A Simple Spectrophotometric determination of nickel in alloy samples using Salicylaldehyde acetoylhydrazone (SAAH)

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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 acetoylhydrazone (SAAH) has been proposed as a new analytical reagent for the direct non- extractive Spectrophotometric determination of nickel (II). The reagent reacts with nickel (II) in a slightly acidic medium (pH 6.5, sodium acetate and acetic acid buffer) to form a yellow coloured 1 : 1(M : L) complex. The reaction is instantaneous and the complex shows absorption maximum (λmax) at 380 nm and remains stable for 3h. The molar absorptivity and sandell's sensitivity are found to be 1.875×10^4 L mol^{-1} cm^{-1} and 0.313 µg cm^{-2} respectively. The system obeys Beer's law in the range for 1.0 - 9.0 µg/ml of nickel (II). The method is highly selective for nickel and successfully used for the determination of nickel in several Standard reference materials such as steels and alloys.

Key words: Spectrophotometric determination, salicylaldehyde acetoylhydrazone, 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 a hard and ductile. Pure nickel shows a significant chemical activity that can be observed when it is powdered to maximize the surface area on which reactions can occur. Naturally occurring nickel is composed of 5 stable isotopes ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni, and^{64}Ni. ^{58}Ni is most abundant (68.08%), ^{62}Ni is the most stable nuclide of all the existing elements[1]. The common oxidation state of nickel is +2, but compounds of Ni, Ni$^+$ and Ni3+ are well known and

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Ni $^{+4}$ has been demonstrated[2]. It is considered corrosion resistant. It is used in many specific and recognizable industrial and consumer products including stainless steel, alnico magnets, coinage, rechargeable batteries, electric guitar strings, microphone capsule and special alloys. It is also used for plating as a green tint in glass. Because of its resistance to corrosion, nickel has been occasionally used as a substitute for decorative silver. Nickel carbonyl is the most toxic nickel compound following acute inhalation exposure. Chronic inhalation of nickel compounds can cause rhinitis, sinusitis, anosmia and in extreme cases perforation of the nasal septum. Since nickel is extensively used in the preparation of alloys and catalysts, its determination is considered as interesting research activity.

This paper describes the non - extractive spectrophotometric determination of nickel (II) using salicylaldehyde acetoylhydrazone (SAAH) in aqueous medium. In continuation of our ongoing work, we report here the spectrophotometric determination of nickel in various alloy samples. A close literature survey reveals that SAAH is so for not been employed for the spectrophotometric determination of nickel (II). This method is far more selective, simple and rapid than the existing spectrophotometric methods. The comparision of spectrophotometric methods for the determination of nickel (II) is given in Table 1.

Results and discussion:

The reagent (SAAH) are easily obtained by condensation reaction. It has been characterized using IR, NMR and Mass spectral data. IR and NMR spectras are shown in

Fig. 1 and Fig. 2 respectively. The infra red spectrum of SAAH showed bands (cm^{-1}) 3074(m), 2946(m), 1681(s), 1616(s), 1574(m), 1339 (m), 1265(s) are respectively assigned to ν (CH) aromatic stretch, ν(CH) aliphatic stretch, ν(C = O) amide stretch,ν(C = N)azomethine stretch, ν(C-C) aromatic stretch, ν (OH) plane bending vibrations, and ν(C-N) stretch vibrations respectively. ^{1}H – NMR spectra (DMSO –d^{6}) showed signals (δ ppm) at 1.95, 6.82 – 6.90, 8.31 and 11.60 due to - CH$_3$, phenyl ring, - OH, and - NH (imino) protons of SAAH

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respectively. Mass spectra shows molecular ion signal at m/z 178. Other peaks are observed at m/z values of 177, 163 and 135 respectively, due to the loss of hydrogen, methyl and acetyl radicals. Based on above spectral data the structure of the reagent is given in Fig 3.

Absorption spectra of 2×10^{-5} solution of SAAH at different pH values were recorded and pKa values were determined spectrophotometrically using Phillip and Merritt method. The bathochromic shift from 270 – 360 nm indicates that in solution on increasing pH the >C=O group of the reagent (SAAH) is enolised and dissociated. The values of SAAH are 3.0 (pK_1) and 8.0 (pK_2) respectively. The pK_1 and pK_2 values are presumably due to keto – enol tautomerism and deprotonation of - OH group respectively.

A 0.01M solution of reagent is stable for 10h. The colour reactions of metal ions with the reagent are summarized in Table 2. In the basic medium (above pH 8.0) the ligand presumably exist in enolic form.

The color reaction of reagent with nickel (II) is instantaneous at room temperature. The order of addition of metal 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 3. Stoichiometry of the complex (M : L = 1 : 1) was determined by Job's continuous variation method and molar ratio method. Sodium acetate (0.2M) – acetic acid (0.2M) buffer (pH 5.0) and equimolar solutions of nickel (II) and reagent were used in these studies. The dissociation constant (α) and concectration (c) of the reagent of 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 $1-\alpha /\alpha^2 c$. The predicted structure of Ni^{II} – SAAH complex is given in Fig 4.

Tolerance limits of foreign ions : The effect of foreign ions which often accompany nickel (II) 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 recommended procedure. An error of 2% in the absorbance of the reaction mixture was considered tolerable. The results

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are given in Table 4. Interference of Zinc (II) is masked with thiocyanate and cadmium (II) is masked with citrate.

Applications : The present method was successfully applied for the determination of nickel in various certified reference materials and the results were presented in Table 5.

Experimental:

Preparation of SAAH : The reaction mixture containing salicylaldehyde (1.043 ml, 0.01 mol) in 5

ml of ethanol, acetoylhydrazide (0.74 gms, 0.01 mol) dissolved in 10 ml of ethanol were taken in 250 ml round bottom flask and refluxed for 3h with stirring. A pale yellow coloured product was separated on cooling the reaction mixture. It was collected by filtration and washed several times with 50 percent cold methanol. This compound was recrystallised from methanol and dried in vaccum. Percetage of yield is 88, m.p -202 -204^{0}C.

The reagent solution (0.01M) was prepared by dissolving 44 mg of the compound in dimethylforamide (DMF) in 25 - ml volumetric flasks. The reagent solution was stable for atleast 10h.

Hydrochloric acid (1M) - sodium acetate (1M) (pH 0.5 – 3.5) ; sodium acetate (0.2M) – acetic acid (0.2M) (pH 4.0 – 6.5) and ammonium chloride (0.2M) – ammonium solutions (0.2M) (pH 7.5 – 10.5) were used in the preparation of buffer solutions.

Preparation of nickel (II) ion solution : A 1 x 10^{-2} M stock solution of divalent nickel was prepared by dissolving 0.25g of nickel sulphate (Merck, Darmstadt) in deionised water containing few drops of concentrated sulphuric acid and made upto the mark in a 100 mL volumetric flask. The resulting solution was standardiised gravimetrically[3].

Recommended procedure : An aliquot of the solution containing nickel in optimum concentration range (Table 2), 10 ml of buffer solution (pH 6.5) and 1 ml 0.01M reagent solution were combined in 25 – ml volumetric standard flask and resulting solution was diluted to the mark with distilled water[4,5]. The absorbance of the solution was measured at 380 nm against reagent (SAAH) blank. The measured absorbance was used to compute the amount of mercury 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.

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Table 1 . Comparison of spectrophotometric methods for the determination ofnickel (II)

Name of the Reference reagent	λmax(nm)	pH	Determination range (µg/mL)	$\varepsilon \times 10^4$ (L mol-1 cm-1)	M:L	
Molybdophosphoric acid	490	4.3	0.0-5.0	0.13	1:1	6
4-methyl-2,3-pentane dienedioxime	370	9.0	0.5-10.0	0.3	1:2	7
Pthalaldehyde dithiosemicarbazone	400		7.5-9.0	0.1-4.5	0.8	1:1 8
Quinolinoldehyde thiosemicarbazone	460	7.5	5.0-25.0	1.6		1:2 9
1-phenyl-1,2-propane dione thiosemicarbazone	395	3.0-6.0	1.8-3.7	1.2	1:1	10
Sailcylaldehyde PM acetoylhydrazone	380		4.0-6.0	1.0-9.0	1.9	1:1

PM – Present method

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Table 2. Chromogenic characteristics of SAAH

Metal ion	λmax (nm)	pH range	Molar absorptivity[a]	Colour of the ion complex
Cu[II]	372	1.0×10^4	5.0 – 7.0	Pale yellow
Ni[II]	380	1.9×10^4	6.5 – 7.5	Yellow
Pb[II]	370	0.9×10^4	8.0 – 9.0	Yellow
Hg[II]	370	1.1×10^4	6.0 – 7.0	Pale greenish yellow
Co[II]	365	1.5×10^4	6.5 – 7.5	Pale yellow

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^{a}L mol^{-1} cm^{-1}

Table 3. Physico – chemical and analytical characteristics o fNi^{II} complex with SAAH

Sl. No.	Characteristics	Ni – SAAH
1.	λ_{max} (nm)	380
2.	pH – range (optimum)	6.5 – 8.0
3.	Mean absorbance	0.235±0.0002
4.	Mole of reagent required per mole of metal ion for 10 fold full color development	
5.	Time stability of the complex (h)	3
6.	Beers law validity range (µg/mL)	1.0 – 9.0
7.	Molar absorptivity (L mol^{-1} cm^{-1})	1.9 x 10^4
8.	Specific absorptivity (ml g^{-1} cm^{-1})	0.319
9.	Sandell's sensitivity (µg/cm^2)	0.313
10.	Composition of the complex as obtained from Jobs and Molar ratio method (M : L)	1 : 1
11.	Stability constant of the complex	6.34 x 10^4
12.	Standard deviation in the determination of 1.90 µg/mL of Ni^{II}	0.0078
13.	Relative standard deviation	3.35
14.	Detection limit (µg ml^{-1})^a	0.1007
15.	Determination limit (µg ml^{-1})^b	0.302

^{a}Detection limit = $\dfrac{\text{Standard deviation} \times 3}{\text{Mean}}$

^{b}Determination limit S/N = 10.

Table 4. Tolerance limit (µg/mL) of foreign ions in the determination of

3.52 (µg/mL) of nickel

Ion added	Tolerance limit	Ion added	Tolerance limit
Bromide	1600	Mo^{II}	38.40
Tartarate	592	Cu^{II}	29.0

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Iodide	507	Mn^{II}	22.0
Sulphate	384	Hg^{II}	8.0
Phosphate	380	Sn^{IV}	6.0
Citrate	354	Co^{II}	5.0
Thiourea	320	Fe^{III}	3.3
Hypo	316	Fe^{II}	2.2
Thiocyanate	248	Zn^{II}	1.3[a]
nitrate	248	Cd^{II}	1.3[b]
Oxalate	176	Al^{III}	0.5
Chloride	142		
EDTA	0.744		

[a]In the presence of 200µg/mL of thiocyanate. [b]In the presence of300µg/mL of citrate..

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Table 5. Determination of nickel in certified reference materials

Name of the certified	Amount of copper¯(%)		
Reference material	Certified Value	Found[a]	%Error
BCM 406[b]	1.55	1.51	0.04
Nickel silver[c]	10.0	10.02	0.02
BAS –106[d]	1.90	1.95	0.05

[a]Average of five determinations.

[b]BCM 406 - Mn 0.61%, Cr 2.1%, Mo 1.00%, Ni 1.52%, Co 0.06%, Cu 0.28%, V 0.0175%.

[c]Nickle silver - Cu 65%, Zn 25% ,Ni 10%.

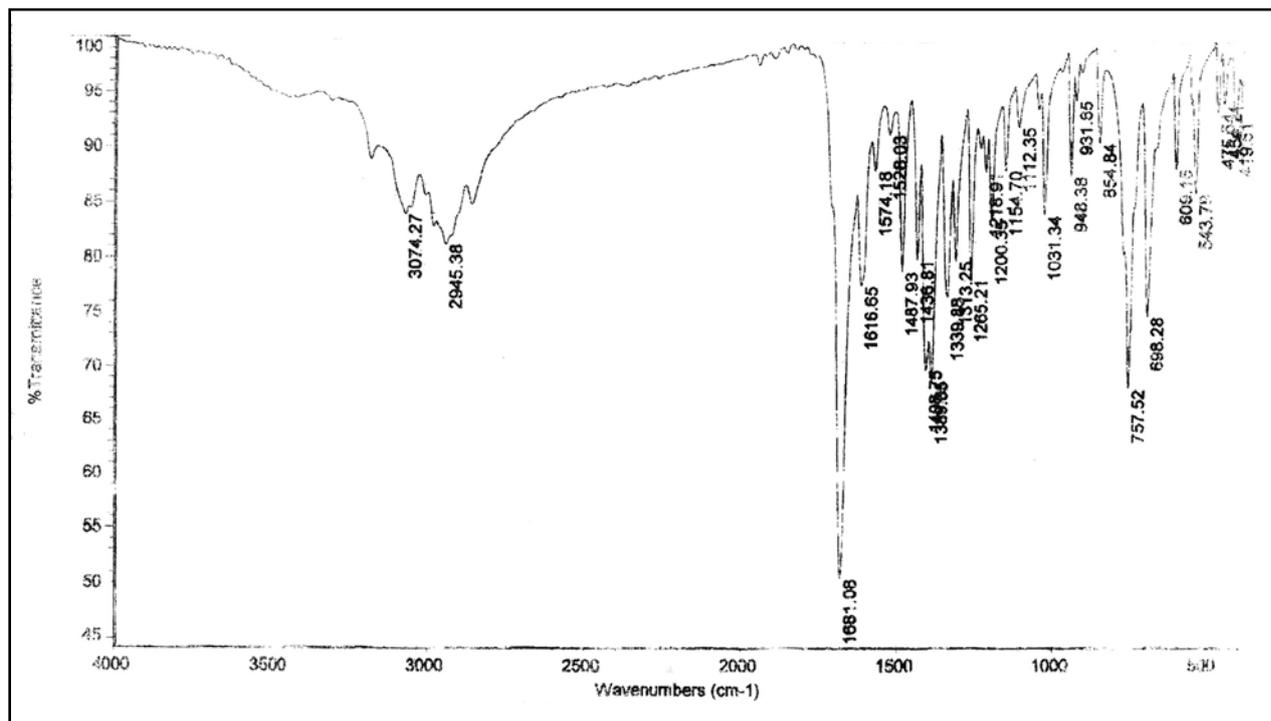[d]BAS-106 - Ni 1.96%, Cu 4,1%, Fe 0.43%, Mn 0.2% and Mg 1.61%.

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Fig. 1. Infrared Spectrum of SAAH in KBr disc

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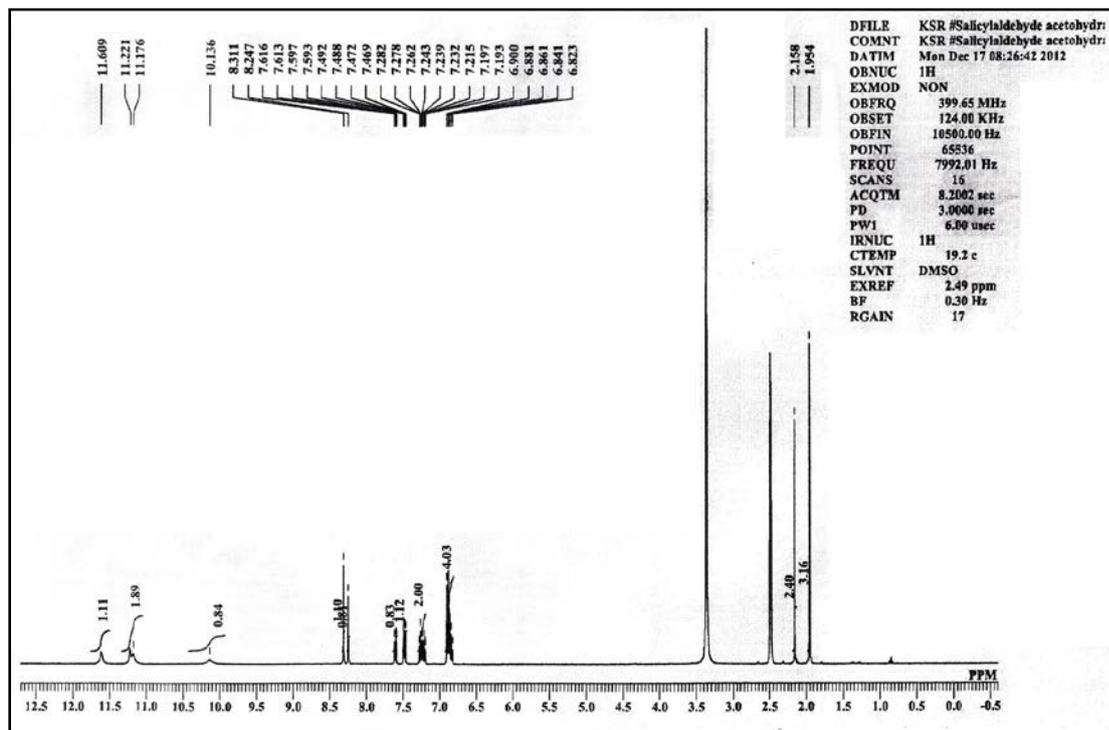
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Fig. 2. ^{1}H-NMR Spectrum of SAAH in DMSO – d$_6$ medium

Fig 3. Structure of reagent (SAAH)
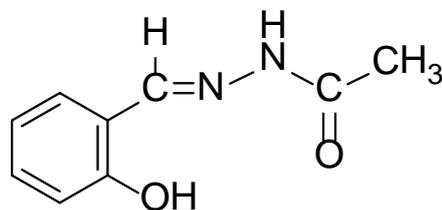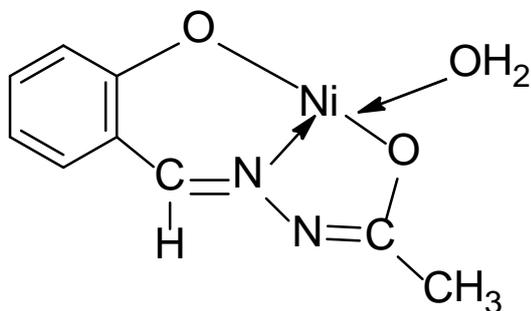

Fig. 4. Predicted structure of Ni – SAAH complex