Research Article

Spectrophotometric Determination of Nickel (II) using 2-Acetylpyridine thiosemicarbazone (APT)

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Abstract For the determination of Nickel (II), a straight forward, sensitive, and accurate spectrophotometric approach has been created. The reagent 2-Acetylpyridine thiosemicarbazone (APT) react with nickel (II) in aqueous solution in the pH range 0.5-12. When 2-Acetylpyridine thiosemicarbazone (APT) was added to nickel (II) in a sodium acetate-acetic acid pH 6 solution, a yellow greenish solution was generated almost instantly. The spectra demonstrated that the nickel (II) complex absorbs the most at 375 nm. Accuracy was maintained for more than 12 hours and the yellow greenish tint was swiftly created. Sequence in which the elements are added (buffer, metal ion, DMF, and reagent) has no influence on the metal complex's absorbance. The determination of nickel in alloy steels, aluminium-based alloys, vegetable oil, and water is effectively accomplished using the current methodology.

Keywords Nickel (II), Spectrophotometry, 2-Acetylpyridine thiosemicarbazone (APT)

Introduction

Nickel is a very important metal for both industrially and biologically. It is one among the essential trace elements along with cobalt, copper, zinc and manganese in the human diet [1-2]. Nickel and cobalt play a direct role in nutritional phenomenon. Ni, or nickel, is an essential trace element that is required in very small amounts for the proper functioning of the human body [3-4].

Some of the important roles of Ni in human physiology are:

- Enzymatic functions: Ni plays a role in the activity of several enzymes in the body, including urease, which helps in the breakdown of urea and plays a role in the metabolism of amino acids.
- DNA synthesis: Ni is involved in the synthesis of DNA and plays a role in the maintenance of the structure of DNA.
- Immune system: Ni is required for the proper functioning of the immune system, and is involved in the production of certain types of white blood cells that help fight infection.
- Bone health: Ni is involved in the metabolism of calcium and may play a role in maintaining bone health.
- Red blood cell production: Ni is involved in the production of red blood cells, which are responsible for carrying oxygen throughout the body [5-6].

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 [7-8].

Ni, or nickel, is an essential micronutrient for plant growth and development, although it is required in very small amounts. Ni plays a crucial role in several physiological processes in plants, including:

- Enzymatic functions: Ni is a component of several enzymes in plants, including urease, which is involved in the metabolism of urea, and hydrogenase, which is involved in nitrogen fixation.
- Photosynthesis: Ni plays a role in the efficiency of photosynthesis, which is the process by which plants convert light energy into chemical energy.
- Plant defense: Ni plays a role in plant defense mechanisms against pathogens and pests. It is involved in the synthesis of certain compounds that protect plants from biotic stress.
- Seed germination: Ni plays a role in the germination of seeds and the development of seedlings.
- Nutrient uptake: Ni can enhance the uptake and utilization of other essential nutrients such as iron and nitrogen [9-10].

Despite its importance, Ni deficiency is a common problem in plants, especially in crops such as rice and wheat. Ni deficiency can lead to reduced growth and yield, as well as increased susceptibility to disease and pests. On the other hand, excessive amounts of Ni can be toxic to plants and can lead to a variety of symptoms, including leaf necrosis, stunted growth, and reduced yield. Therefore, it is important to maintain a proper balance of Ni in plant growth media and soils [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 [14-23].

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

Experimental Work
Preparation of Inorganic Salt Solutions
Nickel (II) solution
Stock solution of Ni (II) (1×10^{-2}M) 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.

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

Description of Instruments Employed in the Present Investigations
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:

- High-speed wavelength scanning is achieved by employing a CPU-controlled scanning device without the use of a sine bar.
- All-in-one corporate spectrophotometer with CRT and printer.
- Single-action operation is enabled by providing backup mode settings.
- 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	$\pm$ 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 halographic 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 compartmen	Inner size: 1100 nm wide
Distance between sample and reference beam	100 nm
Power requirements	With line voltage selector for 100
Weight	42 kgs

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 $\pm$ 0.01 pH.

Instruments used in the characterization of ligands
Infrared spectrophotometer
Using a Perkin-Elmer 983G infrared double beam spectrophotometer, we measured the ligand's infrared spectra, which ranged from 400 to 4000 cm^{-1}. 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

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

Results and Discussion
Effect of pH on the absorbance of the metal complexes
To see if pH has an impact on colour intensity, a metal complex in solution was created using buffer solutions with varying pH values.

One set of standard flasks was filled with 10 ml of buffer solution, 10 ml of metal-ion-reagent solution, and one or two millilitres of dimethylformamide (DMF). The absorbance of each solution (metal complex) was compared to a comparable reagent blank that had been produced according to a predetermined wavelength (X_{max}). After analysing the absorbance versus pH data, the decision was reached on what pH to use.

Effect of reagent concentration on the absorbance
To determine the optimal reagent concentration for complete colour development, the following technique was followed. Every flask included 10 millilitres of buffer solutions as well as the appropriate volume of DMF and a fixed quantity of metal ion. This method yielded the same results each time since each flask had the same aliquot of reagent solution every time. In each flask, distilled water was used to dilute the contents to volume before measuring absorbance at a specific wavelength (X_{max}) against a reagent blank generated in the same way. This experiment determined the needed reagent molar excess for complete colour development.

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 of colours developed.

When 2-Acetylpyridine thiosemicarbazone (APT) was added to nickel (II) in a sodium acetate-acetic acid pH 6 solution, a yellow greenish solution was generated almost instantly. The colour reaction was studied in depth in order to create a spectrophotometric technique for determining nickel concentration in aqueous medium.

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.

Effect of pH on the absorbance of nickel (II) complex
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.
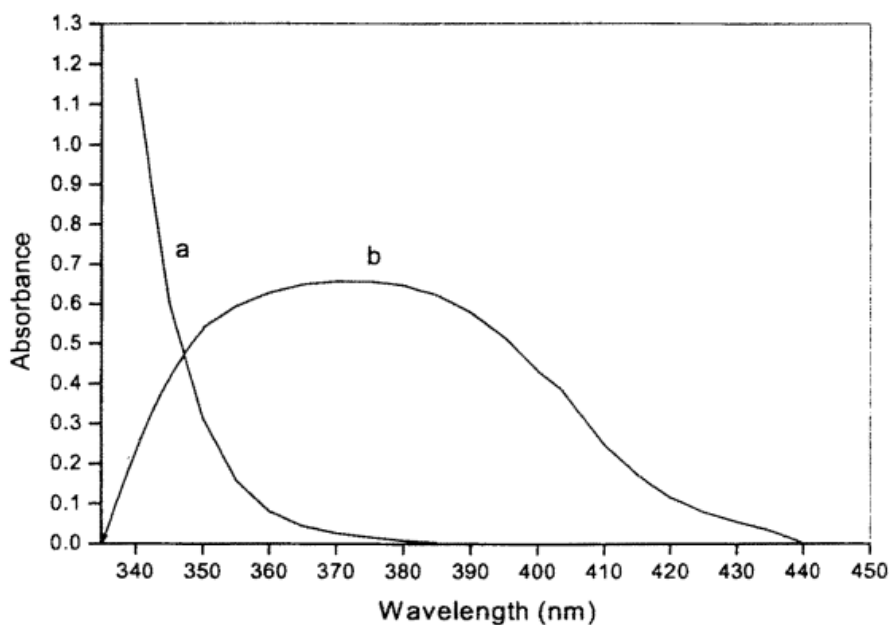
Figure 1: Absorbance spectrum of a) APT Vs Water blank, b) Ni (II) - APT complex Vs APT solution ([Ni (II)] = 4 x 10^{-5}M, [APT] = 4 x 10^{-4}M, pH = 6.0)

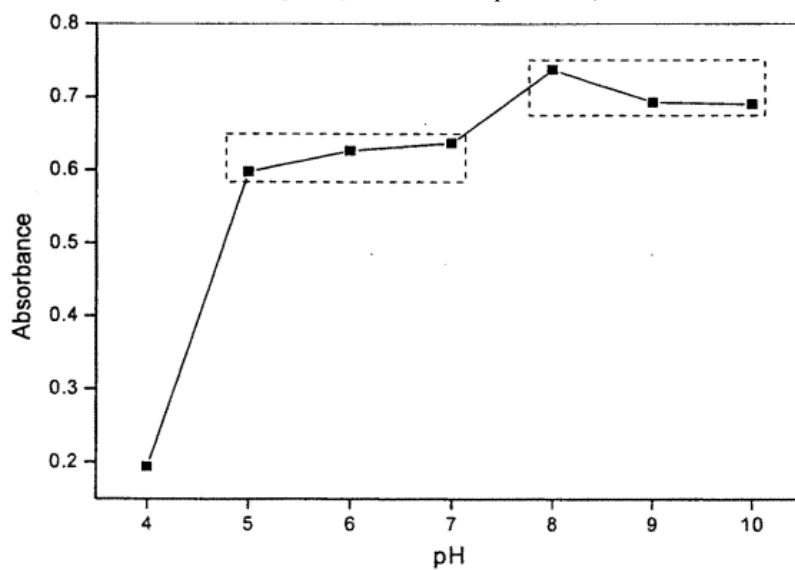*Figure 2: Effect of pH on the absorbance of Ni (II) - APT system ([Ni (II)] = 4 x 10^{-5}M, [APT] = 4 x 10^{-4}M, Wavelength = 375 nm)*

Effect of reagent concentration of the absorption of the nickel (II) - APT complex

Following the process outlined in the research, the reagent to metal ion concentration ratio required for complete colour development was determined. The findings are shown in the table below.

Table 2: Effect of APT concentration on the absorbance of the metal complex ([Ni (II)] = 4 x 10^{-5}M, pH = 6.0, Wavelength = 375 nm)

Ni(II) : APT	Absorbance
1 : 05	0.647
1 : 10	0.634
1 : 15	0.658
1 : 20	0.648
1 : 25	0.623
1 : 30	0.653

The findings in Table suggest that a tenfold molar excess of reagent is essential for complete colour development. Therefore, a minimum of 10 - fold molar excess of reagent is utilized throughout the research

Effect of time on the absorbance of the nickel (II) complex
The stability of the complex's colour over time was tested by measuring the absorbance of the mixture at different intervals over the course of the research. "When measured at 375 nanometers, the nickel (II) 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."

Effect at order of addition of constituents in solution on the absorbance of the metal complex
"Sequence in which the elements are added (buffer, metal ion, DMF, and reagent) has no influence on the metal complex's absorbance."

Applicability of Beer's law
"Using the method described in the research, the sensitivity of the colour reaction and the ability to detect nickel (II) ions were evaluated. As a youngster, I was adopted. In this graph, nickel's absorption is plotted against its concentration (II). The straight line is governed by the equation A375. = 0.1382C + 0.0241 µg/ml."
"Following Beer's law, the system behaves as expected when nickel concentrations range from 0.47 to 4.70 µg/ml (II). In terms of absorption and sensitivity, molar absorptivity and Sandell's sensitivity are 1.6x104 and 0.0352 µg/cm^2 respectively.
Absorbance is measured at 0.284 ml g^{-1} cm^{-1} for the system. Ten observations of 1.172 g/ml nickel had a standard deviation of 0.0094. Relative standard deviation and mean absorbance are 0.341% and 0.032%, respectively, in the experimental data."

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.
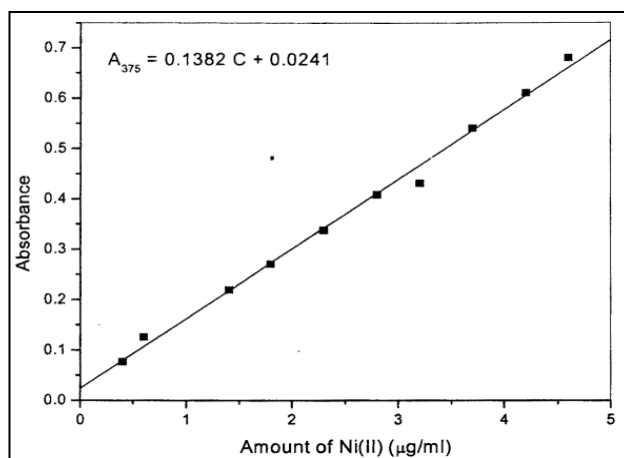
Figure 3: Absorbance Hs Amount of Ni (II) (pH = 6.0, [APT] = 4 x 10⁻⁴ M, Wavelength = 375 nm)

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.

Table 4.15: Tolerance limit of foreign ions in the determination of 2.3452 µg/ml of nickel (II)

Ion added	Tolerance limit (µg/ml)	Ion added	Tolerance limit (µg/ml)
Citrate	1152	Zr (IV)	110
EDTA	1178	Ba (II)	54
Chloride	212	Pb(II)	50
Acetate	282	Sn (II)	50
Nitrate	308	Hg (II)	48
Bromide	317	W (VI)	44
Bicarbonate	360	Cd (II)	27
Thiosulphate	382	Ag (I)	26
Sulphate	384	Mo (VI)	23[a]
Phosphate	387	Sr (II)	21
Thiourea	427	Cr (VI)	12.47
Iodide	507	Mn (II)	11
Iodide	508	Pt(II)	10.25
Oxalate	528	Pd (II)	10.25
Tartarate	592	Tl(III)	10.25
Fluoride	76	Ca (II)	10
		Au(III)	10
		Al (III)	6.5
		Mg(II)	3.0
		Pd(II)	2.6
		V (V)	1.22
		Zn (II)	0.78
		Cu (II)	0.76
		Fe (III)	0.67[b]
		Co (II)	0.66
		Fe (II)	0.6

a. Masked with 200 µg/ml of chloride
b. Masked with 70 µg/ml of fluoride

Composition and stability of the metal complex

The complex's composition was calculated using Job's approach and validated using the molar ratio method. Using the data from Job's figure, the complex's stability constant was computed.

Job's method

The approach outlined in the paper was used for Job's method. Under the experimental circumstances, Job's curve suggests a 1: 2 stoichiometry between the metal ion and the reagent. The equation below is used to compute the complex's stability constant.

$$\beta = \frac{1 - \alpha}{4\alpha^3 C^2}$$

(1)

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.

Molar ration method

The molar ratio approach was employed to estimate the composition of the complex utilizing the basic experimental protocol described in the research. The data are displayed as a graph, which validates the complex's composition.

Conclusion

The current approach is straightforward, less costly, and more exact. The determination of nickel in alloy steels, aluminum-based alloys, vegetable oil, and water is effectively accomplished using the current methodology.

References

[1]. Al-Fartusie, F. S., & Mohssan, S. N. (2017). Essential trace elements and their vital roles in human body. *Indian J Adv Chem Sci*, *5*(3), 127-136.

[2]. Demirel, B., & Scherer, P. (2011). Trace element requirements of agricultural biogas digesters during biological conversion of renewable biomass to methane. *Biomass and bioenergy*, *35*(3), 992-998.

[3]. Asher, C. J. (1991). Beneficial elements, functional nutrients, and possible new essential elements. *Micronutrients in agriculture*, *4*, 703-723.

[4]. Genchi, G., Carocci, A., Lauria, G., Sinicropi, M. S., & Catalano, A. (2020). Nickel: Human health and environmental toxicology. *International journal of environmental research and public health*, *17*(3), 679.

[5]. Al-Fartusie, F. S., & Mohssan, S. N. (2017). Essential trace elements and their vital roles in human body. *Indian J Adv Chem Sci*, *5*(3), 127-136.

[6]. Ni, D., Smyth, H. E., Cozzolino, D., & Gidley, M. J. (2022). Holistic approach to effects of foods, human physiology, and psychology on food intake and appetite (satiation & satiety). *Critical Reviews in Food Science and Nutrition*, 1-11.

[7]. Soetan, K. O., Olaiya, C. O., & Oyewole, O. E. (2010). The importance of mineral elements for humans, domestic animals and plants: A review. *African journal of food science*, *4*(5), 200-222.

[8]. Nielsen, F. H. (2000). Importance of making dietary recommendations for elements designated as nutritionally beneficial, pharmacologically beneficial, or conditioinally essential. *The Journal of Trace Elements in Experimental Medicine: The Official Publication of the International Society for Trace Element Research in Humans*, *13*(1), 113-129.

[9]. Brown, P. H., Welch, R. M., & Cary, E. E. (1987). Nickel: A micronutrient essential for higher plants. *Plant physiology*, *85*(3), 801-803.

[10]. Welch, R. M. (1981). The biological significance of nickel. *Journal of Plant Nutrition*, *3*(1-4), 345-356.

[11]. Kabata-Pendias, A., & Mukherjee, A. B. (2007). *Trace elements from soil to human*. Springer Science & Business Media.

[12]. Gerendás, J., Polacco, J. C., Freyermuth, S. K., & Sattelmacher, B. (1999). Significance of nickel for plant growth and metabolism. *Journal of Plant Nutrition and Soil Science*, *162*(3), 241-256.

[13]. Ahmad, M. S. A., & Ashraf, M. (2011). Essential roles and hazardous effects of nickel in plants. *Reviews of environmental contamination and toxicology*, 125-167.

[14]. Ferreira, S. L., Santos, B. F., de Andrade, J. B., & Costa, A. C. S. (1996). Spectrophotometric and derivative spectrophotometric determination of nickel with hydroxynaphthol blue. *Microchimica Acta*, *122*, 109-115.

[15]. Zhao, S. L., Xia, X. Q., Ma, H. R., & Xi, H. J. (1994). Spectrophotometric determination of nickel with p-acetylarsenazo. *Talanta*, *41*(8), 1353-1356.

[16]. Ferreira, S. L., Costa, A. S., & de Jesus, D. S. (1996). Derivative spectrophotometric determination of nickel using Br-PADAP. *Talanta*, *43*(10), 1649-1656.

[17]. de Sousa, C. S., & Korn, M. (2001). Effects of ultrasonic irradiation on the spectrophotometric determination of nickel with dimethylglyoxime. *Analytica Chimica Acta*, *444*(2), 309-315.

[18]. Ferguson, R., & Banks, C. (1951). Spectrophotometric determination of nickel in calcium metal using 1, 2-cyclohexanedionedioxime. *Analytical Chemistry*, *23*(3), 448-453.

[19]. Reddy, K. H., & Chandrasekhar, K. B. (2001). Simultaneous first derivative spectrophotometric determination of nickel (II) and copper (II) in alloys with diacetylmonoxime benzoylhydrazone.

[20]. Sarma, L. S., Kumar, J. R., Reddy, K. J., Thriveni, T., & Reddy, A. V. (2008). Development of highly sensitive extractive spectrophotometric determination of nickel (II) in medicinal leaves, soil, industrial effluents and standard alloy samples using pyridoxal-4-phenyl-3-thiosemicarbazone. *Journal of Trace Elements in Medicine and Biology*, *22*(4), 285-295.

[21]. Vicente, S., Maniasso, N., Queiroz, Z. F., & Zagatto, E. A. (2002). Spectrophotometric flow-injection determination of nickel in biological materials. *Talanta*, *57*(3), 475-480.

[22]. Ferguson, R., & Banks, C. (1951). Spectrophotometric Determination of Nickel Using 1, 2-Cycloheptanedionedioxime. *Analytical Chemistry*, *23*(10), 1486-1487.

[23]. Mohanapriya, S., & Lakshminarayanan, V. (2007). Simultaneous purification and spectrophotometric determination of nickel present in as-prepared single-walled carbon nanotubes (SWCNT). *Talanta*, *71*(1), 493-497.