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# Spectrophotometric determination of nickel (II) with 2-aminoacetophenone isonicotinoylhydrazone

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# ABSTRACT

A simple, sensitive and accurate spectrophotometric method has been developed for the determination of nickel (II). The reagent 2-Amino acetophenone isonicotinoyl hydrazone (2-AAINH) react with nickel (II) in aqueous solution in the pH range 3.0-11.0 and to form light yellow coloured complex. The complex shows  $\lambda_{max}$  at 470 nm with a molar absorptivity 1.05 x 10<sup>4</sup> L mo1<sup>-1</sup>cm<sup>-1</sup> and Sandell's sensitivity 0.56 x10<sup>-2</sup> µg cm<sup>-2</sup>. Beer's law is obeyed in the concentration range 0.29-6.16 µg mL<sup>-1</sup> of Ni (II). A method for the determination of nickel (II) by second order derivative spectrophotometry has also been proposed. Interference of various diverse ions has been studied. The present method is applied for the determination of nickel in drinking water, aluminium based alloys, alloy steels and vegetable (groundnut) oil samples.

**Keywords:** UV-visible spectrophotometer, Buffer solutions, 2-Amino acetophenone isonicotinoyl hydrazone, derivative spectrophotometry, Nickel (II).

# 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]. Bertrand and Nakamura [2] observed in their experiments on synthetic nutrition that nickel and cobalt play a direct role in nutritional phenomenon. Nickel bound to ribonucleic acid, has special affinity for bone and skin and plays an important role in pigmentation [3]. It has been reported that normal human plasma contains 0.012-0.085  $\mu$ g mL<sup>-1</sup> of nickel (II). Nickel is one of the important alloying element for steel and cast iron. A nickel metallo enzyme is an essential micronutrient [4-6] for plants arose from ureases. Literature survey indicated that several spectrophotometric methods [7-17] were reported for the determination of nickel (II) by using various chromogenic reagents. Hydrazones are important class of analytical photometric reagents, the potentialities of which were reviewed by Singh et al [18].

The present study describe, a simple, rapid, selective and sensitive direct and second order derivative spectrophotometric methods for the determination of trace amount of nickel (II) by compleing with 2-Amino acetophenone isonicotinoyl hydrazone (2-AAINH).

# MATERIALS AND METHODS

# Instrument:

The absorbance and pH measurements were made on a Perkin-Elmer UV-visible (Lambda 25) double beam spectrophotometer fitted with 1cm quartz cells and Elico digital pH meter (model LI-120) respectively. The pH meter has a temperature compensate arrangement. The reproducibility of measurements is within  $\pm$  0.01 pH.

### **Reagents and chemicals:**

The reagent, 2-amino acetophenone isonicotinoyl hydrazone (2-AAINH) was synthesized by condensing equimolar solutions of 2-amino acetophenone and isonicotinoyl hydrazide in alkaline absolute ethanol as described earlier [19]. 1 x  $10^{-2}$  M solution of 2-AAINH was prepared by dissolving 0.255g of the crystallized compound in dimethylformamide and diluting to 100mL. Lower concentrations were prepared by diluting the stock solution appropriately with the solvent.

Stock solution of nickel  $(1 \times 10^{-2} \text{M})$  was prepared by dissolving 0.2808g of NiSO<sub>4</sub>.7H<sub>2</sub>O (AR, Merck) in doubly distilled water. The solution was made up to the mark in 100 ml volumetric flask and standardized gravimetrically using dimethyl glyoxime complexometrically [20]. Lower concentrations were prepared by diluting the stock solution appropriately with distilled water.

The buffer solutions were prepared by mixing appropriate volumes of 0.2M sodium acetate and 0.2M acetic acid (pH 3.0 to 7.0) and 2.0 M ammonium- hydroxide and 2.0 M ammonium chloride (pH 8.0 to 10.0). The pH of these buffer solutions was finally adjusted to the required value by using pH meter.

### **RESULTS AND DISCUSSION**

### **Determination of Nickel (II):**

In different sets of 10 ml volumetric flasks, each containing 4 ml of buffer solution (pH 9.0) and 0.5 ml of 2-AAINH  $(1x10^{-2}M)$ , varying volumes of  $1x10^{-4}$  M or  $1x10^{-3}$  M nickel (II) solution were added and made up to the mark with doubly distilled water. The absorbance was measured at 470 nm against the reagent blank, and the calibration plot was constructed.

The second derivative spectra of [Ni(II)-2-AAINH] colored complex for different concentrations of Ni (II) were recorded in the wave length region 350-600 nm. The derivative amplitudes at 485 nm (Peak) and at 445 nm (valley) were found to be proportional to the concentration of Ni (II) solution. The derivative amplitudes were measured at 485 nm and 445 nm for different concentrations of Ni (II) and plotted against the amount of nickel (II). The plots were linear in the range 0.1-3.0  $\mu$ g mL<sup>-1</sup> at 445nm and 0.1-3.25  $\mu$ g mL<sup>-1</sup> of Ni (II) at 485nm. By substituting the corresponding experimental data in the above equation, the calibration equations were calculated as A<sub>470</sub> = 0.136c -0.042 for zero order data and give the good straight lines.

Nickel (II) forms light yellow coloured complex with 2-amino acetophenone isonicotinoyl hydrazone (2-AAINH). The absorption spectra of 2-AAINH and its Nickel (II) complex were recorded in the wavelength range 350-600 nm at pH 9.0 against the buffer solution and reagent blank respectively is as shown in Fig.1.The spectra show that Nickel (II) complex possesses maximum absorbance at 470 nm where the reagent is showing relatively very low absorbance. Therefore, further analytical studies were carried out at 470 nm using the reagent blank.



Fig. 1: Absorption spectra of a) [Ni (II) – 2- AAINH] Vs reagent blank b) 2- AAINH Vs Buffer blank [Ni(II)] =  $5 \times 10^{-5}$  M; [2- AAINH] =  $2.5 \times 10^{-4}$  M; pH = 9.0

The effect of pH on the colour formation was studied to arrive at the optimum pH. The plot obtained between absorbance data versus pH reveals that the reaction mixture shows constant colour intensity in the pH range 8.0 to 9.5. Hence, the studies were carried out at pH 9.0.

The optimum concentration of the reagent required for the maximum colour formation was studied by measuring the absorbance at 470 nm. The results indicate that a 20-fold excess of the reagent is necessary to develop maximum colouration with a given amount of nickel.

The composition of the complex was determined using Job's method and confirmed by molar ratio method. The results indicate a 1:1 stoichiometry between the metal ion and the reagent under the experimental conditions. The stability constant of the complex calculated from Job's method was found to be  $5.747 \times 10^9$ .

A linear plot was obtained when the absorbance was plotted against the amount of nickel indicating the validity of Beer's law in the range 0.29 -  $6.16\mu g \text{ mL}^{-1}$  of Ni(II). The molar absorptivity of the light yellow coloured solution under the given experimental conditions was calculated as  $1.05 \times 10^4 \text{ L} \text{ mo1}^{-1} \text{ cm}^{-1}$  at 470 nm. The Sandell's sensitivity of the present method was found to be  $0.56 \times 10^{-2}\mu g \text{ cm}^{-2}$ . The regression analysis of the linear curve gave the angular coefficient (m) and correlation coefficient (r) as 0.136 and 0.998 respectively.

### Effect of foreign ions:

The effect of various anions and cations on the determination of Ni(II) under optimal conditions was studied and presented in Table.1. From the results, we can notice that many anions and cations do not interfere in the present method even when presence in more than 100 folds excess. Au (III), V (V), Mo (VI), Mn (II) and Pd (II), are tolerable in 80,80, 45, 30 and 20 fold excess respectively. Co (II) and Cu (II) interfere seriously.

Foreign ion	Tolerance limit (µg mL <sup>-1</sup> )	Foreign ion	Tolerance limit (µg mL <sup>-1</sup> )
Ascorbic acid	1660	Na(I)	450
Tartrate	1500	Cd (II)	740
Bromate	1080	Th(IV)	350
Thiosulphate	1020	Ti(IV)	320
Sulphate	950	Li(I)	270
Citrate	890	Mg(II)	220
Oxalate	840	Pb(II)	200
Thiourea	700	Al(III)	155
Urea	680	Zn(II)	120
Iodide	640	Fe(II)	110
Nitrate	590	Ru(III)	110
Acetate	575	Au(III)	80
Formate	450	V(V)	80
Chloride	385	Mo(VI)	45
Fluoride	250	Mn(II)	30
Cd (II)	740	Pd(II)	20
Te(IV)	600	Cu(II)	5
W(VI)	550	Co(II)	5

Table- 1: Tolerance limits of foreign ions Amount of Ni (II) =  $1.173 \ \mu g \ mL^{-1}$ 

# **Derivative method:**

A sensitive second order derivative spectrophotometric method was developed for the determination of nickel (II). Second order derivative spectra of different solutions containing variable amounts of Ni(II) and a fixed concentration of 2-AAINH, buffer solution (pH 9.0) were recorded in the wavelength region 350-600nm and presented in Fig. 2. The derivative amplitudes were measured at 485m and 445nm and plotted against the amount of Ni(II). Linear plots were obtained in the concentration range  $0.1-3.0\mu \text{g mL}^{-1}$  at 445nm and  $0.1-3.25 \ \mu \text{g mL}^{-1}$  at 485nm. In the second order derivative method, the tolerance limits of both Cu(II) and Co(II) were increased from 5 folds (direct method) to 80 and 65 folds respectively.



# Application to real samples:

The proposed zero order method was employed for the determination of nickel (II) in drinking water and in aluminium based alloys.

The water samples were collected from different places of Anantapuramu district (Andhra Pradesh, India). The water samples (11itre) were collected in clean 2 litre beakers and slowly evaporated to about 25mL. To each sample, 5mL of  $H_2O_2$  was added and evaporated to dryness [21]. It was then dissolved in 20mL of water and filtered to remove insoluble substance. The filtrate was collected in 100mL volumetric flask quantitatively and diluted up to the mark with distilled water.

About 0.4g alloy samples was treated with 15ml of 1:1 HCl. To this 3mL of  $HNO_3$  was added and the contents boiled until dissolution was complete. Then, 10 mL of water and 40 mL of 4N ammonium hydroxide solution were added and filtered through a Whatman filter paper (No.41). The filtrate was collected into 25 mL volumetric flask and made up to the marks with distilled water.

A known aliquot of the sample solutions were taken in a 10mL flask containing 4ml of buffer solution (pH 9.0), and 1mL of the AAINH solution  $(1x10^{-2} \text{ M})$ . The contents were made up to the mark with distilled water and its absorbance was measured at 470 nm against the reagent blank. The amount of nickel (II) present in the sample solution was determined from the predetermined calibration plot. The results are presented in Table.2 and 3 respectively for water and in aluminium based alloys samples. The drinking samples were also analyzed by atomic absorption spectrophotometric method and compared with those obtained by the present method.

Watan Comula	Amount of Ni(II) µg mL <sup>-1</sup>			Recovery (%)		
water Sample	Added	Found*		Present method	AAS method	
		Present method	AAS method	Flesent method	AAS memou	
1	-	1.5	1.48	-	-	
1	1.0	2.52	2.50	100.8	100.0	
	2.0	3.48	3.52	99.4	100.5	
	-	2.0	2.02	-	-	
2	1.0	2.97	3.05	99.0	101.6	
	2.0	4.05	4.00	101.2	100.0	

Table.2: Determination of nickel in drinking water

\* Average of Five determinations

Sample	Contified composition (9/)	Amount of nickel (%)			
Sample	Certified composition (78)	Present	Found*	Recovery (%)	
BAS-20	Cu 4.10; Ni 1.93; Fe 0.43; Mn 0.19; Si 0.29; Mg 1.61; Rest Al	1.93	1.92	99.5	
BAS-85	Cu 0.90; Ni 0.91; Fe 1.15; Mn 0.02; Si 2.04; Mg 0.18; Zn 0.01; Rest Al	0.91	0.93	102.1	

### Table.3: Determination of nickel in aluminum based alloys

\* Average of Five determinations

### Second order derivative method:

The second derivative method was employed for the determination of nickel present in alloy steels and vegetable (groundnut) oil samples.

0.1g of steel sample was weighed accurately and placed in 50mL beaker. 10 mL of 20% (v/v) sulfuric acid was added and carefully covered with a watch glass until the brisk reaction subsided. The solution was heated and simmered after the addition of 5 mL of Con. HNO<sub>3</sub> until all carbides were decomposed. Then, 2mL solution of  $H_2SO_4$  (1:1) was added and the mixture was evaporated carefully until the dense white fumes of the oxides of nitrogen dried off and then cooled at room temperature. After appropriate dilution with water, the contents of the beaker were warmed to dissolve the soluble salts. The solution was then cooled and neutralized with NH<sub>4</sub>OH solution. The resulting solution was filtered through a Whatman (No-41) filter paper into a calibrated flask of known volume. The residue (silica) was washed with a small volume of hot 1%  $H_2SO_4$  followed by water and the volume was made up to the mark with distilled water.

### Preparation of vegetable (ground nut) oil sample solution

100g of hydrogenated groundnut oil (edible) was dried in a hot air oven at  $100^{\circ}$ C and subsequently dissolved in 20ml mixture of 1:2:5 H<sub>2</sub>SO<sub>4</sub>: H<sub>3</sub>PO<sub>4</sub>; HNO<sub>3</sub>. The contents were heated until sulphurous fumes were evolved and the volume was reduced to about 5ml. A little quantity of distilled water was added and filtered through an acid washed Whatman 41 filter paper into a 100ml volumetric flask and made up to the mark with distilled water.

To known aliquots of the samples taken in 10ml volumetric flasks, 5ml of buffer solution of (pH 9.0), 1ml of AAINH  $(1x10^{-2}M)$  were added and the contents were made up to the mark with distilled water. The second derivative spectra were recorded and the amplitude of the derivative curves at 470 nm was measured. The amount of nickel present in the samples was calculated from the derivative amplitude with the help of predetermined calibration plot. The results are presented in Tables.4 and 5.

### Table.4: Determination of nickel in alloy steel samples

Sampla	Certified composition (%)		Amount of nickel (%)	
Sample			Found*	Error (%)
Connor nickel allow	$C_{11}$ 67. Eq. 0.82. Ma 0.09. S: 0.20. N; 21.20	31.20	31.32	+0.38
Copper-mcker anoy	Cu 07, Fe 0.85, Mil 0.08, 51 0.29, NI 51.20.	31.20	31.32	+0.38
Allow NTPC Pall bearing metorial	Ea 65: Cr 15: Cu 4 5: Mn 2: Ni 10.00	10.00	10.15	+1.50
Alloy NIFC Bail bearing material Fe 05, CI 15, Cu 4.5, Mil 2, NI 10.00.		10.00	10.15	+1.50
BCS 364	Cu 80; Sn9.35; Pb9.25; Ni0.28; Sb0.18 ; As 0.065; P 0.056; Zn 0.13; Al 0.002 .	0.280	0.285	+1.78

#### Table.5: Analysis of vegetable oils

Sampla	Amount of nic	Deletive oppor (%)	
Sample	AAS method	Present method*	Relative error (70)
Hydrogenated	0.56	0.54	- 3.57%
ground nut oil	0.0.56	0.575	+0.87

The analytical characteristics of the zero order and second order derivative methods in the present investigations for Nickel (II) show that the derivative method is more sensitive than the zero order method.

# **Comparison of results**

The analytical characteristics of the zero order and second order derivative methods in the present investigations for Ni (II) were compared and presented in Table.6. The results indicated that the derivative methods are more sensitive than the zero order method

Parameter	Zero order	Second	derivative
Analytical wave length (nm)	470	445	485
Beer's law range (µg mL <sup>-1</sup> )	0.29-6.16	0.1-3.0	0.1-3.25
Molar absorptivity(L mol <sup>-1</sup> cm <sup>-1</sup> )	$1.05 \text{x} 10^4$	-	-
Sandell's sensitivity (µg cm <sup>-2</sup> )	0.0056	-	-
Stability constant	5.747x10 <sup>9</sup>	-	-
Angular coefficient (m)	0.136	0.72	0.461
Y-intercept (b)	0.042	0.0110	0.032
Correlation coefficient (r)	0.998	0.9999	0.9999
Standard deviation	$\pm 0.0081$	±0.0065	±0.0062
Detection limit(µg mL <sup>-1</sup> )	0.067	0.023	0.023
Determination limit (µg mL <sup>-1</sup> )	0.205	0.080	0.080

### Table.6: Comparison of results of Nickel (II)

### CONCLUSION

The present method is simple, less expensive and more sensitive. The present method is applied successfully for the determination of nickel in alloy steels, aluminum based alloys, vegetable oil and water.

### REFERENCES

[1] G.H. Bell, J.N. Davidson and H. Scarborough, *Text book of physiology and Biochemistry*. E.S. Living stone Ltd., Edinburgh, **1953**, 2, 80.

[2] G. Bertrand and H. Nakamure, Bull. Soc. Chim. Biol., 1934, 16, 1366.

[3] 3. L. Bernard, *Hawk's physiological chemistry* T.M.H. Publishing Company Ltd., New York , **1965**, 14, 565.

[4] N.E. Dixon, C. Gazzola, R.L Blakey and B. Zerver, J. Am. Chem. Soc., 1975, 97, 4131.

[5] E.J. Hewit, Chemistry and Agriculture special publication No. 36, Chem. Society, London, 1979, 91.

[6] R.M. Welch, J. Plant Nutri., 1981, 3, 345.

[7] S.L.C. Ferreira, B.F.Santos, J.B. De Andrade and A,C, Spinola Costa, *Micro Chimica Acta*, **1996**, 122, 109 - 115.

[8] A.K. Malik, K.N. Kaul, B.S.Lark, W. Faube and A.L. Rao J, Turk J Chem, 2001, 25, 99.

[9] A. Kumar and M. Jain, *Chem Anal*, **1992**, 39,73.

[10] A.K. Bansal and M. Nagar, J Indian Chem Soc, 2006,83, 731.

[11] S.N. Boladani, M. Tewari, A. Agarawal and K.C. Sekhan, Fr J Anal Chem, 1994, 349, 478.

[12] T. Odashima, K. Kohata, K. Yogi and H.Ishii, Bunseki Kagaku, 1995,44(2), 135.

[13] A. Praveenkumar, P.Raveendr Reddy and V.Krishna Reddy, *Indian Journal of Chemistry*, **2007**,46A, 1625-1629.

[14] B. Sritha and T. Sreenivasulu Reddy, *IOSR Journal of applied Chemistry*, 2014, 7(3), 22-26.

[15] Rehana Khanam, Saba Khanam and Rekha Dashora, Oriental Journal of Cemistry, 2014, 30(2), 834-841.

[16] K. Arunabai, G.V.S. Vallinath, K.B. Chandrsekhar and N. Devanna, *RASĀYAN J Chemistry*, 2010,3(3),467-472.

[17] W.J. Barreto, S.R.G. Barreto, I.S.S. Scarmino, D.N. Ishiwaka and M.D. Fatima, *Quim. Nova*, **2010**, 33(1),109-113.

[18] R.B. Singh, P. Jain and R.P.Singh, Talanta, 1982, 29, 77.

[19] M. Gangadharappa, P. Ravindrareddy, V. Krishna Reddy and T. Sreenivasulu Reddy, *Journal of Indian Chemical Society*, **2004**,81(4),525-527.

[20] A.I.Vogel, A Textbook of Quantitative Inorganic Analysis, 1989, 5, 327.

[21] 21. F.D.Snell, Photometric and Fluorometric methods of Analysis, John Wiley New York, 1978.