
Chapter – 5

SPECTROPHOTOMETRIC DETERMINATION OF NICKEL(II)

INTRODUCTION

Nickel usually occurs in +2 oxidation state. It is one of the important alloying elements for steel and cast iron. It is equally important as a catalyst in the hydrogenation of oils. The possibility that nickel may be an essential micro nutrient¹⁻³ for plants arose from urease, which is a nickel metallo-enzyme. Nickel in nature is mainly available in combination with arsenic, antimony and sulphur. The chief ore of nickel is garnierite, a magnesium nickel silicate of variable composition. However, it is capable of forming compounds containing Ni, Ni⁺² and Ni⁺⁴. Previously, nickel was used as a coinage metal. Nickel is used in the steel industry of great tensile strength and toughness.

Nickel is a very important metal for both industrially and biologically. It is a constituent of many materials like alloys, platings, ceramics and electronic circuits. It is used as anode in nickel-cadmium batteries. A nickel-rhodium alloy is used for making reflectors, pen points and other chemical equipment. Cast iron with an improved strength contains 2.5% of nickel. Nickel possesses certain interesting qualities, which make it an important constituent in biological systems⁴. It is one among the essential trace elements along with cobalt, copper, zinc and manganese in the human diet⁵. Bertran and Nakamura⁶ observed in their experiments on synthetic nutrition that nickel and cobalt play a direct role in nutritional phenomenon. Nickel, which is bound to ribonucleic acid, has a special affinity for bone and skin and has been suggested to play an important role in pigmentation⁷. Koch et al.⁸ reported that normal human plasma contains 0.01 to 0.085 ppm of nickel. Nickel is widely distributed in plant and animal tissues⁹.

Many organic reagents are employed for the determination of nickel. Among them oximes, xanthates, Schiff bases, hydrazones, semicarbazones, thiosemicarbazones, dithiols, mercaptanes, dithiocarbamates etc. are some important complexing agents. Dimethyl glyoxime (DMG) is the most widely used reagent for the spectrophotometric determination of nickel¹⁰. The method is empirical and depends on number of experimental conditions. Number of metal ions which react with DMG interfere in this method. The method was used for the determination of nickel in sea water¹¹, food stuffs¹², biological materials¹³, urine¹⁴, soils¹⁵ and oils¹⁶. Nickel is possessing chromophoric properties and gives colour reactions with many organic reagents. Among the several reagents employed, dioximes¹⁷⁻²² are unique in their specificity and are fairly sensitive of which dimethyl glyoxime²³ is the outstanding. The photometric methods for determination of nickel(II) have been reviewed from time to time by several authors²⁴⁻²⁶.

Many semicarbazones and thiosemicarbazones were also used as reagents for the determination of nickel. Some of them are biacetylmonoxime thiosemicarbazone²⁷, ortho-phthalaldehyde thiosemicarbazone²⁸, biacetyl-monoxime-4-phenyl-3-thiosemicarbazone²⁹, Di-2-pyridyl ketone thiosemicarbazone³⁰, methyl thienyl ketone thiosemicarbazone³¹, furointhiosemicarbazone³², quinolin-2-aldehyde thiosemicarbazone³³, 2,2'-dihydroxybenzophenonethiosemicarbazone³⁴, picolinaldehyde thiosemicarbazone³⁵, p-anisaldehyde thiosemicarbazone³⁶ and 2,4-dihydroxyacetophenone thiosemicarbazone³⁷. Salim et al.³⁸ studied 5,5-dimethyl-1,2,3-cyclohexane trione 1,2-dioxime 3- thiosemicarbazone as a reagent for the spectrophotometric determination of nickel. Lemus Gallego et al.³⁹ studied spectrophotometrically nickel(II) complexes with oxime thiosemicarbazones. Various spectrophotometric methods recently proposed for the determination of nickel are

reviewed and listed in Table 5.1. In the present study, the author has employed 2-amino acetophenone isonicotinoyl hydrazone (2-AAINH) for the spectrophotometric determination of nickel (II).

Present investigations

Nickel (II) gives light yellow colour with 2-amino acetophenone isonicotinoyl hydrazone (2-AAINH) in the pH range 3.0- 11.0. By measuring the intensity of the light yellow colour, a spectrophotometric method was developed for the determination of nickel (II) in aqueous medium.

Table 5.1
Analytical results of various spectrophotometric methods for Nickel (II)

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ ($\text{l mol}^{-1} \text{cm}^{-1}$)	Beer's law limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
4-chloro-2-nitroso-1-naphthol and crystal violet	611	-	8.2	-	-	40
2, 2'-dihydroxy benzophenone thiosemicarbazone	380	-	0.154	-	Applied to the analysis of nickel in binary, ternary and quaternary mixtures	41
1-(1,2,4-triazolyl-3-azo)-2-naphthol	523	5.0	3.7	0.2-2.8	Applied to the determination of nickel in steels	42
2-(5-bromo-2-pyridylazo)-5-diethyl amino phenol	560	5.5	12.6	0-15.0	This method has been determined nickel in steels.	43
1-(2-pyridylazo)-2-naphthol-6-sulphonic acid	570	-	5.6	1.0-10.0	-	44
2-(2-thiazolyazo)-5-dimethyl amino benzoic acid	-	5.0-9.5	9.5	0.05-0.5	Cu, Cr, Co, Pd and Fe interfere	45
2-(2-benzothiazolylazo)-5-dimethyl aminobenzoic acid	-	5.0-9.5	12.0	0.05-0.5	Cu, Cr, Co, Pd and Fe interfere	45
Bis (4-phenyl-3-thiosemicarbazone)	460	2.5	2.28	0.2 - 2.0	-	46
Cyclohexylidene - ammonium 2-aminocyclohexylidene -1-dithiocarboxylate	550	6.0-9.0	2.5	-	-	47
Ethylthio xanthate	495	4.0-6.7	-	-	Applied successfully for the determination of nickel in various complex materials.	48
Bromazepam	-	Greater than 11	2.02	-	-	49
O, O'-diethyl dithiophosphate	385	1.0-7.0	0.084	-	The determination of Ni (II) was affected with many diverse ions.	50
Chemical reduction of Ni (II) with formaldehyde	562	5.5-6.0	5.58	-	-	51

Table 5.1 (continued)

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ * (l mol ⁻¹ cm ⁻¹)	Beer's law ** limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
2-(2-thiazolylazo)-P-cresol	580	5.7	2.6	20-70 μg	Applied successfully to determination of nickel in reference samples.	52
3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine	610	6.8	22.1		Applied to the determination of traces of nickel in steels and aluminium chips	53
Ammonium 2-amino-1-cyclohexene-1-dithio carbonate	535	3.0-8.0	2.8	Upto 4.0	Applied to the determination of nickel in vegetable oil.	54
2-(2-(4-methylquinolyl)azo)-5-diethyl amino phenol	-	-	-	-	-	55
P-acetylarsenazo	630	6.0	6.5	0-0.8	Applied to the determination of nickel in aluminium alloy	56
Hydroxy naphthol blue	563	5.2-6.0	1.38	upto 3.2	Co (II), Ti (IV), Al (III), Hg(II), and Cu (II) are interferes	57
Benzothiazolyldiazo amino benzene	550	9.4	19.6	0-7.0	Applied to the determination of nickel in aluminium alloy	58
PAN	568	3.0-10.0	4.8	upto 0.8	Cu (II), Fe (II), Mn (II), Pb (II) and Zn (II) are interferes	59
2-[2-(6-methylbenzothiazolyl)azo]-5-(N-methyl-N- sulfomethyl) aminobenzoic acid.	642	Weak acidic medium	8.81	0-7.0	Applied to the determination of nickel in aluminium alloys and alloy steels.	60
2-[2-(6-methylbenzothiazolyl)azo]-5-(N-ethyl-N- sulfomethyl) aminobenzoic acid.	620	Weak acidic medium	8.22	0-6.0	Applied to the determination of nickel in aluminium alloys and alloy steels.	60
2-[2-(6-methylbenzothiazolyl)azo]-5-(N-ethyl-N- carboxyl methyl) aminobenzoic acid.	625	Weak acidic medium	10.3	0-12.0	Applied to the determination of nickel in aluminium alloys and alloy steels.	60
5-(6-methoxy-2-benzothiazoleazo)-8-amino quinoline	623	-	12.8	0-0.32	Applied to the determination of trace amounts of nickel in aluminium alloy	61

Table 5.1 (continued)

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ * ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	Beer's law ** limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
Azocalix [4] arene	580	Basic medium	12.8	0.17-5.1	Applied to the determination of trace amount of Ni(II) in certified samples.	62
Sodium Isoamyl Xanthate	360	6.0-8.0	1.2	2.0-37.0	Applied to the determination of nickel in stainless steels and Monal alloy	63
Imino dibenzyl and chloro iminodi benzyl	-	-	-	-	Applied to the determination of nickel in industrial effluents and soil samples.	64
O-Carboxyl benzene diazo-amino benzene	540	10.0	33.0	-	The method has been used for the determination of nickel in food samples.	65
1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone	395	Acid medium	-	-	Applied to the determination of nickel in edible oils and seeds.	66
O-Carboxyl phenyl diazo amino benzene	588 & 800	9.0	$2.95 \times 10^{-7} \text{ g mol}^{-1} \text{ cm}^{-1}$	$1.2-41 \mu\text{g g}^{-1}$	Applied to the determination of nickel in water and vegetable samples.	67
3,4-tetra hydroxy-3'- sulfo-5'-nitroazo benzene	490	4.0	1.52	-	The method was applied to the synthetic mixtures	68
Dimethyl glyoximato complex	470	12.0	-	0.26-2.1	The proposed extraction method is applied to the determination of nickel in steel	69
N, N'-bis (3-methyl salicylidene)-ortho-phenylene diamine	430	8.0	9.5	$0-1.0 \times 10^{-5} \text{ M}$ of Ni	Applied to determination of trace amounts of nickel in some natural food samples.	70
2,4-Dihydroxy benzaldehyde isonicotinoyl hydrazone	400	6.0	4.0	0.059-1.17	Applied to the determination of nickel in alloy steels and vegetable oil.	71
2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone	410	6.0	2.05	0.058-2.347	Applied to aluminium based steels and vegetable oil.	72

* and ** unless otherwise indicated

Table 5.1 (continued)

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ * ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	Beer's law ** limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
2-[(2-Mercaptophenylimino)Methyl]Phenol	421	10.5	2.41×10^5	0.011- 0.30	wastewater and standard alloy	73
Bis [3-Hydroxyimino-5-Methyl-Nmethyl]- 2-Imine	415	9.2	1.42×10^3	0.01-40	Extraction	74
3,5-Dimethoxy-4-hydroxy benzaldehyde isonicotinoyl hydrazone	386	9.0	1.22	0.234-2.94	Derivative spectrophotometry	75
Dopasemiquinone	590	7.5	9.3×10^3	3.33×10^{-5} to 1.78×10^{-4} mol L^{-1} .	Heating and time is required. Applied to complex samples, such as inox .etc.	76
4-Hydroxy 3,5 dimethoxy benzaldehyde 4- hydroxy benzoyl hydrazone	408	9.0	3.22	0.058-0.586	Neutral surfactant TritonX-100 (5%) (micellar medium)	77
Cinnamaldehyde 4- hydroxybenzoylhydrazone	400	9.0	2.171	0.146-1.467	Neutral surfactant TritonX-100 (5%) (micellar medium)	77
2-Acetylpyridine-4-methyl-3- thiosemicarbazone	375	6.0	2.16	0.235 - 2.43	Extraction method	78
5-Bromo-2-hydroxyl-3-methoxy benzaldehyde-4-hydroxybenzoic hydrazone	440	6.0	2.01	0.117-2.64	-	79
2-Amino Acitophenone Isonicotinoyl Hydrazone	470	9.0	1.05	0.29–6.16	–	Present method

* and ** unless otherwise indicated

Section i : Zero order spectrophotometric determination of nickel (II)

a. Absorption spectra

The absorption spectra of 2-AAINH and its nickel (II) light yellow coloured complex [Ni- AAINH] were recorded in the wavelength range 350-600 nm at pH 9.0 against the buffer solution and reagent blank respectively. Typical spectra are presented in Fig. 5.i.1. The absorption spectra of nickel (II) complex show maxima at 470 nm, while the reagent blank shows negligible absorbance. Hence, analytical studies were measured at 470 nm.

b. Effect of pH

The effect of pH on the colour formation was studied to arrive at the optimum pH by adopting procedure 3b. A plot was made between pH and absorbance and presented in Fig. 5.i.2. It can be seen that maximum colour was obtained in the pH range 8.0-9.5. Therefore the pH 9.0 was selected for further studies.

c. Effect of reagent concentration

The optimum concentration of the reagent required for the maximum colour formation was arrived at by following the procedure 3c and measuring the absorbance at 470 nm. The results are presented in Table 5.i.1.

The results were indicated that a 20 fold molar excess of the reagent is necessary for maximum colour development which was maintained through the studies.

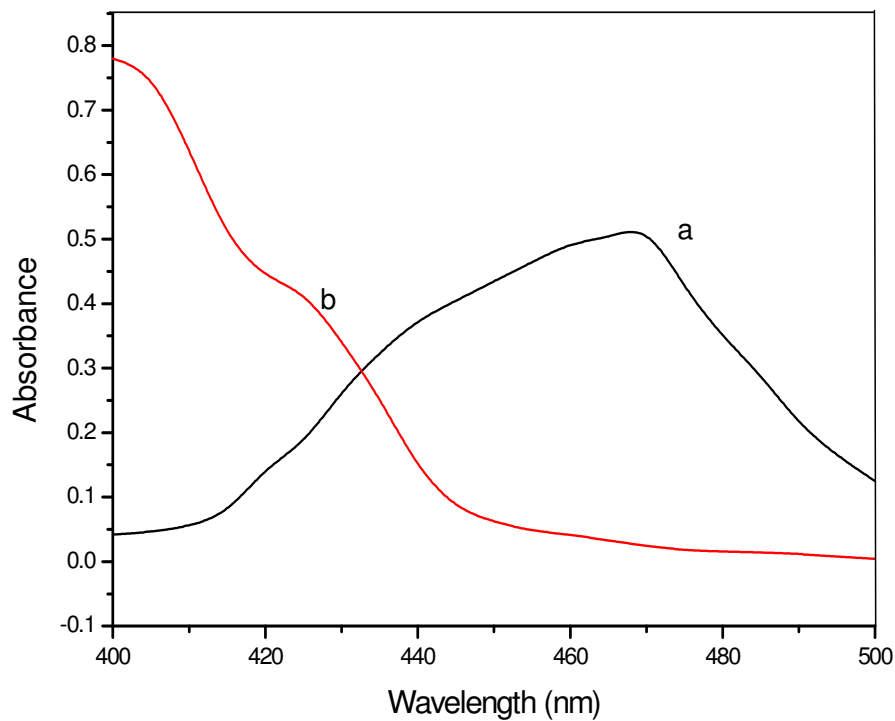


Fig. 5.i.1

Absorption spectra of

a) [Ni(II) – AAINH] Vs reagent blank

b) 2-AAINH Vs Buffer blank

[Ni(II)] = 5×10^{-5} M; [AAINH] = 2.5×10^{-4} M; pH = 9.0

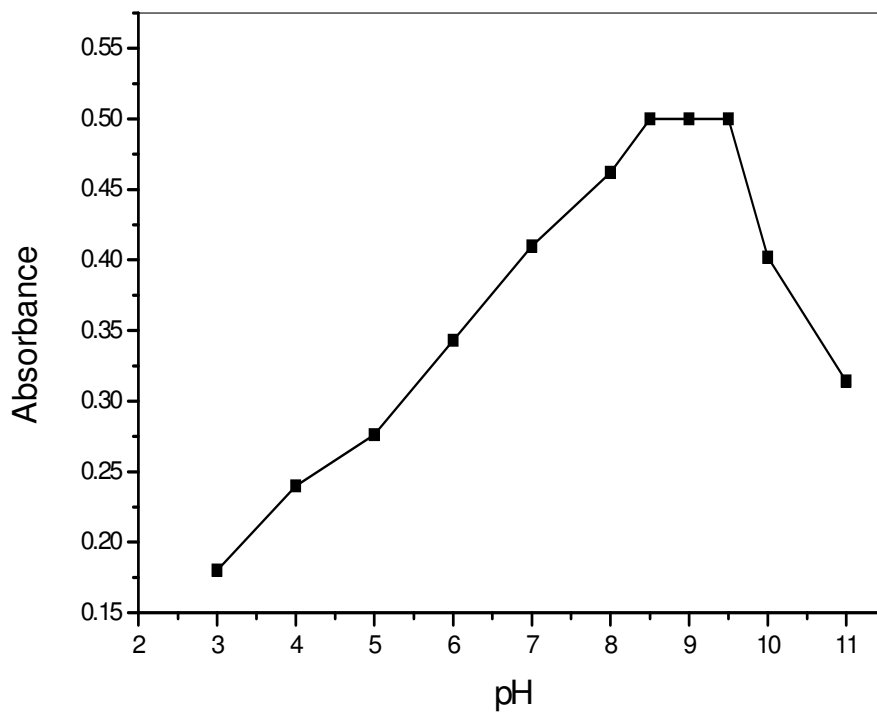


Fig. 5.i.2.

Effect of pH on absorbance of Ni(II) – 2-AAINH

[Ni(II)] = 5×10^{-5} M ; [AAINH] = 2.5×10^{-4} M

Wavelength = 470nm

d. Time stability of the colour of the reaction mixture

The absorbance of the solution was measured at different time intervals to ascertain the time stability of the colour of the complex as described in 3d. It was noticed that the light yellow colour development was instantaneous and remained constant for more than 48 hours.

Table 5.i.1: Effect of 2-AAINH concentration

$$\text{Ni (II)} = 5 \times 10^{-5} \text{ M}$$

$$\text{pH} = 9.0$$

$$\text{Wavelength} = 470 \text{ nm}$$

[Ni(II)] : [2-AAINH]	Absorbance
1 : 5	0.102
1 : 10	0.195
1 : 15	0.215
1 : 20	0.485
1 : 25	0.430
1 : 30	0.425

e. Adherence of the system to Beer's law

The plot between absorbance and the amount of Ni (II) under optimal conditions was established by following the procedure 3e and presented in Fig. 5.i.3. The straight line obeys the equation $A_{470} = 0.136C + 0.042$. Further, Beer's law was obeyed in the range of 0.29-6.16 $\mu\text{g mL}^{-1}$. The molar absorptivity and Sandell's sensitivity were $1.05 \times 10^4 \text{ lit mol}^{-1} \text{ cm}^{-1}$ and $0.0056 \mu\text{g cm}^{-2}$ respectively. The standard deviation for ten determinations of $1.1738 \mu\text{g mL}^{-1}$ of nickel is ± 0.0081 .

Statistical analysis of results

In the spectrophotometric determination of Ni (II), the results were treated by adopting statistical analysis and the results are presented in Table 5.i.2.

The results in the Table 5.i.2 confirm the validity and reproducibility of the present method.

Table 5.i.2: Statistical analysis for the determination of Ni (II)

Parameter	Ni(II) – 2-AAINH
Angular coefficient (m)	0.136
Y-intercept (b)	0.042
Correlation coefficient (r)	0.998
Standard deviation (s)	± 0.0081

f. Effect of foreign ions

The effect of various anions and cations on the determination of Ni (II) under optimal conditions was studied by the procedure in 3f. The results are presented in Table 5.i.3.

Almost all the studied anions do not interfere even when present in more than 200 fold excess. The tolerance limits of the cations are also reasonably high. Further, Pd (II), Mn (II) and Mo (VI) interferes when present in 20-45 fold excess. Cu (II) and Co (II) interferes seriously.

Composition and stability of the complex

The composition of the complex was determined using Job's method and confirmed by molar ratio method.

g. Job's method

For Job's method the procedure described in 3g was adopted. The results present in Fig. 5.i.4 indicate a 1:1 stoichiometry between the metal ion and the reagent under the experimental conditions.

Table 5.i.3: Tolerance limits of foreign ionsAmount of Ni (II) = 1.173 $\mu\text{g mL}^{-1}$

Foreign ion	Tolerance limit ($\mu\text{g mL}^{-1}$)	Foreign ion	Tolerance limit ($\mu\text{g mL}^{-1}$)
Ascorbic acid	1660	Cd (II)	740
Tartrate	1500	Te(IV)	600
Bromate	1080	W(VI)	550
Thiosulphate	1020	Na(I)	450
Sulphate	950	Th(IV)	350
Citrate	890	Ti(IV)	320
Phosphate	880	Li(I)	270
Oxalate	840	Mg(II)	220
Bromide	800	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
		Pd(II)	20
		Cu(II)	5
		Co(II)	5

The stability constant of the complex was calculated from Job's method and obtained as 5.747×10^9 .

h. Molar ratio method

Molar ratio method was followed using the general procedure 3h. The results are presented in Fig. 5.i.5 that confirms a 1:1 complex formation between the metal ion and the reagent.

Applications

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

Two untreated water samples collected from different places around Anantapur town (A.P) have been analyzed after treating the water sample using the procedure 3r and alloys were brought into the solution by the procedure 3(l). The amount of nickel present in drinking water and alloy samples was determined by the following procedure.

Procedure

A known aliquot of the sample solution was taken in a 10 ml flask containing 5ml of buffer solution (pH 9.0), and 1ml of the 2-AAINH solution (1×10^{-2} 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 Tables 5.i.4 and 5.i.5.

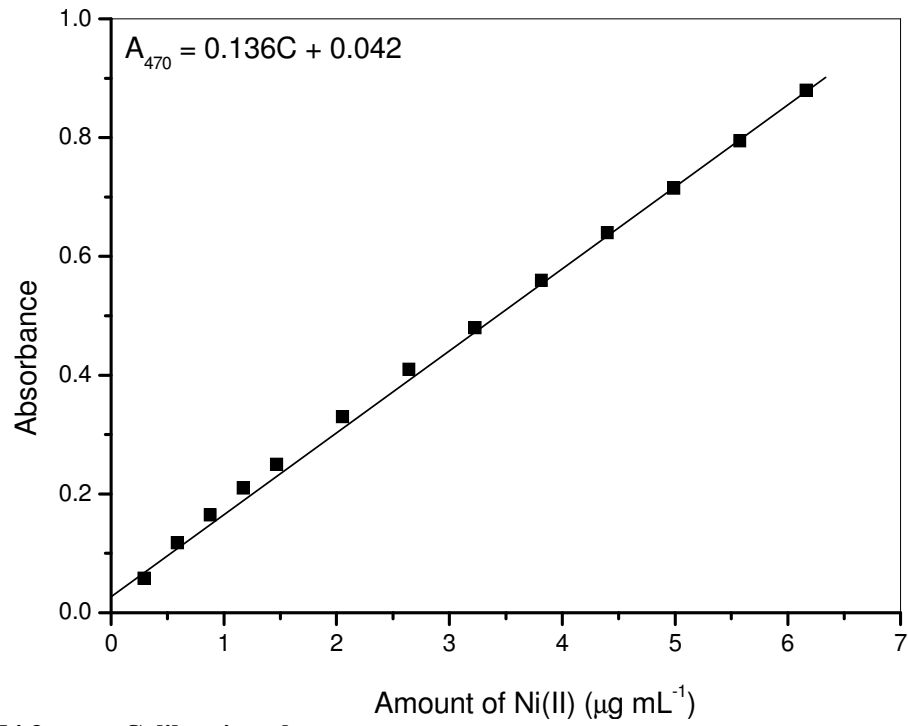


Fig. 5.i.3. Calibration plot
 [2-AAINH] = 8×10^{-4} M
 Wavelength = 470 nm
 pH = 9.0

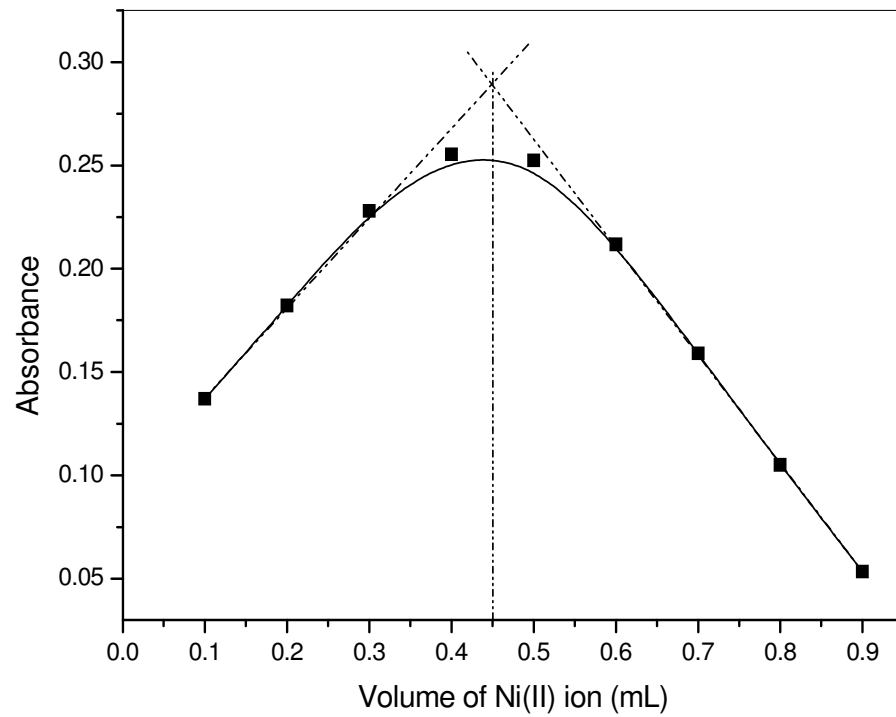


Fig. 5.i.4. Job's curve
 [Ni(II)] = [2-AAINH] = 1×10^{-3} M
 Wavelength = 470 nm ; pH = 9.0

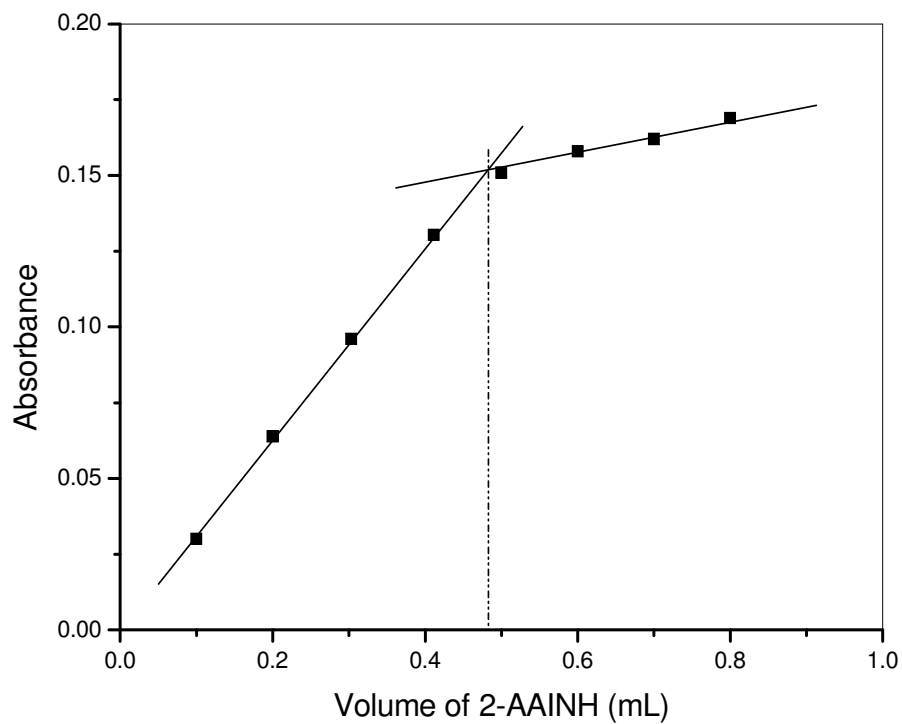


Fig. 5.i.5. Molar ratio plot
 [Ni(II)] = [2-AAINH] = 1×10^{-3} M
 Wavelength = 470nm; pH = 9.0

Table 5.i.4: Determination of nickel in drinking water

Water Sample	Amount of Ni (II) $\mu\text{g mL}^{-1}$			Recovery (%)	
	Added	Found *		Present method	AAS method
		Present method	AAS method		
1	-	1.5	1.48	-	-
	1.0	2.52	2.50	100.8	100.0
	2.0	3.48	3.52	99.4	100.5
2	-	2.0	2.02	-	-
	1.0	2.97	3.05	99.0	101.6
	2.0	4.05	4.00	101.2	100.0

* Average of Five determinations

Table 5.i.5: Determination of nickel in aluminum based alloys

Sample	Certified composition (%)	Amount of nickel (%)		Recovery (%)
		Present	Found*	
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

* Average of Five determinations

Section ii : Derivative spectrophotometric determination of nickel (II)

Nickel (II) forms a light yellow coloured complex with 2- amino acetophenone isonicotinoyl hydrazone (2-AAINH) in basic medium. The coloured solution was systematically studied to develop highly selective first and second derivative spectrophotometric methods for the determination of trace amounts of nickel (II). The results are presented in this section.

The first and second derivative spectra of light yellow coloured nickel (II)-2-AAINH complex were recorded in the wave length region 350-580 nm at pH 9.0 for various amounts of Ni (II) by the procedure described in 3i and are shown in Figs. 5.ii.1 and 5.ii.3 respectively.

The first derivative spectra show a maximum peak at 476 nm. The second derivative spectra show a peak at 485 nm and valley at 445 nm with a zero cross at 462 nm. Therefore 476 nm for first order and 485 nm, 445 nm for second order derivative spectrophotometric determination of nickel were selected respectively.

First derivative method

The first derivative spectra of [Ni (II)-2-AAINH] colored complex for different concentrations of Ni (II) were recorded in the wave length region 350-580 nm and presented in Fig5.ii.1. The derivative amplitudes (zero to peak) at 476 nm was found to be proportional to the concentration of nickel (II) solution. The derivative amplitudes were measured at 476 nm for different concentrations of Ni (II) and plotted against the amount of nickel (II) (Fig5.ii.2). The plot was linear in the range 0.1-3.20 $\mu\text{g mL}^{-1}$ of Ni (II).

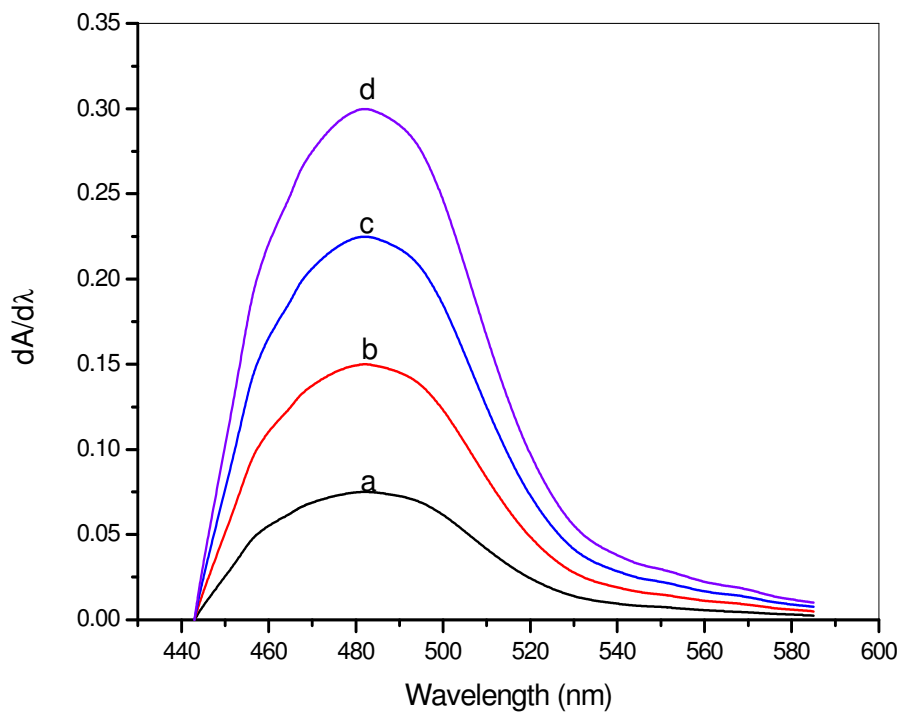


Fig. 5.ii.1. First derivative spectra of
 Ni(II) – 2-AAINH Vs reagent blank
 Ni(II) ($\mu\text{g mL}^{-1}$) = (a) 0.2342; (b) 0.4694; (c) 0.7041; (d) 0.9888

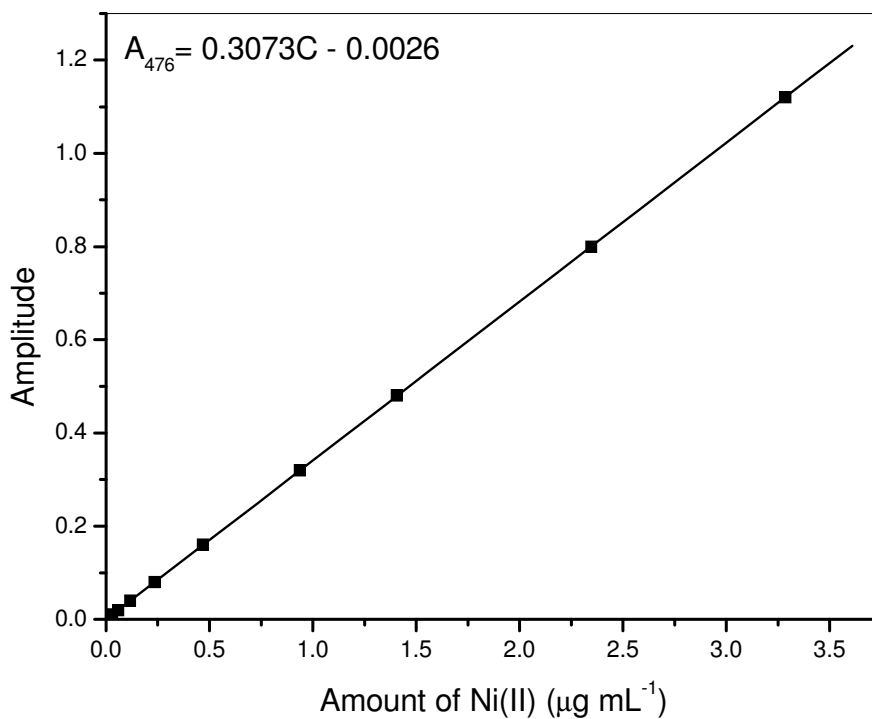


Fig. 5.ii.2. Beer's law plot of first derivative data
 [2-AAINH] = 8×10^{-4} M
 pH = 9.0

Second derivative method

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 and presented in Fig5.ii.3. 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) (Fig5.ii.4). The plots were linear in the range 0.1-3.0 $\mu\text{g mL}^{-1}$ at 445 nm and 0.1-3.25 $\mu\text{g mL}^{-1}$ of Ni (II) at 485 nm.

Effect of foreign ions

The effect of various cations and anions were examined by applying the method to a fixed amount of nickel in the presence of increasing amounts of the ion being studied by following the general procedure 3k. The tolerance limit was taken as the amount that caused an error of $\pm 2\%$ in the absorbance. When compared to the zero order method, the tolerance limits to larger number of ions which were very low in the zero order method, were found to be much higher in the derivative method. This shows the greater selectivity of the derivative methods, when compared to zero order method. The results obtained in the studies are presented in Table 5.ii.1.

Table 5.ii.1: Effect of diverse ions

S. No.	Diverse Ion	Zero Order	First Derivative	Second Derivative
1.	Mo(VI)	45	>100	>150
2.	Mn(II)	30	>100	>150
3.	Pd(II)	20	85	>100
4.	Cu(II)	5	35	80
5.	Co(II)	5	25	65

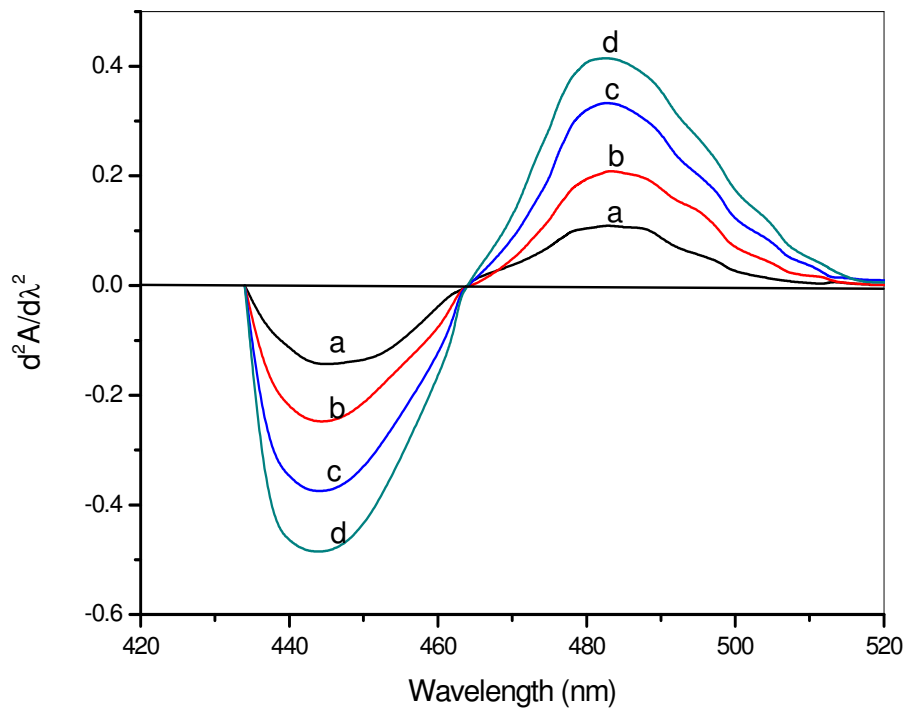


Fig. 5.ii.3. Second derivative spectra of Ni(II) – 2-AAINH Vs reagent blank
 Ni(II) ($\mu\text{g mL}^{-1}$) = (a) 0.2342; (b) 0.4694; (c) 0.7041; (d) 0.9888

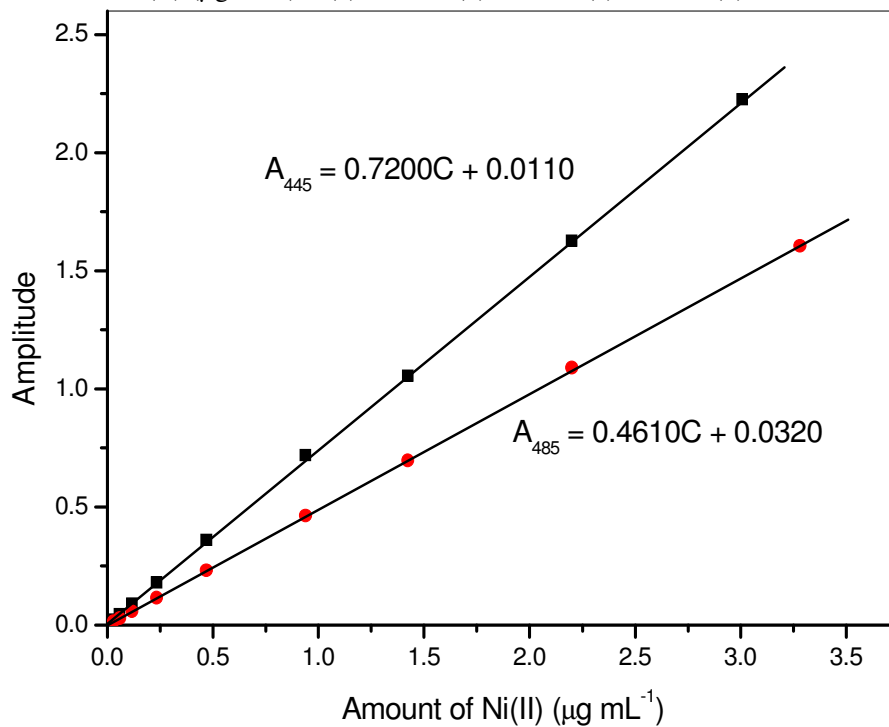


Fig. 5.ii.4. Beer's law plot of Second derivative data
 [2-AAINH] = 8×10^{-4} M
 pH = 9.0

Applications

Ni (II) was determined in alloy steels and vegetable (groundnut) oil samples by second derivative spectrophotometric method. The alloy steel samples and vegetable oil samples were brought into the solution using the procedure 3(l) and 3t respectively.

Procedure

To known aliquots of the samples taken in 10ml volumetric flasks, 5ml of buffer solution of (pH 9.0), 1ml of 2-AAINH ($1 \times 10^{-2}M$) 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 485 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 5.ii.2 and 5.ii.3.

Table 5.ii.2: Determination of nickel in alloy steel samples

Sample	Certified composition (%)	Amount of nickel (%)		Relative error (%)
		Present	Found*	
Copper-nickel alloy	Cu 67; Fe 0.83; Mn 0.08; Si 0.29; Ni 31.20.	31.20	31.32	+0.38
Alloy NTPC Ball bearing material	Fe 65; Cr 15; Cu 4.5; Mn 2; Ni 10.00.	10.00	10.15	+1.50
BCS 364	Cu 80.00; Sn 9.35; Pb 9.25; Ni 0.28; Sb 0.18; Zn 0.13; As 0.065; P 0.056; Al 0.002; Si 0.003.	0.280	0.285	+1.78
Gun metal	Zn 1.37; Sn 9.22; Cu 87.95; Pb 1.13; Fe 0.01; P 0.07; Ni 0.24.	0.240	0.238	-0.83
Monel	Ni 63.01; C 0.15; S 0.002; Mn 0.07; Si 0.05; Fe 2.50; Cu 31.0	63.01	63.95	+1.49

* Average of five determinations

Table 5.ii.3: Analysis of vegetable oils

Sample	Amount of nickel found ($\mu\text{g mL}^{-1}$)		Relative error (%)
	AAS method	Present method*	
Hydrogenated ground nut oil	0.56	0.575	+0.87

* Average of five determinations.

Comparison of results

The analytical characteristics of the zero order, 1st and 2nd order derivative methods in the present investigations for Ni (II) were compared and presented in Table 5.ii.4. The results indicated that the derivative methods are more sensitive than the zero order method.

Table 5.ii.4: Comparison of results of Nickel (II)

Parameter	Zero order	First derivative	Second derivative	
Analytical wave length (nm)	470	476	445	485
Beer's law range ($\mu\text{g mL}^{-1}$)	0.29–6.16	0.1-3.2	0.1-3.0	0.1-3.25
Molar absorptivity ($\text{Lmol}^{-1}\text{cm}^{-1}$)	1.05×10^4	-	-	-
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.0056	-	-	-
Stability constant	5.747×10^9	-	-	-
Angular coefficient (m)	0.136	0.3073	0.72	0.461
Y-intercept (b)	0.042	0.0026	0.0110	0.032
Correlation coefficient (r)	0.998	0.999	0.9999	0.9999
Standard deviation	± 0.0081	± 0.0075	± 0.0065	± 0.0062
Detection limit ($\mu\text{g mL}^{-1}$)	0.067	0.039	0.023	0.023
Determination limit ($\mu\text{g mL}^{-1}$)	0.205	0.125	0.080	0.080

Discussion

The present direct spectrophotometric method is simple, fast, and sensitive for the determination of Ni (II). The metal ion reacts with 2-amino acetophenone isonicotinoyl hydrazone forming light yellow coloured water soluble complex in basic pH condition. The yellow colour was stable for more than 48 hours. The absorption spectrum of [Ni (II) - 2-AAINH] complex showed maximum absorbance at 470 nm, the reagent absorbance was negligible at this wavelength. A 20 fold molar excess of reagent was necessary to obtain maximum colour intensity with a given amount of metal ion.

The complex system was found to obey Beer's law in the range 0.29-6.16 $\mu\text{g mL}^{-1}$ with Molar absorptivity $1.05 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, Sandell's Sensitivity $5.6 \times 10^{-3} \mu\text{g cm}^{-2}$. The present method was applied for the determination of nickel in drinking water and in aluminium based alloys.

The stoichiometric studies on the yellow coloured water soluble complex showed a 1:1 composition. The stability constant of the complex was calculated as 5.747×10^9 . The analytical results obtained by the proposed method are in good agreement with the amounts of Ni (II) added. In order to improve the sensitivity and selectivity of the analytical method proposed, an attempt has been made to develop derivative spectrophotometric methods for the determination of nickel (II), in which Beer's law range is improved and tolerance limits of interference ions such as Co (II), Cu (II) and Pd (II) which were low in the direct method were improved in derivative method. The derivative method was applied for the determination of nickel in alloy steels and vegetable oil samples. The results of the present method were compared with those of some of the reported spectrophotometric methods and are presented in Table 5.ii.5.

The results reveal that the present method is non-extractive, comparable in its sensitivity and selectivity with some of the reported methods establishing its place among the spectrophotometric methods for the determination of nickel.

Table 5.ii.5: Analytical results of various spectrophotometric determinations for Nickel

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	Beer's law* limits ($\mu\text{g mL}^{-1}$)	Remarks	Ref. No
4-chloro-2-nitroso-1-naphthol and crystal violet	611	-	8.2	-	-	40
2, 2'-dihydroxy benzophenone thiosemicarbazone	380	-	0.154	-	Applied to the analysis of nickel in binary, ternary and quaternary mixtures	41
2-(5-bromo-2-pyridylazo)-5-diethyl amino phenol	560	5.5	12.6	0-15.0	This method has been determined nickel in steels.	43
O, O'-diethyl dithiophosphate	385	1.0-7.0	0.084	-	The determination of Ni (II) was affected with many diverse ions.	50
Ammonium 2-amino-1-cyclohexene-1-dithio carbonate	535	3.0-8.0	2.8	Upto 4.0	Applied to the determination of nickel in vegetable oil.	54
Hydroxy naphthol blue	563	5.2-6.0	1.38	upto 3.2	Co (II), Ti (IV), Al (III), Hg(II), and Cu (II) are interferences	57
2-[2-(6-methylbenzothiazolyl)azo]-5-(N-methyl-N- sulfomethyl) aminobenzoic acid.	642	Weak acidic medium	8.81	0-7.0	Applied to the determination of nickel in alluminium alloys and alloy steels.	60
2-[2-(6-methylbenzothiazolyl)azo]-5-(N-ethyl-N- sulfomethyl) aminobenzoic acid.	620	Weak acidic medium	8.22	0-6.0	Applied to the determination of nickel in alluminium alloys and alloy steels.	60
2-[2-(6-methylbenzothiazolyl)azo]-5-(N-ethyl-N- carboxyl methyl) aminobenzoic acid.	625	Weak acidic medium	10.3	0-12.0	Applied to the determination of nickel in alluminium alloys and alloy steels.	60
Sodium Isoamyl Xanthate	360	6.0-8.0	1.2	2.0-37.0	Applied to the determination of nickel in stainless steels and Monal alloy	63

Table 5.ii.5 (continued)

Reagent used	λ_{\max} (nm)	pH	$\epsilon \times 10^4$ ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	Beer's law* limits ($\mu\text{g mL}^{-1}$) M of Ni	Remarks	Ref. No
N, N'-bis (3-methyl salicylidene)-ortho-phenylene diamine	430	8.0	9.5	$0-1.0 \times 10^{-5}$	Applied to determination of trace amounts of nickel in some natural food samples.	70
2,4-Dihydroxy benzaldehyde isonicotinoyl hydrazone	400	6.0	4.0	0.059-1.17	Applied to the determination of nickel in alloy steels and vegetable oil.	71
2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone	410	6.0	2.05	0.058-2.347	Applied to aluminium based steels and vegetable oil.	72
5-Bromo-2-hydroxyl-3-methoxy benzaldehyde-4-hydroxybenzoic hydrazone	440	6.0	2.01	0.117-2.64	-	79
2-Amio Acetophenone Isonicotinoyl Hydrazone	470	9.0	1.05	0.29-6.16	Applied to aluminium based steels, drinking water and vegetable oil	Present method

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