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"A Comparative Study on Physio-Chemical and Analytical Properties of Nickel (II) Complexes with 2-Acetylpyridine thiosemicarbazone (APT) and 2- Acetylpyridine semicarbazone (APS)"

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Abstract. *For comparative study of Nickel (II) complexes derived from 2-Acetylpyridine thiosemicarbazone (APT) and 2-Acetylpyridine semicarbazone (APS) spectrophotometric approach has been created. The complexes have been prepared and characterized on the basis of spectrophotometric determination. Nickel (II) with 2-Acetylpyridine thiosemicarbazone and 2-Acetylpyridine semicarbazone produce immediate colour reactions. For 60 minutes, the absorbance of both complexes stays constant. Spectrophotometric data of colour reaction between Nickel (II) with APT and APS are included for comparison. In both procedures, a 10-fold molar excess of reagent is adequate for complete colour development. The determination of nickel in alloy steels, vegetable oil, and water is effectively accomplished using this methodology.*

Keywords: *Nickel (II), Spectrophotometry, 2-Acetylpyridine thiosemicarbazone ,2-Acetylpyridine semicarbazone.*

1. INTRODUCTION:

The semicarbazone and thiosemicarbazone usually behave as chelating ligands and usually react with metallic cations giving complexes. Thiosemicarbazone are now well established as an important class of Sulphur donor ligands particularly for transition metal complexes. The metal nickel is crucial for both industrial and biological purposes. Together with cobalt, copper, zinc, and manganese, it is one of the crucial trace elements needed in the human diet [1-6]. Nutritional phenomena are directly influenced by nickel and cobalt. Ni, often known as nickel, is a crucial trace element that the human body needs in extremely minute levels to operate properly [7-8].

Among Ni's crucial functions in human physiology are the following:

- Enzymatic activities: Ni affects the activity of various enzymes in the body, such as urease, which aids in the urea breakdown process and is involved in amino acid metabolism.
- DNA synthesis: Ni contributes to the synthesis of DNA and is necessary for the preservation of DNA's structural integrity.
- Immune system: Ni is necessary for the immune system to operate correctly and is involved in the development of specific types of white blood cells that aid in the fight against infection.
- Bone Development: Ni is involved in calcium metabolism and may be important for supporting bone health [9-10].

It's important to note, however, that excessive amounts of Ni can be toxic and can lead to various health problems. Therefore, it's important to maintain a balanced intake of Ni through a healthy and varied diet [11-13].

Nickel is one of the important alloying elements for steel and cast iron. Literature survey indicated that several spectrophotometric methods were reported for the determination of nickel (II) by using various chromogenic reagents [14-15].

The current study describes, a easy, selective and sensitive direct spectrophotometric methods for the comparison and determination of trace amount of nickel (II) by complexing with 2-Acetylpyridine thiosemicarbazone (APT) and 2-Acetylpyridine semicarbazone.

2. EXPERIMENTAL WORK:

2.1 Preparation of Inorganic Salt Solutions

2.1.1 Nickel (II) solution

Stock solution of Ni (II) (1 x 10'2M) was prepared ($NiSO_4.7H_2O$) with double distilled water containing few drops of concentrated H_2SO_4 and made up to 100ml. The stock solution was standardized gravimetrically.

2.1.2 Preparation of Buffer Solutions

The conventional techniques described in the literature were used to create the buffer solutions. The following solutions were used to make buffers.

pH	Constituents
0.5-3.0	1M Sodium acetate + 0.1M hydrochloric acid
3.5 -6.0	0.2M Sodium acetate + 0.2M acetic acid
6.5 - 7.5	1M Sodium acetate + 0.2M acetic acid
8.0-12.0	2M Ammonia + 2M ammonium chloride

2.2 Details of Instruments Employed in the Present Investigations

2.2.1 UV-visible double beam recording spectrophotometer

The present investigation made use of a UV-160A double beam spectrophotometer. Shimadzu Corporation in Japan created it. The following are some of its most notable characteristics:

1. High-speed wavelength scanning is achieved by employing a CPU-controlled scanning device without the use of a sine bar.
2. All-in-one corporate spectrophotometer with CRT and printer.
3. Single-action operation is enabled by providing backup mode settings.
4. Ease of data processing because the received spectrum is available simply talking to CRO.

Table 1: Specifications of UV 160a Spectrophotometer

Measuring wavelength range	200-1100 nm
Spectral band width	2 nm
Wavelength readability	0.1 nm increment
Wavelength scanning speed	Monochromator setting speed is nearly - 3600 nm/min Fast nearly 2400 nm/min Medium nearly 1500 nm/min Slow nearly 480 nm/min
Wavelength accuracy	± 0.5 nm with automatic wavelength correction
Light source switching	Automatic wavelength change is possible between 295 and 364 nm.
Photometric system	Double beam system
Recording system	Printout of measured data and calculated results
Multicomponent	Samples from various sources are included. Mixed samples can be used as standards to determine up to eight different components. Up to sixteen (16) standards' worth of data can be kept in the backup memory.

Light sources	Halogen lamp, 50 W, 2000-hour life span, socket type, deuterium lamp, automated sensitivity control, monochromator, monochromator.
Mono chromator	Aberration - corrected concave halo graphic grating with / = 4.2
Detector	A matched pair of silicon photodiode
Recorder	Computer controlled thermal graphic printer
CRT	9-inch with graphic function 240 x 320.
Sample compartment	Inner size: 1100 nm wide
Distance between sample and reference beam	100 nm
Power requirements	With line voltage selector for 100
Weight	42 kgs

2.2.2 ELICO digital pH meter

The pH of buffer solutions is measured with an ELICO digital pH meter (Model LI 610), made by M/s ELICO private limited, Hyderabad, India. The devices are equipped with a system to automatically adjust for changes in temperature. The reproducibility of measurements is within ± 0.01 pH.

2.3 Instruments used in the characterization of ligands

2.3.1 Infrared spectrophotometer

Using a Perkin-Elmer 983G infrared double beam spectrophotometer, we measured the ligand's infrared spectra, which ranged from 400 to 4000 cm1. Anhydrous conditions were used to form a thin pellet from 10 mg of finely powdered material, which was then fully mixed with spectral grade KBr. IR spectrum of ligands were recorded using this device

2.3.2 Absorption spectra of reagent solutions and metal complexes

It was necessary to make up to the specified concentration of dimethyl formamide (DMF) in a 25-ml volumetric flask using an aliquot of reagent (typically 1 ml of 1 x 10'2M) solution, and this was done by adding distilled water to a 10 ml volumetric flask containing buffer solution. The reagent solution's absorbance was compared to a water blank. The absorbance versus wavelength relationship was shown using a graph.

In order to determine the absorption spectra of a complex (metal + reagent), the following approach was used. Metal complexes were produced in a 25 ml standard flask by adding 10 ml of buffer, acceptable amounts (1 ml or 2.5 ml) of DMF and the appropriate concentration of metal ions to the flask. It was decided to compare the absorbance of the complexes against a reagent blank that had been made identically. It was decided on the analytical wavelength based on an absorbance vs. wavelength plot.

2.3.3 Effect of time on the absorbance of reaction mixture and stability

There were 10 ml of buffer solution, metal ion and reagent and DMF added to a 25-ml calibrated flask, then the solution was diluted up to the mark with distilled water. The colour 56 complex solution's absorbance was compared to a reagent blank generated in the same way but over a longer period of time. This experiment established the stability of the compound and the time elapsed until the entire spectrum

2.3.4 Results and Discussion

Ni (II) - APT complex was investigated, and the optimal pH was determined using the method research, the complex's greatest absorbance occurs in the pH range of 4.0 to 7.0. As a result, pH 6 is used in following experiments. In pH range of 8.0 to 10.0, 2-acetylpyridine semicarbazone (APS) interacts with nickel (II) to produce a light-yellow tinted complex. The colour reaction was studied in order to create a spectrophotometric technique for measuring nickel (II) in an aqueous media.

2.3.5 Absorption spectra of APS, APT and its Nickel complex in aqueous solutions

Following the techniques outlined in the research, “the absorbance of the complex in solution was measured at pH 8.5 against a reagent blank in the wavelength range of 250 to 600 nm. a. The spectra are shown in Figure 1. At 350 nm, the compound has the highest absorption. As a result, all further research was conducted at this wavelength.” Absorption spectra of 2-Acetylpyridine thiosemicarbazone (APT) and metal complex Following the techniques specified in the research, the absorption spectra of the nickel (II) complex in solution against reagent (APT) blank and that of the APT against water blank were recorded at pH 6. A wavelength range of 250 nm to 600 nm is used. Figure shows typical

absorption spectra. The spectra demonstrate that the nickel (II) complex absorbs the most at 375 nm, whereas the reagent blank absorbs the least. As a result, the wavelength of 375 nm has been selected for further analysis.

2.3.6 Effect of reagent concentration on the absorbance of the complex

With the approach described in the study, we looked at the impact of the reagent concentration on complex absorbance at 350 nm. In order to achieve full colour development, researchers found that just a five-fold molar excess of the reagent was necessary.

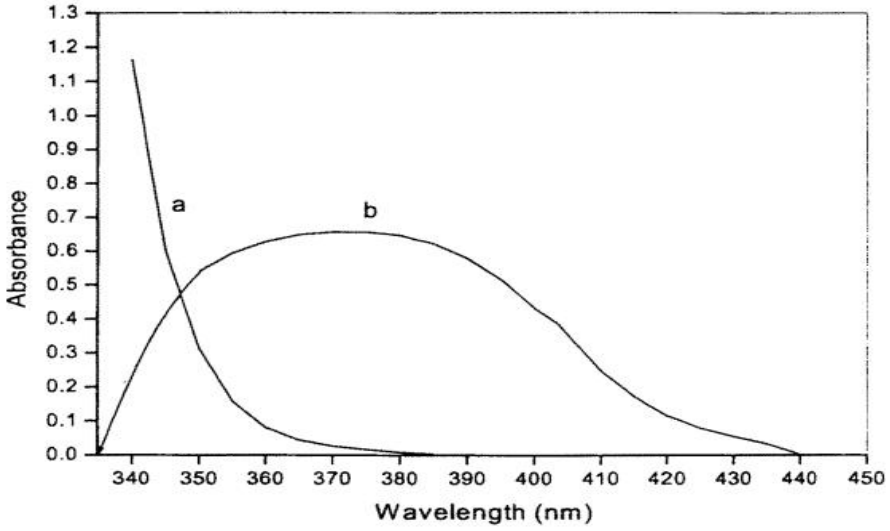


Figure 1: *Absorbance spectrum of a) APT Vs Water blank b) Ni (II) - APT complex Vs APT solution*

([Ni (II)] = 4 x 10^{-5}M, [APT] = 4 x 10^{-4}M, pH = 6.0)

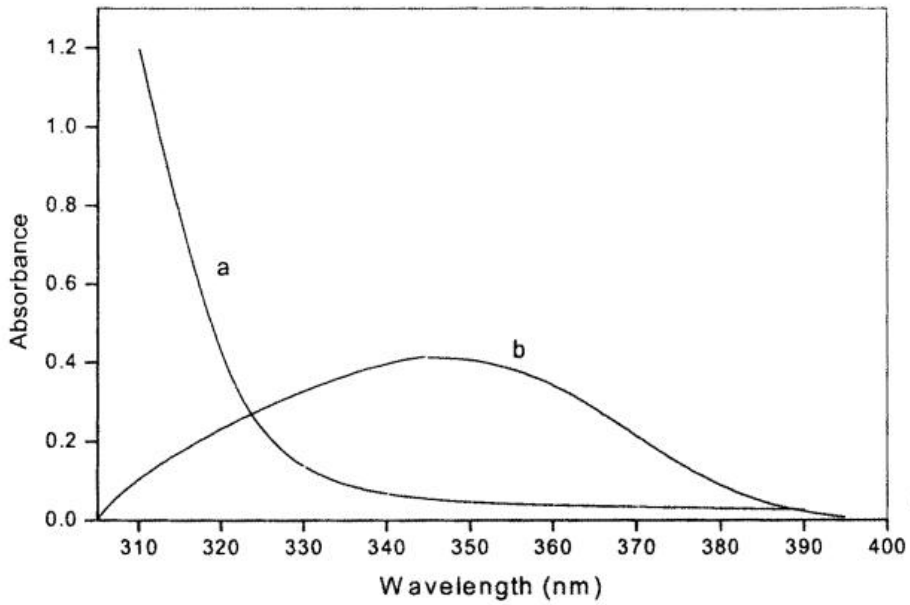


Figure 2: *Absorbance spectrum of a) APS Vs Water blank b) Ni (II) - APS complex Vs APS solution*

([Ni (II)] =1.6x10^{-5}M, [APS] = 4x 10^{-4} M, pH = 9.0)

2.3.7 Effect at pH on the absorbance of the Ni (II) – APT Ni (II) – APS and complexes

"Buffer solutions were prepared with different pH values, which allowed researchers to examine the effect of the pH on colour intensity. Figure depicts the link between pH and absorbance. The pH of the buffer (ammonium chloride - ammonium hydroxide) solution was selected because the complex exhibited a maximum and stable absorbance in the range of 8-10." The influence of pH on the absorbance of the Ni (II) - APT complex was investigated, and the optimal pH was determined using the method research, as shown in fig. According to the graph, the complex's greatest absorbance occurs in the pH range of 4.0 to 7.0. As a result, pH 6 is used in following experiments:

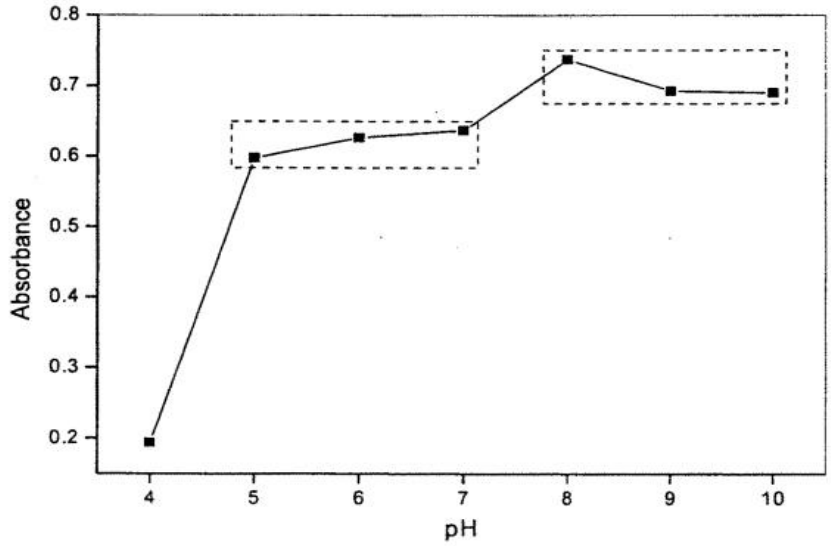


Figure 3: *Effect of pH on the absorbance of Ni (II) - APT system [Ni (II)] = 4 x 10^{-5}M, [APT] = 4 x 10^{-4}M, Wavelength = 375 nm*

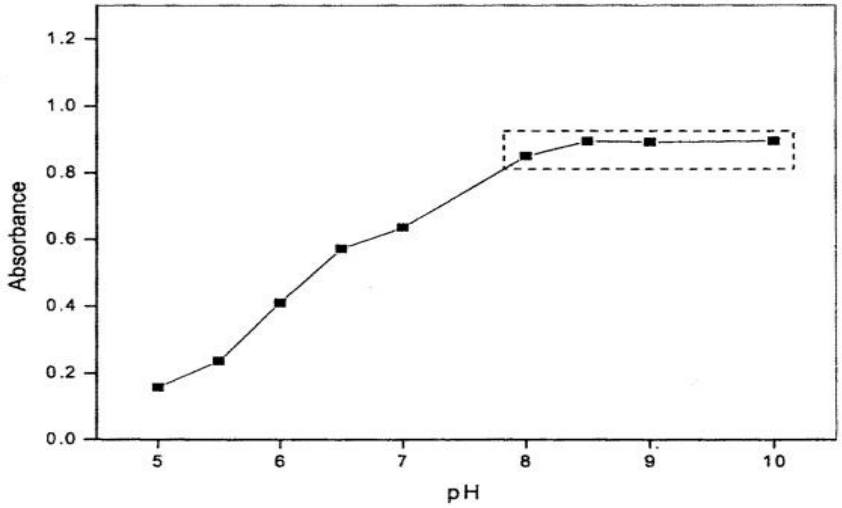


Figure 4: *Effect of pH on the absorbance of Ni (II) - APS system ([Ni (II)] = 1.6x10^{-5}M, [APS] = 4x 10^{-4} M, Wavelength = 350 nm*

2.3.8 Effect of time on the absorbance of both complexes

At 350 nm, the nickel (II) complex's absorbance was measured at different time points over a period of several minutes. There is a near-instantaneous colour interaction between APS and nickel (II), which results in a constant absorbance for 75 minutes. When measured at 375 nanometers, the nickel (II) – ATP complex's absorbance was found to be very low. Accuracy was maintained for more than 12 hours and the yellow greenish tint was swiftly created.

2.3.9 Order of addition of constituents on the absorbance of the complex

The absorbance of the nickel (II) - APS and nickel (II) – APT complexes in solution is unaffected by the sequence in which the elements (buffer, nickel (II), DMF, and APS) are added to the solution.

2.4 Applicability of Beer's law

"The applicability of Beer's law to the existing system was explored using the research approach. In the range of 0.094 - 0.940 g/ml, the calibration graph shows that the system follows Beer's law (II). The straight line is governed by the equation A_{350} = 0.4682C + 0.0308. 2.81x104 Lit Mol-1 cm-1 Ni (II) Absorbance and Sandell's sensitivity for Ni (II) are 0.021 µg/cm2 for Ni (II). There is a 0.479-ml g-1 cm-1 specific absorptivity for the system in question. There is a 0.0144 standard deviation in the 0.47 µg/ml Ni (II) measurement. Relative standard deviation and mean absorbance are 1.02 percent and 0.642-20.0024 percent, respectively, for a sample of 10 measurements."

2.5 Tolerance limits of foreign ions

By measuring the absorbance of a nickel complex containing 2.34 µg/ml of nickel, the influence of different cations and anions often associated with metal ions on the detection of nickel (II) under ideal circumstances was investigated. Using the technique outlined in the paper, nickel was tested in the presence of various concentrations of foreign ions. An absorbance value inaccuracy of less than 2% was regarded acceptable. To test the reagent's selectivity, the impact of different foreign ions was studied using the technique described in study. The goal of this experiment was to determine the tolerance limits for difference.

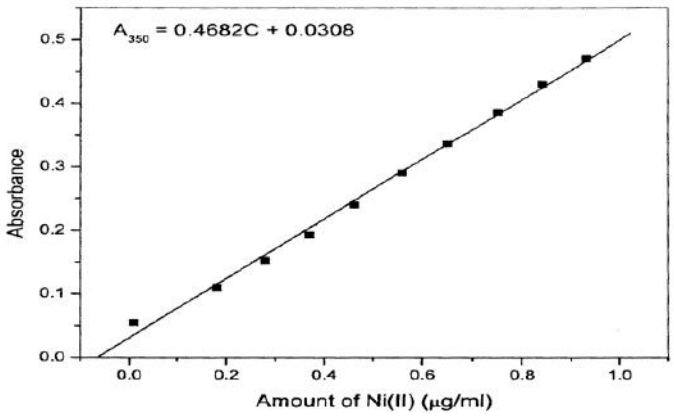


Figure 5: *Absorbance Vs Amount of Ni (II) (pH = 9.0, [APS]= 6 x 10^{-4} M, Wavelength = 350 nm)*

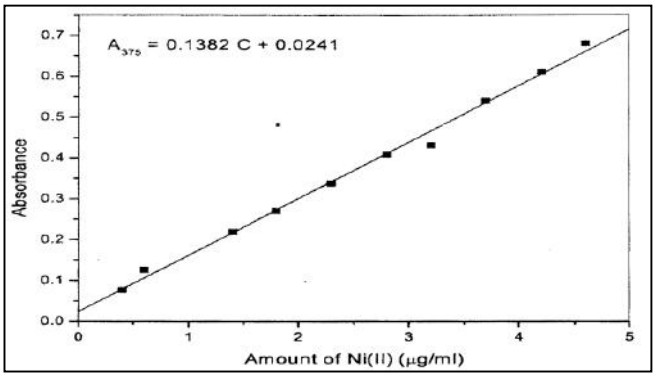


Figure 6: *Absorbance Vs Amount of Ni (II) (pH = 6.0, [APT]= 4 x 10^{-4} M, Wavelength = 375 nm)*

Ions that form a chain The amount of foreign ion that results in a 2% error in absorbance was selected as a tolerance limit. Reference samples were also prepared in accordance with research guidelines. On the other hand, the tolerance limit values for metal ions that are connected to each other are lower.

2.6 Composition and stability constant of Ni (II) APT and Ni (II) APS complex

"Job's continuous variation and molar ratio method was used to determine the nickel (II) complex's composition. An analysis was performed using the data from Job's plot in order to calculate the stability constant of nickel (II)."

2.7 Job's continuous variation method

"Job's methods are being examined. According to Job's plot, three moles of reagent APS react with one mole of metal ion. Consequently, the ratio is one to three. The complex's stability constant was calculated using the following equation, as the complex's composition is 1:3 (M: L)".

$$\beta = \frac{1-\alpha}{27\alpha^4 C^3} \quad (1)$$

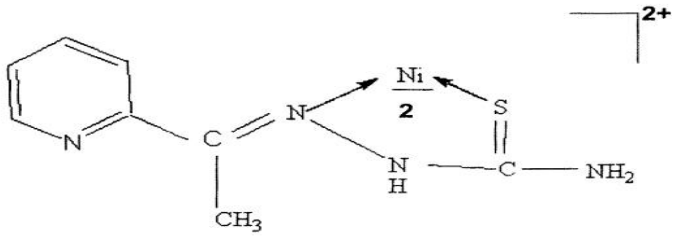
There is a correlation between Job's plot and the values (0.07131) α and C (5.6 x 10-6). 1.3 x 1014 is determined to be the stability constant. Under the experimental circumstances, Job's curve suggests a (1: 2) stoichiometry between the metal ion and the reagent APT. The above equation is used to compute the complex's stability constant. The α and C values of 0.0604 and 2.4 x 10^{-6}, respectively, were discovered. The complex's stability constant is found by replacing these values in the preceding equation. 1.84 x 10^{14} is the value calculated.

2.8 Molar ratio method

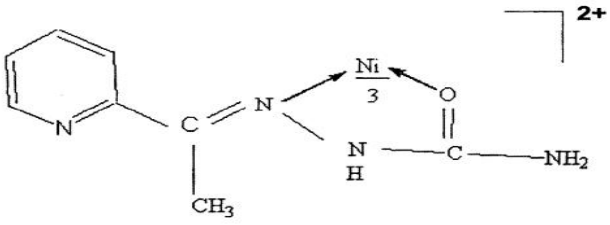
The complex's composition was also established using the molar ratio approach, as detailed in the study. 1 ml of 2 x 10^{-4} M nickel (II) solution was added to 10 ml of buffer (pH 8.5) solution in a set of (ten) 25-ml standard flasks. Each flask received known aliquots (1-10 ml) of reagent (2 x10^{-4} M) solution. The absorbance was measured against a comparable reagent blank after the contents were plotted with distilled water. The complex's composition was determined via a molar ratio plot, which revealed 1: 3 ratio (M: L) for nickel (II) - APS and 1: 2 (M: L) ratio for nickel (II) - APT. As a result, the molar ratio approach confirms the composition found by Job's method.

3. RESULT:

The APS-based spectrophotometric approach is mole sensitive (Ɛ=2.8 x 104 lit mol-1 cm-1). When compared both approach, APS produces a 1:3 (M: L) complex, while APT produces a 1: 2 (M: L) complex with nickel (II). As a result, it is impossible to compare metal complex stability constants. In the determination of nickel (II) using APT reagent, the standard deviation is lower, but the tolerance limit values for foreign ions are higher. As a result, the APT reagent may be used to determine metal ions in a selective manner. Because the APS approach is more sensitive, it is used to determine the amount of nickel in different samples. The findings are really promising. Based on the composition of the complexes produced in solution state using Job's approach, the structures of the complexes are provisionally ascribed below



Tentative structure of $[Ni(APT)_2]^{2+}$ complex



Tentative structure of $[Ni(APS)_3]^{2+}$ complex

Figure 7: *Structure of Ni (II) APT and APS*

Table 2: Physio-Chemical and analytical characteristics of Ni (II) with APT and APS

S. No.	Characteristics	Ni - $(APT)_2$	Ni - $(APS)_3$
1	λ_{max} (nm)	375	350
2	Mean absorbance	0.341 ± 0.008	0.642 ± 0.002
3	pH range (optimum)	5.0 – 7.0	8.0 – 10.0
4	Mole of reagent required per mole of metal ion for full colour development	10 fold	10 fold
5	Time stability of the complex (in minutes)	12 hrs	75
6	Beer's law validity range (µg/ml)	0.47 – 4.70	0.094 – 0.94
7	Molar absorptivity (lit $mol^{-1}cm^{-1}$)	1.6×10^4	2.8×10^4
8	Specific absorptivity (ml $g^{-1}cm^{-1}$)	0.284	0.479
9	Sandell's sensitivity (µg of Ni(II) cm^{-2})	0.0352	0.021
10	Composition of the complex as obtained in Job's and molar ratio methods (M : L)	1 : 2	1 : 3
11	Stability constant of the complex	1.84×10^{14}	1.32×10^{14}
12	Standard deviation	0.0094	0.0144
13	Relative Standard deviation (RSD), (co-efficient of variation)	0.032%	1.024%

4. CONCLUSION:

This method is very sensitive for comparison between nickel (II) 2-Acetylpyridine thiosemicarbazone (APT) and nickel (II) 2-Acetylpyridine semicarbazone (APS). Sulphur containing ligands are good chromogenic reagents for the spectrophotometric determination of transitions metal ions pollutants. Metal complexes of Sulphur containing ligands show very intense colours. The colour reactions have been exploited for the spectrophotometric determination of toxic metal ions.

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