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Non-Extractive Spectrophotometric Determination of Nickel In Alloy Samples Using Salicylaldehyde Isonicotinoylhydrazone

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ABSTRACT

A very simple, highly selective and non - extractive Spectrophotometric method for the trace amounts of nickel (II) has been developed. Salicylaldehyde isonicotinoylhydrazone (SAINH) has been proposed as a new analytical reagent for the direct non- extractive Spectrophotometric determination of nickel (II). The reagent reacts with nickel in a basic medium (pH 7.5, sodium acetate and acetic acid) to form a yellow coloured 1: 1(M : L) complex. The reaction is instantaneous and the maximum absorption was obtained at 385 nm and remains stable for 1h. The molar absorptivity and Sandell's sensitivity were found to be 1.81 x 10^4 L mol^{-1} cm^{-1} and 0.32 µg cm^{-2} respectively. Linear calibration graphs were obtained for 1.0 -10.0 µg ml^{-1} of nikel(II). The method is highly selective for nickel and successfully used for the determination of nickel in several standard reference materials (steels and alloys).

Keywords: Spectrophotometric determination, salicylaldehyde isonicotinoylhydrazone, alloy and steel samples, molar absorptivity and Sandell's sensitivity.

INTRODUCTION

Nickel is a silvery white, lustrous metal with a slight golden tinge. It is hard and ductile. Pure nickel shows a significant chemical activity, can be observed when it is powdered to maximize the exposed surface area on which reactions can occur, but larger pieces of the metal are slow to react with air at ambient conditions due to the formation of a protective oxide surface.

Naturally occurring nickel is composed of 5 stable isotopes ^{58}Ni,^{60}Ni,^{61}Ni,^{62}Ni and ^{64}Ni and^{58}Ni is the most abundant (68.08%),^{62}Ni is the most stable nuclide of all the existing elements [1]. The common oxidation states of nickel is +2, but compounds of Ni, Ni^{+} and Ni^{3+} are well known and Ni^{4+} has been demonstrated [2].Because of the nickel slow rate of oxidation at room temperature, it is considered as a corrosion resistant. Because of this it has been occasionally used as substitute for decorative silver. It is used for plating metals such as iron and brass, for chemical apparatus and in certain alloys that retain a high silvery polish such as german silver. Compound of nickel is used as catalyst for hydrogenation. Enzymes of some microorganisms and plants contain nickel as an active site which makes the metal an essential nutrient for them. It is used in many specific and recognizable industrial and consumer products including stainless steel, alnico magnets, coinage, rechargeable batteries, electric guitar strings, microphone capsules and special and alloys. Nickel is absorbed by inhalation and ingestion. The immediate effects of nickel carbonyl exposure are respiratory tract irritation and neurological effects, nausea, vomiting, diarrhea and head ache. Delayed effects include pulmonary oedema, pnuemonitus and in severe case causes death.

In natural water environment, nickel concentration is generally small because of its occurrence in a colloidal form. It is easily accumulated in the biological environment, particularly in the phytoplankton or other aquatic plants which are sensitive bio- indicators of water pollution. Since nickel is extensively used in the preparation of alloys and catalysts, its determination may be considered as interesting research activity. Various spectrophotometric methods used for the determination of nickel are summarized in table 1 [3-13].

Table 1. Spectrophotometric methods for the determination of nikel (II) with different reagents

Name of the reagent	λ_{max} **(nm)**	pH	Beers law(ppm)	Molar absorptivity **(ε)** **L mol^{-1} cm^{-1}**	M:L	Ref
Molybdophosphoric acid	490	4.3	0.0-5.0	$0.13x10^4$	1:1	3
4-(5-utiro-2-thiozolylazu resorcinol)	540	6.5	4.0	$1.0x10^4$	1:1	4
Sodium isoamylxanthate	360	6.0-8.0	0.2-2.7	$1.2x10^4$	1:2	5
Pthalaldehyde dithiosemicarbazone(PADT)	400	7.5-9.0	Upto4.5	$0.81x10^4$	1:1	6
Quinolaldehyde thiosemicarbazone(QAH)	460	7.5	5.0-25.0	$1.6x10^4$	1:2	7
Salycilaldehyde thiosemicarbazone(SAT)	370	6.5-7.0	0.5-5.0	$0.98x10^4$	1:1	8
Acenapthaquinone thiosemicarbazone(ANQT)	420	6.3-8.4	Upto14.7	$0.28x10^4$	1:2	9
Diacetylmonoxime-4-phenyl-3-thiosemicarbazone(DAMOPT)	375	5.2-10.0	-	$1.7x10^4$	-	10
2-hydroxy-4-isopropoxy acetophenone thiosemicarbazone (HIAT)	400	9.0	1.6-4.4	$0.08x10^4$	1:2	11
2-(2-Furanylmethylene)hydrazine carbothioamide (FMHC)	440	5.8	0.36-6.0	$0.72x10^4$	1:2	12
1-phenyl-1,2-propanedione-2-thiosemicarbazone(PPDOT)	395	3.0-6.0	1.8-3.7	$1.2x10^4$	1:2	13
Salicylaldehyde isonicotinoylhydrazone(SAINH)	378	1.0-10.0	7.5	$1.81x10^4$	1:1	Present method

MATERIALS AND METHODS

Preparation of SAINH: Salicylaldehyde (1.05 ml, 0.01mol) and isoniazid (0.69g, 0.01 mol dissolved in 3 mL of ethanol) were mixed in a clean round bottom flask. Suitable quantity of (~10mL) of ethanol was added to the reaction mixture and refluxed with stirring for 2 h. A pale yellow coloured product was separated out on cooling. It was collected by filtration, washed several times with hot water. This compound was recrystalized from methanol and dried in vacuum. Yield is 2.8 g, melting point is 250 – 252°C.

Preparation of SAINH solution: It was prepared by taking 0.060 g of SAINH reagent substance in a 25mLstandard flask. The regent substance was dissolved in 10 mL of DMF and diluted upto the mark with the same solvent.

Preparation of nickel (II) ion solution *:* Stock solution (1×10^{-2}M) of Ni(II) was prepared by dissolving requisite quantity (0.25 g) of nickel sulphate ($NiSO_4.7H_2O$) in doubly distilled water containing a few drops of conc.H_2SO_4 and made upto 100-ml volumetric flask. The stock solution was standardized gravimetrically [14].

Recommended procedure *:* An aliquot of the solution containing nickel in optimum concentration range , 10 ml of buffer solution (pH 7.5) and 1 mL of 0.01M reagent solution were combined in 25 mL volumetric standard flask and resulting solution was diluted to the mark with distilled water. The absorbance of the solution was measured at 385 nm against reagent (SAINH) blank. The measured absorbance was used to compute the amount of nickel from predetermined calibration plot.

Preparation of Alloy sample *:* 100 mg of alloy sample was dissolved in aquaregia and evaporated on hot water bath to dryness. The residue was dissolved in minimum amount of dilute hydrochloric acid and transferred into 50 mL standard flask quantitatively. The contents were diluted to the mark with distilled water.

Instrumentation: Perkin – Elmer (Lamda 25), UV – Visible spectrophotometer equipped with 1.0 cm (path lenth) quartz cell and Elico model LI- 610 pH meter were used in the present study.

RESULTS AND DISCUSSION

The reagent (SAINH) are easily obtained by condensation reaction and is shown in Fig 1.

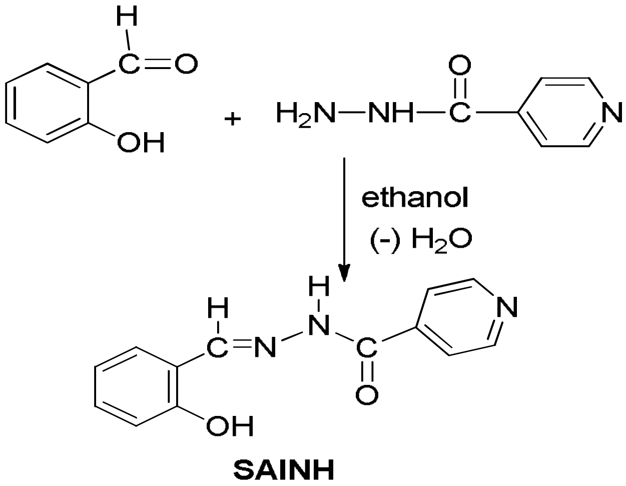


Fig 1. Condensation reaction of SAINH

It has been characterized using IR, NMR and Mass spectral data. The infrared spectrum of SAINH showed bands (cm^{-1}) at 3271(m), 3120(m), 3051(m), 1649(s), 1619(s), 1535(m),1473(s), 1290(s), 768(s), 711(s) and 682(m), are respectively assigned to ν (NH) secondary stretching, ν (C-H) stretching, (isoniazid), ν (C-H) aromatic stretching (salicylaldehyde), ν (C=0) isonicotinoyl stretching, ν (N-H) plane bending, ν (C- C) aromatic ring stretching, ν (C-H) asssymetric bending, ν (C-N) streching vibrations, ν (C-H) aromatic oop bend(salicylaldehyde) and ν (N-N) stretch and ν (C-H) aromatic oop bending respectively. This spectrum is shown in Fig 2.

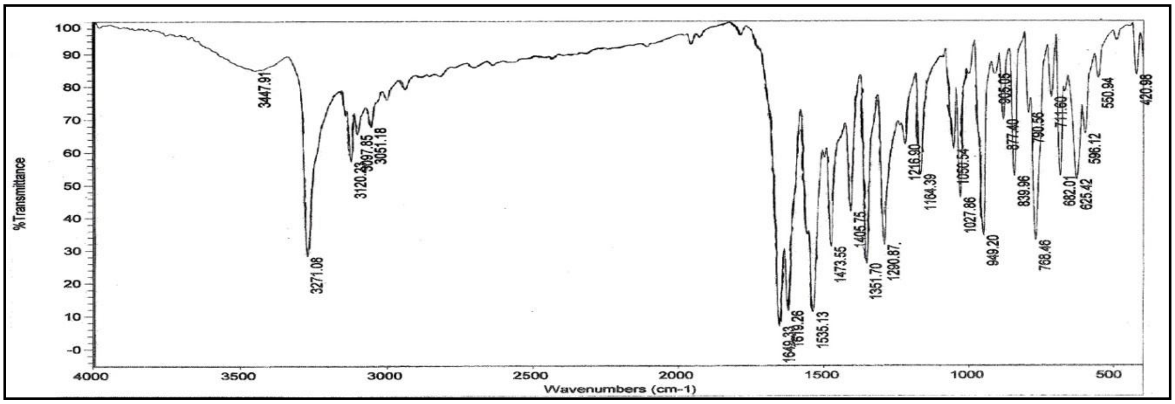
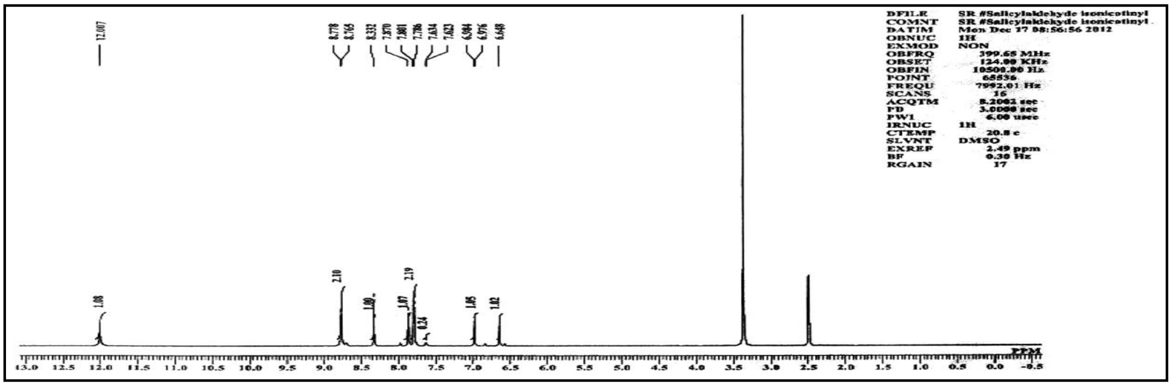


Fig 2. Infrared Spectrum of SAINH in KBr disc

^{1}H – NMR spectra (DMSO –d^6) showed signals (δ ppm) at 6.65, 7.786-7.801 and 8.33 due to - CH$_3$, - OH (aliphatic), phenolic and - NH$_2$ protons of SAINH respectively. NMR spectrum is shown Fig 3.



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COMNT    SR #Salicylaldehyde isonicotinyl
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OBNUC    1H
EXMOD    NON
OBFRQ       399.65 MHz
OBSET       124.00 KHz
OBFIN     10500.00 Hz
POINT        65536
FREQU      7992.01 Hz
SCANS          16
ACQTM       8.2002 sec
PD          3.0000 sec
PW1          6.00 usec
IRNUC    1H
CTEMP        20.8 c
SLVNT    DMSO
EXREF        2.49 ppm
BF           0.30 Hz
RGAIN          17
```

Fig 3. ^{1}H-NMR Spectrum of SAINH in DMSO – d$_6$ medium

Massspectra shows molecular ion signal at m/z 241. Other peaks are observed at m/z values of 240 and 163 respectively due to the loss of -H and -C$_5$H$_4$N radicals (Fig 4). Based on above spectral data the structure of the reagent is given in Fig 1.

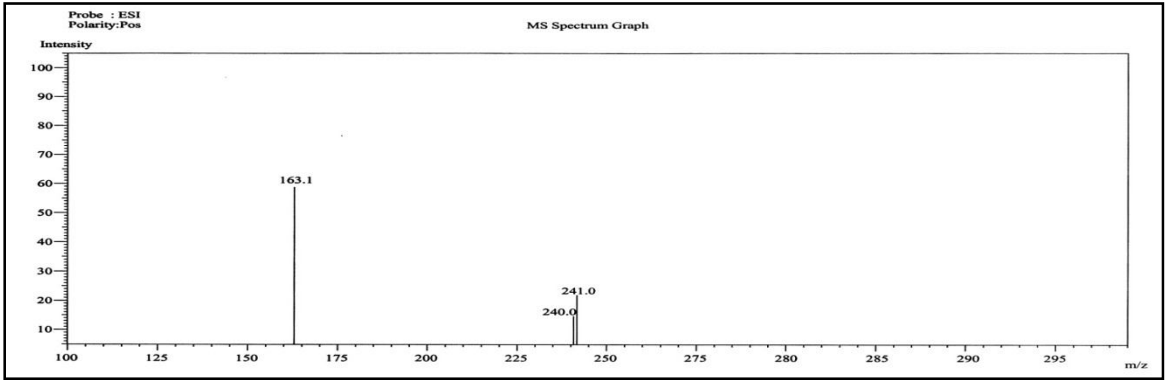

Fig 4. Mass Spectrum of SAINH in DMSO – d$_6$ medium

Absorption spectra of 2x10^{-5} solution of SAINH at different pH values were recorded and pKa values were determined spectrophotometrically using Phillip and Merrit method [15]. The bathochromic shift from 295 – 365 nm indicates that in solution on increasing pH the >C=0 group of the reagent (SAINH) is enolised and dissociated. The values of SAINH are 4.2(pK_1) and 9.0 (pK_2) respectively. The pK_1 and pK_2 values are presumably due to keto – enol tautomerism and deprotonation of - NH group respectively.

A 0.01M solution of reagent is stable for 1h. The colour reactions of reagent with nickel (II) are instantaneous at room temperature. The order of addition of nickel ion, reagent and buffer has no effect on the absorbance of the complex. Various physico – chemical and analytical characteristics of nickel complex are summarized in Table 2.

Table 2. Physico – chemical and analytical characteristics of Ni(II) – SAINH complex

S. No.	**Characteristics**	**Results**
1	λ_{max} (nm)	385
2	pH range (optimum)	7.0 – 8.0
3	Mean absorbance	0.235 ± 0.0004
4	Mole of reagent required per mole of metal ion for full colour development	10 fold
5	Time stability of the complex (in minutes)	1 hr
6	Beer's law validity range (μg/ml)	1.0 – 10.0
7	Molar absorptivity (lit $mol^{-1}cm^{-1}$)	1.81×10^4
8	Specific absorptivity (ml $g^{-1}cm^{-1}$)	0.308
9	Sandell's sensitivity my of Cu(II) cm^{-2}	0.320
10	Composition of the complex as obtained in Job's and molar ratio methods	1 : 1
11	Stability constant of the complex	13.48×10^4
12	Standard deviation in the determination of 1.17 μg/ml of Ni(II) for ten determinations	0.0060
13	Relative Standard deviation (RSD) %	2.55
14	Y–intercept	–0.0064
15	Angular co–efficient	0.0826
16	Detection limit (μg/ml)	0.0765
17	Determination limit (μg/ml)	0.2297

Stoichiometry of the complex (M : L = 1 : 1) was determined by Job's continuous variation method and molar ratio method. Sodium acetate (1M) –acetic acid (0.1M) buffer (pH 7.5) is used in these studies. The dissociation constant (α) and concentration (c) of the reagent at intersecting point were used in the calculation of stability constant of the complex. Stability constant of the complex 1: 1 (M : L) complex is given by $1\text{-}\alpha / \alpha^2 c$. The predicted structure of Ni (II) – SAINH is given in Fig 5.

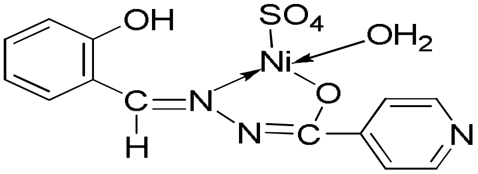

Fig 5. Predicted structure of Ni – SAINH complex

Tolerance limits of foreign ions *:* The effect of foreign ions which often accompany nickel has been studied by adding different amounts of foreign ions to fixed amount of nickel (II) in solution. The colour reaction was studied as described in the standard procedure. An error of ±2% in the absorbance of the reaction mixture was considered tolerable. The results were presented in Table 3. Larger amounts of Cd(II) and Co(II) do not interfere in the presence of masking agent thiocyanate.

Table 3. Tolerance limit of foreign ions in the determination of 4.69 µg ml^{-1} of Nickel

Ion added	**Tolerance limit µg/ml**	**Ion added**	**Tolerance limit µg/ml**
Citrate	544.2	U(VI)	95.2
Iodide	504.2	W(VI)	59
Phosphate	392	Cd(II)	27a
Oxalate	352	Mn(II)	22
Tartrate	296	Cr(VI)	12.5
Nitrate	248	Pb(II)	8.2
Sulphate	192	Co(II)	2.4a
Bromide	160	As(I)	4.1
Chloride	142	Ti(II)	2.4
Carbonate	120	Pt(IV)	2.0
Acetate	94	Pd(II)	0.90
Fluoride	78	Zn(II)	0.23
Thiourea	31		

a : Masked with 200µg ml^{-1} of thiocyanate

APPLICATIONS

The present method was successfully applied for the determination of nickel in various certified Reference materials and the results were presented in Table 4.

Table 4. Amount of nickel(%) present in various alloy samples

Sample	**Amount of Nickel* in µg/ml**		**Error**
	Taken	**Found**	
BCM- 406[a]	1.5210	1.5230	0.2%
Nickel[b] Silver	10.0560	10.0520	0.4%
BAS – 106[c]	1.9315	1.9375	0.6%

* Average of three determinations

a = low alloy steel : Mn 0.61%, Cr 2.1%, Mo 1.00%, Ni 1.52%, Co 0.006%, Cu 0.28%, V 0.017%
b = Nickel silver : Cu 65%, Zn 25%, Ni 10%
c = BAS – 106 : Ni 1.93%, Cu 4.1%, Fe 0.43%, Mn 0.2% and Mg 1.61%CC

CONCLUSIONS

The synthesized reagent salicylaldehyde isonicotinoylhydrazone (SAINH) is characterized by analytical and spectral studies. The reagent forms a yellow coloured complex with nickel (II). The Ni (II)-SAINH complex structure is predicted and various physico-chemical and analytical characteristics are determined. This reagent SAINH is successfully used for the determination of nickel (II) in various alloy samples.

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