

A NEW SPECTROPHOTOMETRIC PROCEDURE FOR THE DETERMINATION OF NICKEL (II) USING 6-PHENYL-2, 3-DIHYDRO-AS-TRIAZINE- 3-THIONE

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Abstract

A spectrophotometric procedure for the determination of Nickel (II) based on the complex formation with 6-phenyl-2, 3-dihydro-as-triazine-3-thione (PDTT) was developed. A yellow compound forms and is easily extractable by chloroform at $\text{pH} > 6$. The mole ratio between Nickel (II) and PDTT is 1:4. The absorbance of the complex obeys Beer's law over the concentration range of 1-7 μg of Ni (II) per ml chloroform. This procedure can be carried out in the presence of many cations and anions without appreciable interference.

Introduction

Many spectrophotometric procedures based on complex formation with organic dyes have been reported for determination of Ni (II) [1-5].

6-Phenyl-2, 3-dihydro-as-triazine-3-thione (PDTT) forms a yellow complex with Ni (II) which is easily extractable by chloroform over a wide range of pH [6-14]. PDTT is prepared as prescribed by Lalezari and Golgolab [6]. This reagent was used by Edrissi, Massomi and Lalezari [7] for the gravimetric determination of palladium and thallium, and was also employed by Maghssoudi and Shamsa [8] for the spectrophotometric determination of Hg (II), and by Maghssoudi and Fawzi [9] for the spectrophotometric determination of Cu (II).

The purpose of this investigation is to study the Ni (II)-PDTT complex and establish another spectrophotometric procedure for the determination of Ni (II).

Experimental Section

Apparatus. A Bausch and Lomb model Spectronic 20

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with 1 cm glass cells was used for all absorbance measurements.

Reagents and Chemicals. A 4N sodium hydroxide solution, 2N tataric acid solution, and 0.002M solution of PDTT in 4N NaOH were used. The 0.002M solution of PDTT in NaOH should be freshly prepared before use.

Nickel sulfate solution. A 0.01M nickel sulfate solution was prepared. Solutions with lower concentrations were prepared by proper dilution.

Solutions of Diverse Ions. 1% solutions were prepared by dissolving measured amounts of salts of the corresponding ion in distilled water. In some cases, diluted acids were added to prevent hydrolysis.

General Procedure. In a 100 ml separatory funnel, 10-70 μg Ni (II), 5ml PDTT solution 0.002M, 2ml tataric acid 2M were transferred. The mixture was shaken thoroughly and the formed complex was extracted by 5,3 and 2ml chloroform. The extracts were collected in a 10ml volumetric flask and brought to volume with chloroform. The absorbance of the extracts was measured at 410 nm versus chloroform.

Results and Discussion

Absorption Curves. Absorption curves with different concentrations of Ni(II)-PDTT complex (corresponding to Ni(II) of 2.5, 3.5, 4.5 ug per ml chloroform) and PDTT alone in chloroform are shown in Fig.1. The absorption measurements were made in the wavelength range of 250-600 nm. The complex in chloroform showed maximum absorptions at 410 and 270 nm where PDTT alone in chloroform showed at 350 and 260 nm. All spectrophotometric measurements were made at 410 nm, since the absorption of PDTT at this wavelength was negligible. The molar absorptivity of the complex was 8.3×10^3 when the absorbance was 0.71 and Ni(II) concentration was 50 ug/10ml chloroform.

Effect of pH. The pH of the aqueous layer was changed from 1 to 14. The results showed complete

extraction at $\text{pH} > 6$.

Stability of Color. The Ni(II)-PDTT complex was very stable and began to fade slowly after 5 days. The complex was also stable toward buffers with pH 6 or more. However, buffers with pH less than 6 broke the complex.

Conformity to Beer's law. The absorbance of Ni(II)-PDTT complex at different concentrations of Ni(II) was plotted versus the concentrations of Ni(II). The complex follows Beer's law at 410 nm over the concentration range of 1-7 $\mu\text{g Ni}^{2+}$ /ml chloroform (Fig 2).

Nature of the complex. The composition of the complex was determined by the continuous variation method [10] as follows: The total molar concentration of the mixture ($\text{Ni}^{2+} + \text{PDTT}$) was kept constant at three different concentrations, 1, 0.75 and 0.4 mM. The

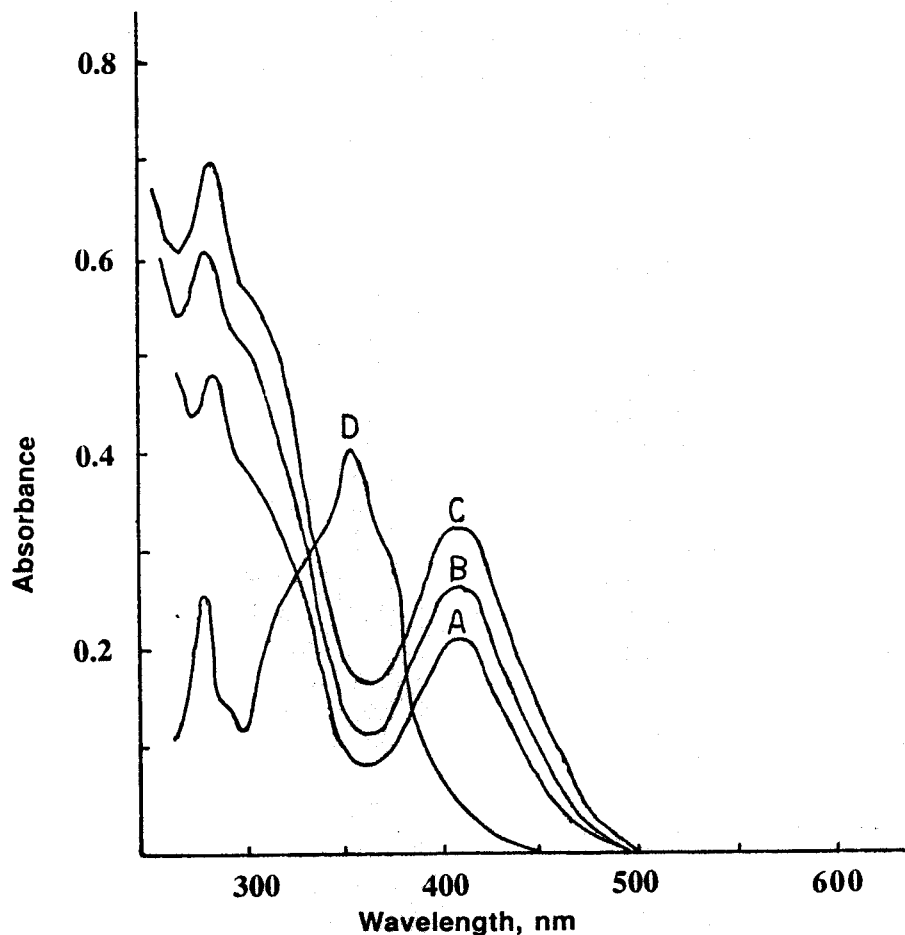


Figure 1. Absorption curves of Ni(II)-PDTT complex in Chloroform
(A) 2.5 ug / ml chloroform (B) 3.5 ug / ml chloroform
(C) 4.5 ug / ml chloroform of Ni(II)

method was completed by following the general procedure. Spectrophotometric measurements were carried out at 410 nm and the absorbances of the solutions were drawn versus the mole fraction of Ni²⁺

The maxima occur at 0.2 mole fraction of Ni²⁺ indicating a 1:4 ratio of Ni²⁺ to PDDT in the complex (Fig 3).

Determination of the optimum amount of reagent.

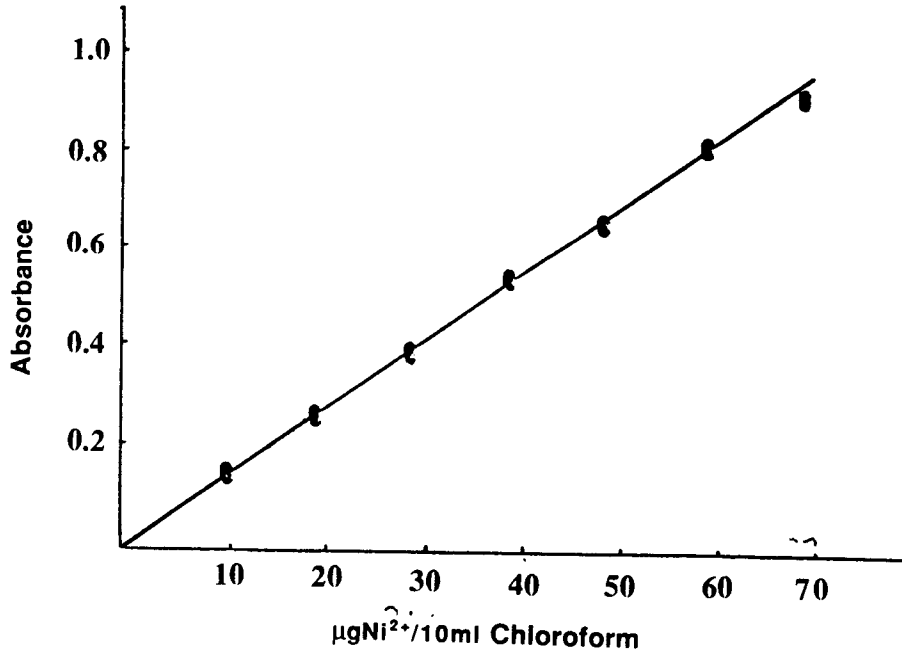


Figure 2. Calibration curve of Ni(II) -PDDT complex at 410 nm

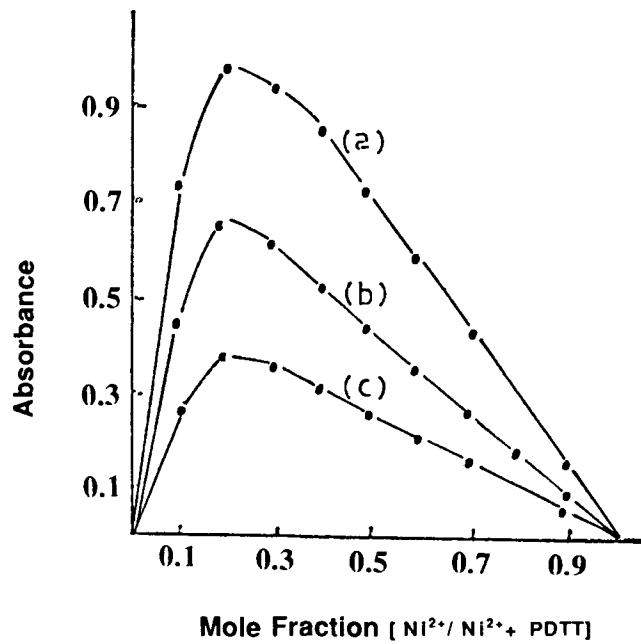


Figure 3. Composition of Ni(II) -PDDT complex by continuous variation method (a) 1.0 mM of Ni (II) (b) 0.75 mM of Ni (II) (c) 0.4 mM Ni(II)

For this purpose the mole ratio method was employed [11]. The concentration of Ni^{2+} was kept constant at 0.001 M, while the PDTT concentration was varied between 0.001 M and 0.015 M. Spectrophotometric measurements were carried out as mentioned in the general procedure. The absorbance was plotted against the mole ratio of the reagent to metal. A continuous increasing in absorbance occurs as the concentration of PDTT increases up to the ratio 5 to 1 of PDTT to Ni^{2+} . After the PDTT concentration was increased, the absorbance of the complex did not change, therefore a little more than this ratio was used in all determinations of Ni^{2+} .

Effect of Diverse Ions. To determine the effect of diverse ions, a standard nickel sulfate solution containing 60 μg Ni^{2+} and the ion in question were placed in a separatory funnel, to which an excess of the reagent solution was added. The method was completed as mentioned under the general procedure. The following ions in the form of the salts indicated were studied:

1. Fe^{2+} ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)
2. Mg^{2+} ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$)
3. Co^{2+} ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
4. Bi^{3+} (BiCl_3)
5. Ag^+ (AgNO_3)
6. Hg^{2+} (HgCl_2)
7. Cu^{2+} ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)
8. Mn^{2+} ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$)
9. Zn^{2+} (ZnCl_2)
10. Sb^{3+} (SbCl_3)
11. Cr^{3+} ($\text{Cr}_2(\text{SO}_4)_3$)
12. Sn^{2+} ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$)
13. Na^+ (NaCl)
14. F^- (NaF)
15. Br^- (NaBr)
16. CH_3COO^- (CH_3COONa)
17. I^- (NaI)
18. CN^- (NaCN)
19. NO_3^- (NaNO_3)
20. SO_4^{2-} (Na_2SO_4)
21. $\text{S}_2\text{O}_3^{2-}$ ($\text{Na}_2\text{S}_2\text{O}_3$)
22. $\text{Cr}_2\text{O}_7^{2-}$ ($\text{K}_2\text{Cr}_2\text{O}_7$)
23. K^+ (KCl)
24. Li^+ (LiNO_3)
25. NH_4^+ (NH_4Cl)
26. UO_2^+ ($(\text{CH}_3\text{COO})_2\text{UO}_2 \cdot 2\text{H}_2\text{O}$)
27. Hg^{1+} [$\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$]
28. Ti^{1+} [CH_3COOTi]

The following three groups are tolerated by $>10^5 \mu\text{g}$ Na^+ , K^+ , Li^+ , NH_4^+ , UO_2^{2+} , $\text{Cr}_2\text{O}_7^{2-}$, SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, F^- , Cl^- , Br^-

and I^- . These ions do not interfere with the formation and extraction of $\text{Ni}(\text{II})$ -PDTT complex, because they do not produce interfering products with PDTT, NaOH or tartaric acid.

Fe^{2+} , Ba^{2+} , Mg^{2+} , Ca^{2+} , Cd^{2+} and Sr^{2+} do not give complexes with PDTT. However, they precipitate by NaOH, and the formed precipitates have physical interference. This precipitation can 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.

The following ions are tolerated by the indicated amounts:

- Fe^{2+} (5 mg), Bi^{3+} (10 mg), Sb^{3+} (10 mg), Hg^+ (1 mg), Sn^{2+} (10 mg), Mn^{2+} (30 mg), Cr^{2+} (10 mg), Zn^{2+} (20 mg) (20 mg Zn^{2+} is tolerated after washing the extracts with dilute NaOH solution), Ag^+ (100 μg), Co^{2+} (100 μg), Ti^{2+} (100 μg), Cu^{2+} (100 μg), and CN^- (20 μg).

Silver and cobalt form products with NaOH solution which interfere with the formation and extraction of the $\text{Ni}(\text{II})$ -PDTT complex.

Thallium, copper and mercury form complexes with PDTT which have an absorption -at 410 nm. The interference of silver could be eliminated by using a suitable masking agent. It was observed that $\text{Ni}(\text{II})$ can be analyzed in the presence of high concentrations of iodide. Since iodide can mask silver without affecting nickel in the face of NaOH, therefore it was possible to analyze successfully nickel in the presence of silver without prior separation of the latter. A concentrated solution of potassium iodide was used as a masking agent. For eliminating the cobalt interference, a chloroform solution of PDTT was used to extract the Ni^{2+} content. The extract was washed with diluted NaOH solution to remove the excess of PDTT. To analyze Ni^{2+} in the presence of Hg^{2+} , no suitable masking agent was found. However, it seems possible to follow the analysis by masking Ni^{2+} itself by CN^- and following the general procedure [8]. The difference in absorbance before and after the addition of CN^- will correspond to the amount of Ni^{2+} present.

Precision and Accuracy. A set of six identical samples, each with a final Ni^{2+} content of 30 μg were treated according to the recommended procedure, and their absorbances were measured. This was repeated with a final Ni^{2+} content of 70 μg for another set of six samples.

The accuracy varied from 99.2% at 30 ug to 99.7% at 70 ug. The percentage of the relative standard deviation varied from 0.75% at 30 ug to 0.42% at 70 ug of Ni²⁺

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