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Research Article

ANALYTICAL APPLICATIONS OF 3-ACETYLPYRIDINE THIOSEMICARBAZONE (3-APT): SIMPLE AND SENSITIVE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL (II) IN SOIL AND ALLOY SAMPLES

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ABSTRACT

Nickel (II) reacts with 3-acetylpyridine thiosemicarbazone (3-APT) and forms an yellow colored complex with sodium acetate and acetic acid buffer at pH 6.0. The absorbance value of the Ni (II)–3-APT complex was measured at different intervals of time at 430 nm, to ascertain the time stability of the complex. The complex was instantaneous and stable for more than 5h. The system obeyed Beer's law in the concentration range of 0.35-3.53 µg/ml of nickel (II), with an excellent linearity and a correlation coefficient of 0.999. The molar absorptivity and Sandell's sensitivity of the complex species were found to be 1.6×10^4 L mol^{-1} cm^{-1} and 3.6×10^{-3} $\mu g/cm^2$ at 430 nm, respectively. Hence, a detailed study of the of nickel (II) with 3-APT has been undertaken with a view to develop a rapid simple and sensitive spectrophotometric method for the determination of nickel (II) when present alone or in the presence of diverse ions which are usually associated with nickel (II) in soil and various standard alloy samples have been tested for the determination of nickel for the purpose of validation of the present method.

Key Words: *Nickel (II), 3-acetylpyridine Thiosemicarbazone, UV-VIS Spectrophotometry, Dithiozone Method*

INTRODUCTION

Nickel is present in small amounts in soil, plant and animal tissues. The main source of nickel comes from the hydrogenation of oils, iron factories, from the combustion of coal, diesel and residual oils, tobacco smoke, chemicals and catalysts (Sharma, 1997). It is used in nickel plating and also in the manufacture of alloys along with iron, copper, aluminum, chromium, zinc and molybdenum. Nickel containing steels are highly resistant to corrosion. Because of its high melting point (1453°C), nickel is also used in the production of heat-resistant steels and cast iron. Nickel-plated steels are used in the manufacture of some food processing vessels and many other pieces of equipment. The interest in the determination of nickel has grown considerably in recent years, owing to its involvement in some essential metabolic processes (Judith *et al.,* 1998). Nickel is relatively non-toxic and does not cause any serious human health hazard, despite the fact that acid foods take up nickel during cooking. The nickel deposited in the human body from nickel vessels is not readily absorbed and causes no detectable hazard. However, a high incidence of respiratory tract neoplasia among workers in nickel refineries and carcinogenic properties of this metal have been reported (Sharma, 1997). Thioemicarbazones consider as a promising analytical reagents owing to their ability to form intense colored complexes with various metal ions (Reddy *et al.,* 1985; Garg and Jain, 1988; Singh and Ishi, 1991). They are widely employed in spectrophotometric and extractive spectrophotometric analysis, atomic absorption spectrometry and solid–liquid separation. The nickel (II)–thiosemicarbazone complexes have intense colors and high molar absorptivities when compared with the analogous thiosemicarbazone complexes. A literature survey indicated that only a few thiosemicarbazones (Salinas *et al.,* 1986, Asuero 1983; Reddy *et al.,* 1984; Sigh *et al.,* 1982; Jadhav and Kulkarni, 1992; Desai and Desai, 1996; Cristofol *et al.,* 1991; Kumar *et al.,* 1997; Attah, 2009; Patel *et al.,* 2010) have been explored for the extractive spectrophotometric determination of nickel (II) and 3-acetylpyridine thiosemicarbazone (3-APT) has so far not been used as an analytical reagent for the determination of nickel (II). In the present work, 3-APT has been examined in order to evaluate its usefulness as a spectrophotometric reagent for nickel (II). Further, the potentially of this method has been tested successfully by analyzing nickel (II) present in soil and standard alloy samples. For the determination of nickel at micro levels there are several frequently adopted methods using analytical techniques such as AAS, ICP–OES, ICP–AES, ICP–MS, X-ray fluorescence spectroscopy, spectrophotometry, spectrofluorometry and other such techniques. Among these, the spectrophotometric methods are preferred as they are cheaper and easier to handle and have comparable sensitivity.

MATERIALS AND METHODS

Experimental

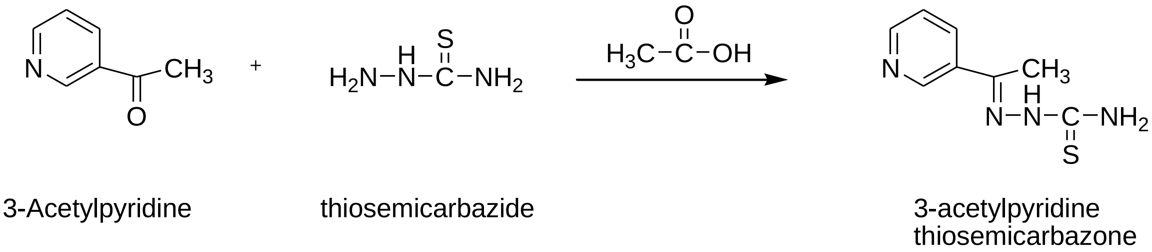
Instrumentation

A Perkin-Elmer lambda 25 UV–VIS spectrophotometer with a 1.0 cm quartz cell was used for absorbance studies. An Elico LI-120 digital pH meter was used for pH adjustment. A Perkin–Elmer 2380 atomic absorption spectrometer was used for the comparison of results.

Reagents and Samples

3-acetylpyridine (0.050mol) was dissolved in 5.0 ml of ethanol and mixed in a flask containing thiosemicarbazide (0.050mol) dissolved in 10.0 ml of a hot water and the reaction mixture was added 2 to 3 ml of acetic acid. The resulting reaction mixture was refluxed on a water bath for 30 min. It was allowed to stand at room temperature until pale yellow crystals were formed (Kumar et al. 2007). These were separated and recrystallized from ethanol (Scheme 1).

The molecular formula and molecular weight of 3-APT are $C_8H_{10}N_4S$ and 194gm respectively. The compound was characterized by IR and ^{1}H-NMR spectral data. Infra red spectrum of 3-APT shows bands at 3450(s), 3288(s), 3239(s), 3043(m), 1577(s), 1537(s), 1497(s), 1364(w), 1147(m), 832(s) and 681(s)cm^{-1} corresponding to ν(N–H) (asymmetric and symmetric), ν(C–H) aromatic stretch, ν(C=N)stretching(Schiff base), ν(C–H) aromatic ring, ν(C–H)of pyridine ring, ν(N–H) stretch(primary amide), ν(C=S), ν(C–H)-oop bend (aromatic) and ν(C–C)-oop bend aromatic ring vibrations. ^{1}H-NMRspectrum of 3-APT ($CDCl_3$+DMSO–d_6) showed signals at 2.63 (3H, s) –CH_3, 8.16 (1H, s) due to pyridine, 8.22 (3H, m), C(s)-NH_2, 8.64 (1H, s), =N-NH and 12.01 (1H, s) corresponds to H-C=N group attached to carbon atom of thiosemicarbazone.



Scheme 1: Preparation of 3-acetylpyridine thiosemicarbazone (3-APT)

Preparation of Standard Solution of Nickel (II)

A total of 6.73 g of $(NH_4)_2Ni(SO4)_26H_2O)$ [ammonium nickel sulfate hexahydrate] was weighed, dissolved in double-distilled water containing a few drops of concentrated sulfuric acid and made up to one liter. The stock solution was then standardized gravimetrically using dimethylglyoxime (Vogel, 1061). The required dilute solutions of nickel (II) were prepared by diluting the stock solution with double-distilled water. All reagents used were of analytical reagent grade unless otherwise stated.

Buffer Solutions

1.0 M Hydrochloric acid and 1M sodium acetate (pH 0.5-3.0), 0.2 M of NaOAc and 0.2 M AcOH (pH 4.0-7.0) and 2.0 M NH_4Cl - 2.0 M NH_4OH (7.0-10.0) buffer solutions were prepared in distilled water. Suitable portions of these solutions are mixed to get the desired pH.

Analytical Procedure for Soil Samples

The samples of soil were dried in open air to prevent them from mineral concentration. The dried sample was pulverized to a convenient size in a mortar for the purpose of analysis. Ten grams of the powdered soil, 10 ml nitric acid and 1ml of sulphuric acid were transferred into a 100 ml standard flask. A pre-cleaned glass funnel was inserted and heated on a hot plate at approximately 290°C until nitrogen oxide fumes just give off. The digestion was repeated with three heating steps after the final addition of nitric acid until the nitrogen oxide fumes and the sulphite have disappeared. The flask was cooled for about 2min and the funnel was rinsed with a small volume of deionized double-distilled water in the flask and the contents were transferred into a 25mL calibrated flask and made up to the mark with deionized double-distilled water. The concentration of nickel was determined by the general procedure described.

Analytical Procedure for Standard Alloy Samples

A total of 0.1 g of each oven-dried (110°C) alloy sample was dissolved in 15 ml of aquaregia. The solution was heated to near dryness and nitrate was expelled from the residue, using 5ml of concentrated hydrochloric acid. Each residue was extracted into double-distilled water, separately, and made up to 100 ml.

General Procedure

To an aliquot of a working standard solution containing 0.1–10 µg ml^{-1} nickel(II) in 25.0 ml volumetric flasks were added pH 6.0 buffer (10.0 ml), 1 × 10^{-2}M reagent solution (1 ml) and make up to the mark with double distilled water. The absorbance's of all the solutions were measured at 430nm against the reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra of The Reagent and Ni(II)–3-APT Complex

An aliquot of solution contains 10.0 ml of buffer solution (pH=6.0), 1.0 ml of 1 × 10^{-3}M nickel(II) solution and 1.0 ml of 1×10^{-2} M 3-APT solutions were added. The absorption spectrum of the reagent solution against the solvent blank, and the absorption spectrum of the solution containing nickel (II) complex against the reagent blank is given in (Figure 1). From the spectra, it is clear that the Ni (II)–3-APT complex and the reagent have maximum absorbance at 430 and 390 nm, respectively. The reagent has a minimum absorbance at the maximum absorbance of the complex and does not interfere in the determination of nickel (II). Hence, further absorbance measurements of the complex were carried out at 430 nm.

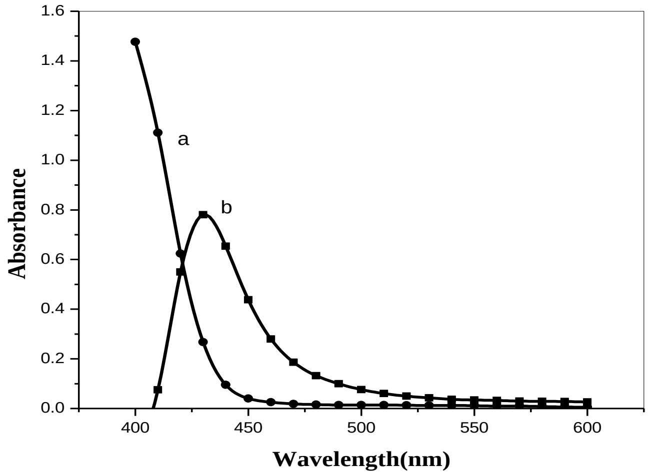


Figure 1: Absorption Spectra of a. 3-APT Vs Water blank, b. Ni(II) –3-APT Vs 3-APT, Ni(II): 1.0 ml of 1 ×10^{-3} M, 3-APT: 1.0 ml of 1 ×10^{-2} M, pH:6.0, λmax 430 nm.

Effect of pH on The Extraction of Ni (II)–3-APT complex

A preliminary study showed that the formation of Ni (II)–3-APT complex was affected by the hydrogen ion concentration. The optimum pH range for the absorbance was determined by using buffers such as sodium acetate–hydrochloric acid (pH 1.0–3.5), sodium acetate–acetic acid (pH 3.6–6.9) and ammonium chloride–ammonium hydroxide (pH 7.0–11.0). In each case, a mixture containing 10.0 ml of buffer solution (pH=6.0), 1.0 ml of 1×10^{-3}M nickel(II) solution and 1.0 ml of 1×10^{-2} M 3-APT solutions were added and the solutions are made up to the mark with double distilled water for 25.0 ml volumetric flask. The absorbance's of all the solutions was measured at 430 nm using their respective reagent blanks. This indicates that the complex shows constant and maximum absorbance in the pH range 5.0—7.0 we have used buffer having pH 6.0 in subsequent studies.

Effect of Reagent Concentration on the Absorbance of Ni (II)–3APT complex

The effect of reagent concentration on the formation of the Ni(II)–3-APT complex was studied using 10.0 ml of buffer solution (pH=6.0), 1.0 ml of 1×10^{-3}M nickel(II) solution and 1.0 ml of 1×10^{-2} M 3-APT solutions were added and make up to the mark with double distilled water for 25.0 ml volumetric flasks. The absorbances of these solutions were measured at 430nm, against their corresponding reagent blanks. This study has revealed that a ten-fold molar excess of the 3-APT to that of nickel is necessary for maximum complex development of the metal ion. Hence, a tenfold molar excess of the reagent was maintained for maximum complex of nickel (II).

Time Stability of the Color Reaction

The absorbance value of the Ni (II)–3-APT complex was measured at different intervals of time at 430 nm to ascertain the time stability of the color of the complex. It was observed that the color remained constant for more than 5 h. Physico-chemical and analytical properties of nickel (II) complex of 3-APT are summarized in Table 1.

Table 1: Physico – Chemical and Analytical characteristics of Ni-(3-APT)$_2$ complex

Characteristics	**Results**
λ_{max} (nm)	430
pH - range (optimum)	5.0-7.0
Mean absorbance	0.549 ± 0.0013
Mole of reagent required per mole of metal ion for full color developed	10
Time stability of the complex (in hrs)	5
Beer's law validity range (µg/ml)	0.35-3.53
Molar absorptivity (L mol^{-1} cm^{-1})	1.6×10^4
Specific absorptivity (ml g^{-1} cm^{-1})	0.284
Sandell's sensitivity (µg/cm^2)	0.0036
Composition of complex as obtained Jobs and molar ratio methods (M:L)	1 : 2
Stability constant of the complex	1.74×10^{11}
Standard deviation in the determination of 1.174 µg/ml of Ni (II) for ten determinations	0.0038
Relative standard deviation (RSD)%	1.7
Y intercept	-0.010
Angular coefficient (m)	0.273
Correlation coefficient (ν)	0.999
Diction limit	0.021
Determination limit	0.061

Applicability of Beer's law to the Ni(II)–3-APT complex

Known aliquots of 25.0 ml solutions containing constant volumes of 10.0 ml of buffer solution (pH=6.0), 1.0 ml of 1×10^{-2} M 3-APT and varying amounts of nickel(II) ranging from 0.1–10.0 µg ml^{-1} were prepared. The absorbance's of all the solutions were measured at 430nm, against their corresponding reagent blanks. From the experimental data, it was found that the complex system obeys Beer's law in the concentration range 0.35 – 3.53µg ml^{-1} of nickel (II). The straight line obeys the equation $A_{430} = 0.2724\ C - 0.0101$. The molar absorptivity and Sandell's sensitivity of the method are 1.6×10^4 L mol^{-1} cm^{-1} and 3.6×10^{-3} µg cm^{-2} of Ni (II) respectively. The specific absorptivity of the system is found to be 0.284 ml g^{-1} cm^{-1}. The standard deviation in the determination of 2.12 µg ml^{-1} of Ni (II) is 0.003 for ten determinations. The relative standard deviation and the mean absorbance are 0.64 percent and 0.572 ± 0.0013 respectively.

Determination of the Composition of Ni (II)–3-APT complex

The composition of the Ni (II) complex with 3-APT was studied using Job's method of continuous variation, and the mole ratio method. Spectrophotometric investigation of the metal complex was conducted to obtain the composition of the complex. The composition of the complex was established by Job's method of continuous variation.

Equimolar solutions of nickel (II) and 3-APT ($2\text{x}10^{-4}$ M) were prepared. The metal and reagent solutions were mixed in different proportions, keeping the total volume constant at 10.0 ml. To each solution, 10.0 ml of buffer (pH 6.0) and the metal and reagent solutions were mixed in different proportions, keeping the total volume constant at 10.0 ml solution. The solutions make up to the mark with double distilled water. The absorbance values of the solutions were recorded at 430 nm, against their respective reagent blanks. From the above experimental results, it is evident that one mole of nickel (II) reacts with two moles of 3-APT, showing the composition of the complex to be 1:2. This composition was verified using the molar ratio method. From jobs continuous variation method the stability constant of the complex was found to be $1.74\ \text{x}\ 10^{11}$.

Effect of Foreign Ions on the Extraction of Ni (II)–3-APT complex

Known amounts of various cations and anions were added to a fixed amount of nickel(II) in order to study the effect of interference of these ions on the extraction and determination of nickel(II), using the analytical procedure described in the Experimental section. An error of 72% in the absorbance reading was considered to be tolerable.

Cations like aluminum(III), uranium(VI), indium(III) and iron(II) do not interfere, even when present up to 4000 µg. Manganese(II), tungsten(VI), barium(II) and magnesium(1I) do not have any effect up to 2500 µg, whereas zinc(II), lead(II), selenium(IV), cerium(IV), copper(II) and palladium(II) interfere seriously with the extraction of nickel(II). Anions like fluoride, chloride, bromide, tartrate, thiosulphate and oxalate do not interfere when present up to 4000 µg or more. Thiocynate, thiourea and phosphate interfere seriously, whereas EDTA masks nickel (II) completely due to the higher stability of the Ni(II)–EDTA complex. Sulfate, acetate and citrate do not interfere when present up to 2000 µg. The interference of zinc(II), lead(II) selenium(IV), cerium(IV), copper(II), cadmium(II) and palladium(II) can be eliminated by using 1.0 ml of 0.5% thiosulphate solution.

The present method when compared with other existing spectrophotometric methods was found to be more sensitive and selective. It also offers advantages like reliability and reproducibility in addition to its simplicity, instant color development and low interference. 3-APT is cheap, stable at high temperatures, and easy to dispense and store. The reagent 3-APT was more stable when complexed with Ni (II) and the color of the complex was stable for more than 5h. 3-APT reacts nickel selectively when associated with the following metal ions: Al (III), U(VI), In(III), Fe(II), Mn(II), W(VI), Ba(II), Mg(1I), fluoride, chloride, bromide, tartrate, thiosulphate and oxalate. 3-APT is a stable reagent for the determination of nickel (II).

Applications of the developed method

The developed extractive spectrophotometric method for nickel (II) has been successfully applied for its determination in Soil and standard alloy samples.

Determination of nickel (II) in soil samples

Soil samples were collected from around Kadapa, Andhra Pradesh, India. Each aliquot was analyzed for nickel (II) by the general procedure which was given in the experimental section. Nickel (II) present in soil samples was determined from the calibrated plot (Beer's law plot) using 3-APT it was shown in Table 2.

Table 2: Determination of nickel (II) in soil samples

Sample	Amount of Ni(II)[a] found μg/g Present method	SD	%RSD
Kadapa	21.8	0.2005	0.92
Mangampet	23.6	0.2336	0.99
Proddatur	20.1	0.1969	0.98
Yerraguntla	18.6	0.1674	0.90
Mydukur	19.8	0.1742	0.88

[a] *Average of three determinations*

Table 3: Determination of Nickel (II) in standard alloys

Sample	Composition	Amount of Nickel [a] in μg/ ml		% of Recovery
		Certified	Found	
BAS – 106	Ni 1.93, Cu 4.1; Fe 0.43; Mn 0.2; Mg 1.61.	0.939	0.936	99.68
NTPC Alloy	Ni 10; Cr 15; Fe 6.5; Cu 4.5; Mn 2.1.	0.939	0.938	99.89
Nickel base super alloy (CM 247 LC)	Ni, 61.91;Cr,8.1; Mo,0.5;Al,5.6;Ta, 3.2; Zr,0.015;C,0.06; Co, 9.0;W, 9.5; Ti,0.7; Hf, 1.4; B, 0.025	61.90	61.88	99.96
Nickel base super alloy (IN 718	Ni, 54.9;Cr,18;Mo, 3; Fe, 19; Co, 5.1	54.88	54.86	99.96
Alloy steel (BCS 233	Ni, 11.22; Co, 23.4; Sn, 7.95; Mn,0.235; Cu,5.09	11.20	11.18	99.82
Alloy steel (BCS 266)	Ni, 1.33; Al,7.95; Co, 23.4; Cu, 3.33	13.28	13.26	99.84
Low alloy steel (BCS 253)	Ni, 2.92;Mo,0.94; Cr, 0.34;V,0.220; Cu, 0.495	2.90	2.85	98.27
Low alloy steel (BCS 251)	Ni, 5.15;Mo,0.185; Mn, 0.165; Co, 0.007; Cu, 0.090	5.13	5.12	99.8

[a] *Average of three determinations*

Determination of nickel (II) in Standard Alloy Samples

The present method was also applied for the determination of nickel(II) content in standard alloy samples such as nickel base super alloys (CM 247 LC and IN 718), alloy steels (BCS 233 and 266) and low alloy steels (BCS 253 and 251). An appropriate aliquot of each solution was analyzed for nickel (II) employing the recommended procedure given in Materials and methods, using 3-APT and the results was shown in Table 3.

Conclusion

Few thiosemicarbazones are used in the extractive spectrophotometric determination of nickel (II). In the present investigation, the authors introduced a new reagent, 3-acetylpyridine thiosemicarbazone (3-APT) to the field of spectrophotometric determination of nickel (II). The reagent was found to be sensitive when compared to earlier reported reagents. The selectivity of the reagent was further improved by the use of proper masking agents to suppress the interference of diverse metal ions. The results from the present developed method clearly demonstrate the usefulness of 3-APT as an extracting agent for the determination of nickel (II) in soil and standard alloy samples.

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