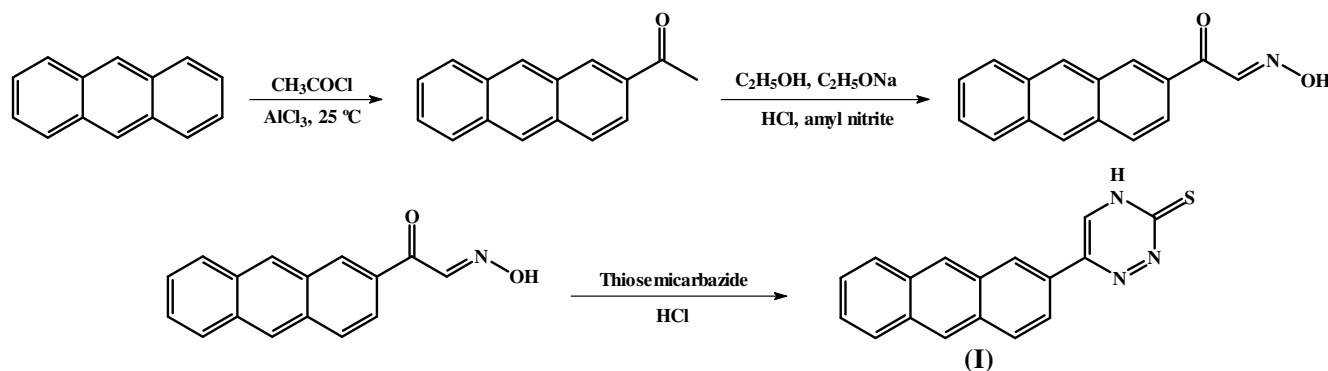


Fig. 1. Synthesis of 6-(anthracen-2-yl)-2,3-dihydro-1,2,4-triazine-3-thione

under anhydrous conditions and reflux for 50 h at 55 °C, 2-anthracenyl glyoxal aldoxime was produced. In a 100 mL flask thiosemicarbazide was added to 2-anthracenyl glyoxal aldoxime in acidic media and reflux for 3.5 h. The yellow coloured product was separated by filtration and crystallized from CH₃OH-H₂O to give the complexing reagent, 6-(anthracen-2-yl)-2,3-dihydro-1,2,4-triazine-3-thione (ADTT). The synthesis scheme is shown in Fig. 1.

Spectrophotometric measurements were performed using a Shimadzu UV-160 double beam UV visible spectrophotometer (Shimadzu, Kyoto, Japan) with a fixed band width of 2 nm. The zero order spectrums was produced in the range of 230-650 nm using a 1 cm quartz cell against a reagent blank prepared under similar conditions. The derivative spectra at different orders (1-4) were obtained in the same wavelength range and different slit width ($\Delta\lambda$).

For preparing standard copper solution, accurately weighed amount of elemental copper (0.500 g) was dissolved in hot conc. HNO₃. After cooling, 50 mL of HNO₃ (1:1) was added and the volume was adjusted to 500 mL by distilled water. The final concentration of copper(II) solution would be 1 mg/mL. The same procedure was adopted for preparing nickel(II) solution as for copper solution by utilizing elemental nickel to reach a final concentration of 1 mg/mL for nickel(II).

A 0.004 M solution of reagent was prepared by dissolving suitable amount of the reagent in 2 M NaOH. The reagent solution was prepared daily as it was not stable.

Derivatization reaction: One mL of standard solutions of copper(II), nickel(II) or a mixture of copper(II) and nickel(II) was transferred to a 100 mL separatory funnel. 1 mL of reagent solution, 1 mL of 1 M tartaric acid and 1 mL of 2 M sodium hydroxide were added and mixed thoroughly. The resulting colored complex was extracted with chloroform. The chloroform layer was separated, mixed, dried over anhydrous sodium sulfate and transferred to a volumetric flask of 10 mL volume and adjusted to the volume with chloroform.

Spectrophotometric measurements: Zero order spectra of complexes produced by using standard solutions of copper(II) (10 µg/mL) and nickel(II) (10 µg/mL) was reported in the wavelength range of 230-650 nm. The first, second, third and fourth derivative spectra of those solutions were obtained in the same range at different $\Delta\lambda$ values.

Calibration solutions: Synthetic standard solutions of copper(II) in the range of 5-35 µg/mL in the presence of fixed

concentration of nickel(II) (5 µg/mL) was prepared by using standard solutions. A second series of synthetic standard solutions of nickel(II) in the range of 5-35 µg/mL in the presence of fixed concentration of copper(II) (5 µg/mL) was also prepared. The measured amplitude obtained at selected wavelength in derivative spectra was constructed over the concentration range of 5-35 µg/mL for nickel(II) or copper(II). The statistical data was calculated for six series of calibration curves.

Accuracy and precision: Two series of standard solutions of copper(II) solutions containing 5, 10 and 35 µg/mL plus nickel(II) (5 µg/mL) and nickel(II) solutions containing 5, 10 and 35 µg/mL plus copper(II) (5 µg/mL) were prepared and analyzed according to the discussed method. Each analysis was performed in triplicate in one day and during three consecutive days. The coefficient of variation and the percentage of deviation between added and measured concentrations were calculated.

Composition of the complex: The stoichiometry of the nickel-reagent and copper-reagent complex was studied by mole ratio method. According to this method a fixed concentration of copper or nickel was used for complexing reaction by using various concentrations of complexing reagent. The maximum absorbance was obtained to find out the stoichiometry of the reaction. It was found that up to 6 times of reagent solution was adequate to obtain maximum absorption.

RESULTS AND DISCUSSION

Spectra of reagent: 2-Acetylanthracene was obtained with high purity of 75 %. ¹H NMR (CDCl₃, δ): 8.73-8.32 (m, 3H, H₁, H₃, H₉), 8.15-7.94 (m, 4H, H₄, H₅, H₈, H₁₀), 7.64-7.43 (m, 2H, H₆, H₇), 2.76 (s, 3H, CH₃). IR (KBr, ν_{\max} , cm⁻¹): 1669 (C=O).

The reagent was obtained with high purity of 95 %. ¹H NMR (DMSO-*d*₆, δ): 8.89-8.62 (m, 3H, H₁, H₃, H₄), 8.30-7.84 (m, 4H, H₅, H₈, H₉, H₁₀), 7.69-7.59 (m, 2H, H₆, H₇), 6.91 (s, 1H, CH). Ms (m/z, %): 289 (M⁺, 20), 216 (18), 201 (100), 199 (40), 176 (20), 101 (20), 60 (34).

Spectral characteristics: The zero order absorption spectra of complexes of copper(II) and nickel(II) are shown in Fig. 2. A maximum absorbance of 308 and 410 nm was observed for copper(II)-reagent and nickel(II)- reagent complex respectively.

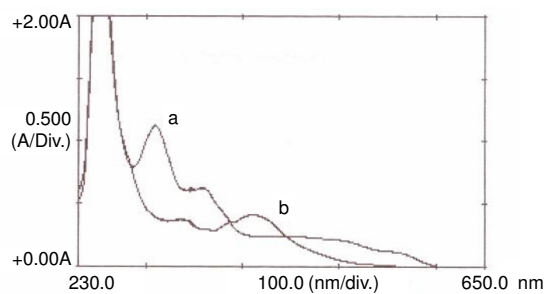


Fig. 2. Zero-order spectra of (a) Cu(II)-reagent and (b) Ni(II)-reagent complexes

Optimization of the experimental condition: It has been observed that maximum absorption of complex formation was resulted in basic conditions. The composition of the cation-reagents complex was studied by mole ratio method. By increasing the concentration of the complexing reagent the absorbance value of both complexes was elevated. The cation-reagent stoichiometric ratios were found to be 1:6 for both complexes. A large excess of reagent was used for completion of the reaction.

Derivative spectrophotometric method: Zero order spectra of copper(II) and nickel(II) complexes showed distinct overlap which prevents the simultaneous determination of these ions. The cation-reagent complexes were subjected to one to fourth order derivative spectrophotometric analysis at different $\Delta\lambda$ values. The recorded spectra were examined to find out suitable spectrum and wavelength to be used for simultaneous determination of the cation complexes. By using the zero crossing technique, it has been concluded that simultaneous determination of cation complexes would be possible by using the first, second, third and fourth order derivative spectrum at different wavelength. The related spectra are shown in Figs. 3-7. The detailed information is also shown in Table-1.

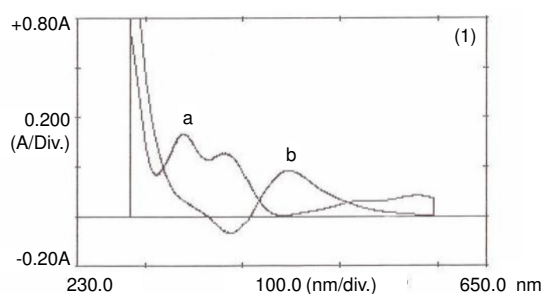


Fig. 3. First-derivative spectra of (a) Cu-ADTT complex and (b) Ni-ADTT [447nm, zero crossing for Ni(II)]

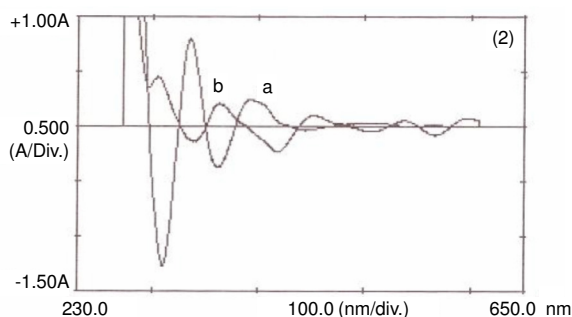


Fig. 4. Second-derivative spectra of (a) Cu-ADTT complex and (b) Ni-ADTT [387nm, zero crossing for Cu(II)]

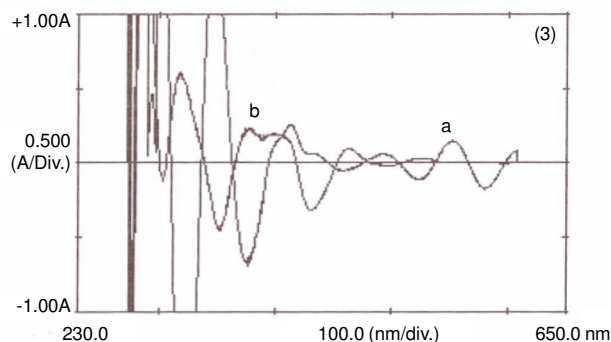


Fig. 5. Third-derivative spectra of (a) Cu-ADTT complex and (b) Ni-ADTT [554 nm, zero crossing for Cu(II)]

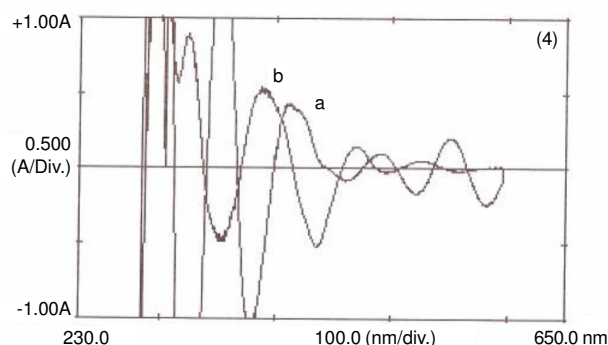


Fig. 6. Third-derivative spectra of (a) Cu-ADTT complex and (b) Ni-ADTT [400 nm, zero crossing for Ni(II)]

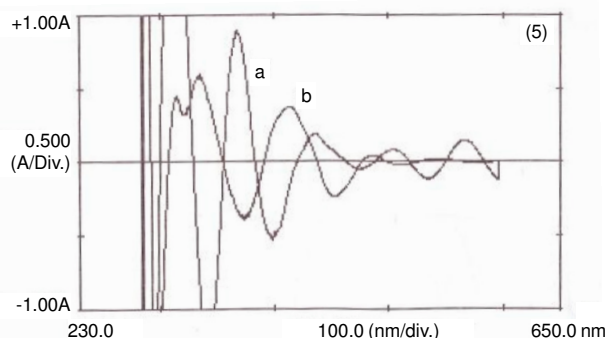


Fig. 7. Fourth derivative spectra of Ni-ADTT and Cu-ADTT complex [385 nm, zero crossing for Ni]

TABLE-1
FIRST, SECOND, THIRD AND FOURTH DERIVATIVE SPECTROPHOTOMETRIC DATA FOR DETERMINATION OF COPPER(II)-REAGENT AND NICKEL(II)-REAGENT

Method	Analyte ion	Wavelength (nm)
First-order $n = 9$ ($\Delta\lambda = 36$ nm)	Ni ²⁺	447.0
Second-order $n = 7$ ($\Delta\lambda = 24.5$ nm)	Cu ²⁺	387.5
Third-order $n = 9$ ($\Delta\lambda = 31.5$ nm)	Ni ²⁺	400.0
Third-order $n = 7$ ($\Delta\lambda = 24.5$ nm)	Cu ²⁺	554.0
Fourth-order $n = 9$ ($\Delta\lambda = 27$ nm)	Ni ²⁺	385.5

Linearity: According to the data from derivative spectra, synthetic mixtures of Cu²⁺ in the range of 5-35 $\mu\text{g/mL}$ in the presence of Ni²⁺ (5 $\mu\text{g/mL}$) and Ni²⁺ in the range of 5-35 $\mu\text{g/mL}$ in the presence of Cu²⁺ (5 $\mu\text{g/mL}$) were prepared and the measured amplitude at selected wavelengths in derivative spectra were constructed *versus* the concentration of each

TABLE-2
STATISTICAL DATA OF CALIBRATION CURVES OF NICKEL(II)-REAGENT IN THE PRESENCE OF COPPER(II) (5 µg/mL)

Parameters	First-order (447 nm)	Third-order (400 nm)	Fourth-order (385.5 nm)
Linearity range	5-35 µg/mL	5-35 µg/mL	5-35 µg/mL
Regression equation	$Y = 0.00627x - 0.01608$	$Y = 0.0137x - 0.0236$	$Y = -0.0055x - 0.00895$
SD of slope	1.03×10^{-4}	1.67×10^{-4}	1.79×10^{-4}
RSD of slope (%)	1.65	1.22	-3.25
SD of intercept	4.9×10^{-3}	9.2×10^{-3}	7.8×10^{-3}
Correlation coefficient (r^2)	0.9994	0.9993	0.9994

cation. Six calibration series were constructed and the statistical values calculated are shown in Tables 2 and 3. Beer's law is validated by the high value of the observed correlation coefficients. The limit of quantification of nickel(II) or copper(II) in all conditions with CV < 4.73 % was found to be 5 µg/mL. The detection limits were 0.30 µg/mL for nickel and 1.40 µg/mL for copper.

mixtures of copper(II) in the presence of nickel(II) and nickel in the presence of copper(II). The concentration of metal ions was determined using the measured amplitude of each derivative spectra and the suitable calibration curve. The results are illustrated in Tables 4 and 5.

Conclusion

This paper proposed a new reagent for the simultaneous determination of copper and nickel by different orders of derivative spectrophotometry. The measurements have been done in third and fourth-order were more accurate with lower CV % and error. The present method is simple and selective for the simultaneous determination of copper and nickel.

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Accuracy and precision: The accuracy and precision of the method were determined by using three sets of synthetic

TABLE-4
ACCURACY AND PRECISION DATA FOR DETERMINATION OF COPPER(II) IN THE PRESENCE OF NICKEL(II) (5 µg/mL)

Added (µg/mL)	Second order (387.5 nm)			Third order (554.0 nm)		
	Found (µg/mL)	CV (%)	Error (%)	Found (µg/mL)	CV (%)	Error (%)
Within-day (n = 3)						
5.00	4.97 ± 0.15	3.05	0.66	4.83 ± 0.09	1.81	-3.29
15.00	15.18 ± 0.11	0.72	1.21	15.32 ± 0.05	0.32	2.14
35.00	35.00 ± 0.02	0.06	0.001	35.04 ± 0.06	0.17	0.12
Between day (n = 9)						
5.00	4.89 ± 0.23	4.73	-2.25	4.80 ± 0.17	3.61	-4.03
15.00	15.21 ± 0.17	1.08	1.41	15.18 ± 0.15	0.98	1.22
35.00	34.96 ± 0.19	0.56	-0.12	34.99 ± 0.35	1.00	-0.03

TABLE-5
ACCURACY AND PRECISION DATA FOR DETERMINATION OF NICKEL(II) IN THE PRESENCE OF COPPER(II) (5 µg/mL)

Added (µg/mL)	Within-day (n = 3)			Between-day (n = 9)		
	Found (µg/mL)	CV (%)	Error (%)	Found (µg/mL)	CV (%)	Error (%)
First order						
5.00	5.12 ± 0.17	3.36	2.57	5.11 ± 0.18	3.47	2.14
15.00	15.23 ± 0.26	1.73	1.56	15.10 ± 0.36	2.36	0.64
35.00	35.35 ± 0.36	1.02	1.00	35.22 ± 0.25	0.72	0.62
Third order						
5.00	5.15 ± 0.12	2.31	2.98	5.08 ± 0.11	2.20	1.67
15.00	15.25 ± 0.19	1.24	1.66	15.21 ± 0.21	1.35	1.44
35.00	34.78 ± 0.02	0.06	0.64	34.87 ± 0.16	0.46	0.38
Fourth order						
5.00	4.97 ± 0.07	1.38	-0.49	9.94 ± 0.18	306	1.18
15.00	15.32 ± 0.26	1.72	2.13	15.16 ± 0.19	1.26	1.07
35.00	34.98 ± 0.12	0.35	0.05	34.92 ± 0.33	0.96	0.23

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