A decorative border with floral and scrollwork motifs framing the page.

***DETERMINATION  
OF  
NICKLE (II)***

## Determination of Nickel (II)

The main use of Nickel, are in important alloys, electroplating materials and catalysts. The recovery of nickel from ores, alloy, catalysts etc. is commercially important. It is used for hydrogenation of oils and other organic substances. Probably the largest use of nickel is in the manufacturing of stainless steels, and nickel – chrome resistance wire. It is also used in alloys for electronic and space application. It is therefore necessary to separate the variety of materials. Solvent extraction method is an efficient method for the extraction and separation from the other materials

Spectrophotometric determination of nickel have been reviewed by number of analysts<sup>1-3</sup>. Some method also have been developed for spectrometric determination for nickel<sup>4-7</sup>. Several workers<sup>8-10</sup> have used cycloheptane for spectrometric determination for nickel.

Reagent containing sulphur, nitrogen and/or oxygen donor atoms combine with nickel (II) to form coloured complex, which can be extracted into organic solvents. The organic extract can be utilized for spectrometric determination for nickel.

### Procedure for Extraction of Nickel (II)

1 ml solution containing 1 mg of Nickel, taken in a beaker, and mixed with 2 ml of 0.4M sodium acetate solution and 1 ml of 6.0 % isonitrosothiocamphor in alcohol. The pH of the solution was adjusted up to the desire value, with dilute solution of hydrochloric acid or sodium hydroxide, keeping total volume of 10 ml with purified water. The mixture was transferred in a separating funnel and equilibrated for one minute with an equal volume of chloroform. The two phases are allowed to separated out.

The compound was analyzed as anal. Calcd. For  $C_{20}H_{28}N_2O_2S_2Ni$  :

C 53.21%; H 6.20%; N 6.20%; S 14.18%. and Ni 13.01%,

Found C 53.20; H 6.24%; N 6.26%; S 14.12%. and Ni 13.04%

### **Procedure for Spectrophotometer determination of Nickel (II)**

To an aqueous solution (4 ml) containing 50 mcg of Nickel, in a beaker added, 2 ml of 0.4 M sodium acetate solution and 1 ml of 6% Isonitrosothiocamphor in alcohol was added. The pH of solution was adjusted to 7 with the help of dilute solution of hydrochloric acid or sodium hydroxide. The volume of solution maintained up to 10 ml & transfers this mixture into a separator funnel. Mixed the content for one minute with 10 ml of chloroform. The organic layer was collected in a test tube and absorbance of same was taken at 450nm against reagent blank. The amount of Nickel is determined with a calibration curve which was prepared as follows.

A series of solutions containing known amount of Nickel were treated as above prescribed method and a graph of absorbance against concentration of Nickel was plotted. ( Table 8)

### **Procedure for mole ratio curve:**

To a series of solutions containing 8mcg amount of Nickel & increasing amount of reagent in 1 ml of alcohol were added. The colour was developed and extracted with benzene as described above ; absorbance was measured at 450 nm (Table 9)

### **Stability of complex:**

The absorbance of the solution does not deteriorate up to 1 hour. (Refer. Table 10 )

### **Effect of pH:**

It was observed that in pH range colour extracted in solvent was stable up to 60 min. (Refer. Table 11 )

**Results and Observation:**

The extraction of Nickel with isonitrosothiocamphour has been studied at the pH range 1 to 10 . Nickel can be quantitatively extracted by benzene from an aqueous alcoholic solution at 7 – 8 bellow and above of this range the percentage of Nickel decreases .

The selection of organic solvent s are arranged in the following order.  
(Table12)

Benzene>Carbontetrachloride>Chlorobenzene>Butanol>Ether  
> Chloroform>Toluene

## Validation of Analytical Technique <sup>11-13</sup>

**Parameter:** The analytical procedure is prepared for the following parameter.

1. **Specificity:-** Specificity is carried out to check the interference due to diluents in analysis.

**Acceptance Criteria:** The absorbance proves that there is no interference due to diluents indicating method is specific.

2. **Linearity :** Linearity is established by demonstrating that the results obtained, are directly proportional to that concentration. The Solution were prepared at different concentrations level and absorbance was measured.(Table 14)

A graph of concentration v/s absorbance was plotted which is Linear.(Table.2)

3. **Accuracy:** Accuracy of the method was established by recovery experiment known amount of Nickel was added in three different concentration and analysis was performed.

Sr.No.	Qty. added in ppm	Absorbance	Quantity recovered in ppm	% Recovery
1	0	0	0	--
2	75 ppm	0.519	74.68 ppm	99.56 %
3	100 ppm	0.695	100.0 ppm	100.00 %
4	125 ppm	0.869	125.03 ppm	100.02 %
Mean recovery.				99.79%

Mean recovery of 3 level is calculated, which is 99.79% and is in acceptable limit, indicating that method is accurate under the prescribed conditions.

**4. Precision:** Precision of the method was established by performing assay 3 time by same analyst.

Sr. No.	Conc. of Nickel in ppm	Absorbance	% of Nickel
1	100 ppm	0.690	99.28%
2	100 ppm	0.691	99.42%
3	100 ppm	0.698	100.43 %
Mean			99.71 %

Mean of 3 analysis is 99.71 % and is in acceptance limit, indicated that method is validated.

**5. Robustness:** The robustness is proceeded by obtaining the analytical results on the portion of same sample by different analyst.

Sr.No.	Conc. of Nickel in ppm	Analyst	Absorbance	% of Nickel
1	100 ppm	Analyst I	0.696	100.14%
2	100 ppm	Analyst II	0.691	99.42%
3	100 ppm	Analyst III	0.693	99.71 %
Mean				99.75 %

Mean of results of all three analysts is 99.75 % which is in acceptable limit, and indicated that the method is validated.

**Table 8**

**Absorbance measurement of Nickel (II) in Benzene with the help of Isonitrosothiocamphor at different wavelength .**

Concentration of Nickel : 100 ppm  
Volume of chloroform : 10 ml  
Time of equilibrium : 1 min.

Sr. No.	Wavelength	Absorbance
1	350	0.626
2	355	0.618
3	360	0.617
4	365	0.599
5	370	0.596
6	375	0.598
7	380	0.608
8	385	0.615
9	390	0.629
10	395	0.633
11	400	0.630
12	405	0.641
13	410	0.642
14	415	0.650
15	420	0.652
16	425	0.654
17	430	0.658
18	435	0.660
19	440	0.664
20	445	0.666
21	442	0.671
22	442	0.675

Cont.

23	443	0.677
24	444	0.681
25	445	0.682
26	446	0.688
27	447	0.691
28	448	0.692
29	449	0.694
30	450	0.695
31	451	0.693
32	452	0.694
33	453	0.684
34	454	0.682
35	455	0.680
36	456	0.675
37	457	0.671
38	458	0.670
39	459	0.665
40	460	0.660
41	465	0.657
42	470	0.659
43	475	0.648
44	480	0.649
45	485	0.638
46	490	0.627
47	495	0.618
48	500	0.594
49	505	0.540
50	510	0.532



**Cont.**

51	520	0.515
52	530	0.490
53	540	0.355
54	550	0.264
55	560	0.216
56	570	0.188
57	580	0.174
58	590	0.157
59	600	0.147
60	610	0.126

**Table 9**

**Effect of Reagent concentration on the absorbance of Nickel (II) and Isonitrosothiocamphor.**

Concentration of Nickel : 100 ppm  
Organic phase : 10ml Benzene  
Time of equilibrium : 1 min.  
Wavelength : 450 nm

Sr.No.	Volume of Isonitrosothiocamphor	Absorbance
1	0.1	0.551
2	0.2	0.585
3	0.3	0.592
4	0.4	0.630
5	0.5	0.664
6	0.6	0.684
7	0.7	0.692
8	0.8	0.695
9	0.9	0.695
10	1.0	0.695
11	1.5	0.695
12	2.0	0.695



**Table 10**

**Absorbance of Nickel (II) in chloroform with Isonitrosothiocamphor as function of time.**

100 ppm of Nickel (II) in 10 ml of chloroform at pH 7 equilibrated with respect to different time at 450nm.

Sr.No.	Time in minute	Absorbance
1	1	0.691
2	2	0.691
3	3	0.691
4	4	0.691
5	5	0.691
6	10	0.691
7	30	0.691
8	60	0.691
9	90	0.688
10	120	0.688

**Table 11**

**Absorbance of Nickel (II) with the help of Isonitrosothiocamphor in chloroform at different pH**

Concentration of Nickel : 100 ppm  
Organic phase : 10 ml Benzene  
Wavelength : 450 nm.

Sr.No	pH	Absorbance	% extraction
1	1.0	0.085	12.2 %
2	2.0	0.134	27.9 %
3	3.0	0.276	39.7 %
4	4.0	0.510	73.3 %
5	5.0	0.638	91.79 %
6	6.0	0.695	100.00 %
7	7.0	0.695	100.00 %
8	8.0	0.695	100.00 %
9	9.0	0.687	98.8 %
10	10.0	0.672	96.6 %

**Table 12**

**Extraction of Nickel (II) with Isonitrosothiocamphor using different solvent**

Organic phase : 10 ml

Time of equilibrium : 1 min.

Sr.No.	Solvent	Absorbance	% extraction
1	Benzene	0.691	100.0%
2.	Carbon tetra chloride	0.585	100.0%
3.	Chlorobenzene	0.461	98.5%
4.	Butanol	0.451	97.0%
5.	Ether	0.211	92.0%
6.	Chloroform	0.208	85.5%
7.	Toluene	0.095	82.3%

**Table 13**

**Absorption measurement of Nickel (II) extracted with different concentration of benzene at pH 7**

Concentration of Nickel : 100 ppm  
Organic phase : 10 ml Benzene  
Time of equilibrium : 1 min.  
Wavelength : 450 nm

Sr.No.	Volume of Benzene	Absorbance
1	5	>1
2	10	0.691
3	15	0.462
4	20	0.346
5	25	0.275
6	50	0.137

**Table 14**

**Calibration Curve for Nickel (II)**

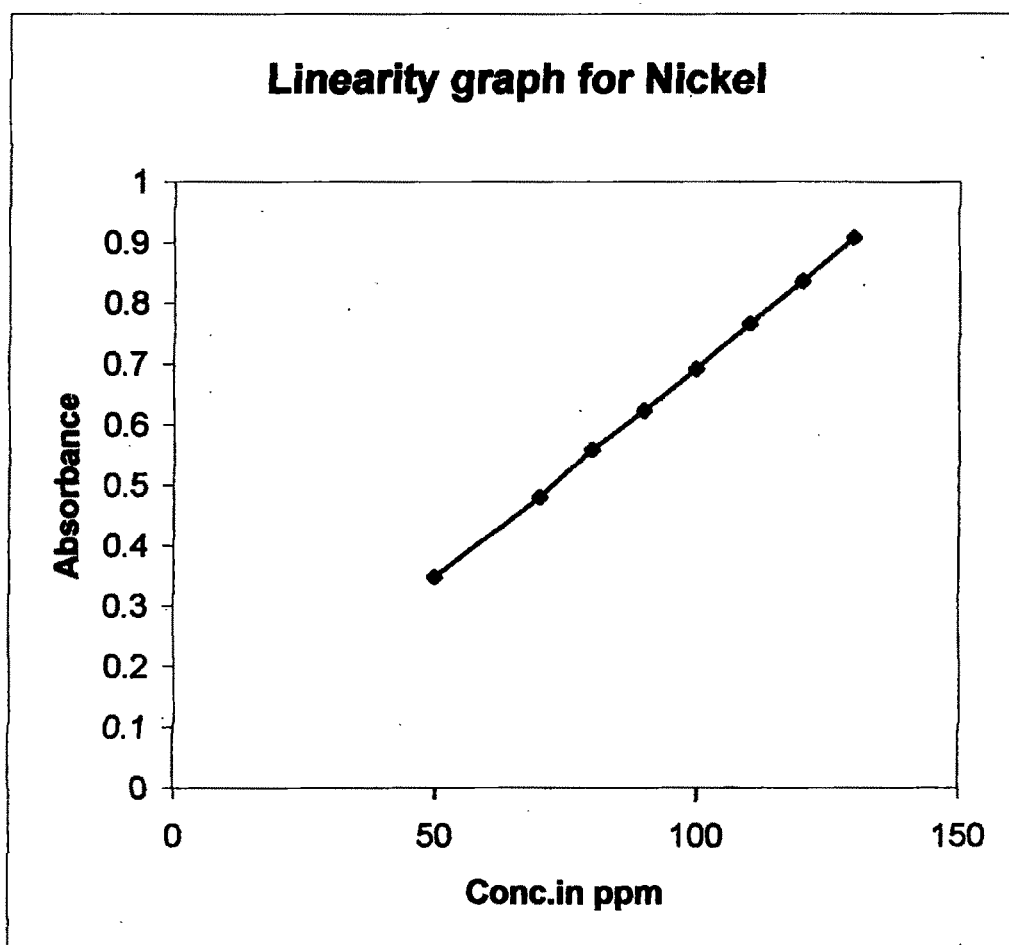
Organic phase : 10 ml Benzene  
Time of equilibrium : 1 min.  
Wavelength : 450 nm

Sr.No.	Conc. Of Nickel in ppm	Absorbance
1	50	0.348
2	70	0.480
3	80	0.559
4	90	0.622
5	100	0.691
6	110	0.766
7	120	0.835
8	130	0.907

# Linearity graph for Nickel

Calibration curve for Nickel at 450 nm in Benzene

Conc. of Nickel in ppm	Absorbance
50	0.348
70	0.48
80	0.559
90	0.622
100	0.691
110	0.766
120	0.835
130	0.907





## **Infrared studies of Nickel (II) Complex with isonitrosothiocamphor**

The energy of radiations belonging to first octaves in the infra red region are of the same order of magnitude as rotation and vibration energies of molecules, consequently, strong interaction of infrared radiations and matter are to be expected. If the vibration of the molecule differ in frequency from those of the incident radiation, no interaction take place. However, if the molecule vibrates with the some frequency, it absorb (under certain conditions) a certain amount of energy and rise to a higher energy level (exited state) This transition is discrete (quantized) and results in an increase in the amplitude of the vibration. The absorbed energy is the difference between the energy of the two level.

Classical electrodynamics & modern quantum theory shows that the interaction of radiation and matter, resulting either in absorption or emission of energy, is possible only when a dipole moment vibration is involved. Consequently only vibrations or rotations of the molecule resulting in a change in dipole moment are infrared active.

Molecular spectra enable the direct derivation of discrete energy level of a molecule. From these level one can obtain detailed information about the motions of electrons and nuclei in the molecule.

The studies of electronic motions provide the theoretical backgrounds for understanding of chemical valance. From the vibrational frequency one can calculate with great accuracy, the force between the atoms in a molecule and heat of dissociation of a molecule. From the rotational frequency one can calculate very accurately nuclear distance and can obtained accurate information about molecular geometry.

The range of functional group determined with the help of infrared are as bellow:

1. **Nitroso compound** : N=O bond is stable in nitroso compounds is characterized by a stretching vibration in the range <sup>14</sup> 1621 -1488 cm<sup>-1</sup>

Nitroso compound tend to dimerise, secondary primary nitroso compound readily rearrange to oxime. In monomeric state absorbs in the 1621-1488 cm<sup>-1</sup> <sup>15</sup> region, but in the solution they exist preferably as dime rise and then absorbs near 1290 cm<sup>-1</sup>

2. **→C-CH<sub>3</sub> group**: The mode of → C-CH<sub>3</sub> gives an observation at about <sup>15</sup> 2872 cm<sup>-1</sup>

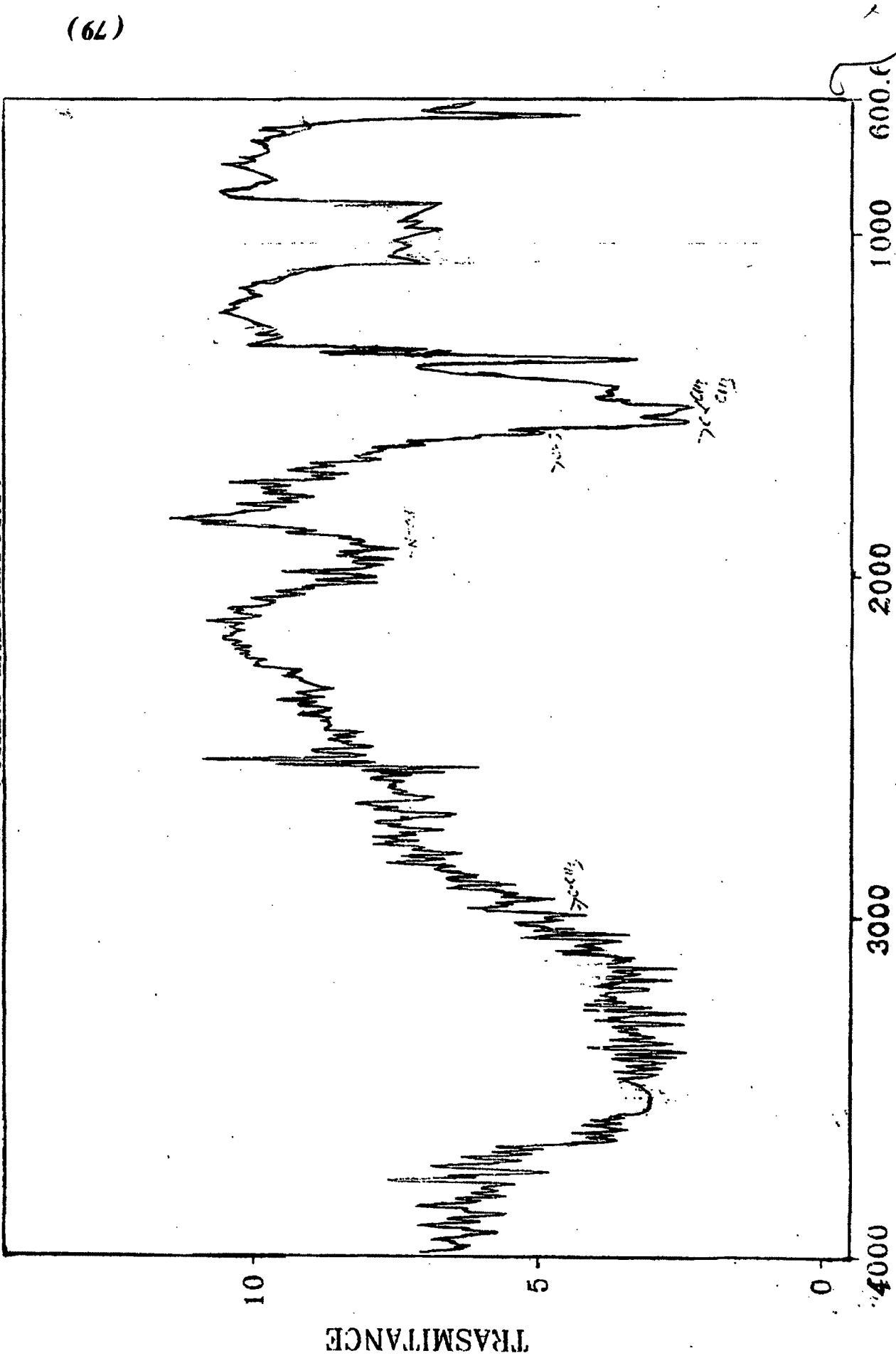
3. **>C=S group** : The range of >C=S group occurs in the range<sup>16</sup> of 1000-1400 cm<sup>-1</sup>

4. **>C<**  $\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$  **group** : The frequency of  $\begin{matrix} \text{CH}_3 \\ >\text{C}< \\ \text{CH}_3 \end{matrix}$  is at about <sup>17</sup> 1340 -1460 cm<sup>-1</sup>

Two new bands around 470 and 350 cm<sup>-1</sup> appeared in the spectra of all the complexes, which could be assigned to complete vibrations having contribution from  $\nu$  MN and  $\nu$  MS.

$\nu$  - OH in free ligend disappear in the complex, and a new weak new band at 280 cm<sup>-1</sup> appears. This indicates the deprotonation of the ligend molecule during the complexation. Further, the intensity of  $\nu = \text{C} -$  decreases and it shifts to downward direction in the complex indicating thereby complexation of oxygen side of the ligend.

*Handwritten notes:*  
A large question mark is drawn to the right of the paragraph above.  
Below it, the text "No. needed here" is written vertically.  
Further down, "this is wrong" is written with a line pointing to the underlined word "complexation" in the paragraph above.



PARTY : SANJAY KUMAR SINGH      WAVENUMBER [cm-1]      B.NO. : .

M.P.I.F : 3      R.NO. : .

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