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Development of pH Dependent Solid Phase Spectrophotometric (SPS) Determination of Ni (II) with Pyridine-2, 6-Dimethanol as an Analytical Reagent

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Abstract: *An analytical reagent, pyridine-2, 6-dimethanol (PDM) is proposed for the direct spectrophotometric determination of nickel (II) ions. The proposed method is a rapid, selective, sensitive and very simple. The PDM reacts with Ni (II) ions forming green coloured soluble complex at room temperature. The maximum molar absorbance was at 390 nm at pH 4.5.The Beer's law is obeyed in the concentration range of 0.01 to 60 µg /ml of Ni (II) ions. The molar absorptivity and the stability constant of the complex were* $1.597x10^4$ *L* $mol^{-1}cm^{-1}$ *and* $2.37x10^6$ *respectively. Several extractive parameters that considered for the complexation and extraction of Ni (II) ions such as pH, equilibrium time, effect of temperature, concentration of metal ions, effect of interfering ions, elution studies, electronic spectra, IR spectra, magnetic properties, molar conductance of the adsorbent matrix were studied. The stoichiometry of extracted species was studied by Job's method and Mole-Ratio method which was found to be 1:2. The quantitative recovery of the metal ion was achieved by using 2N* HNO_3 *(20 ml). The proposed method has been successfully applied for the determination of nickel (II) in various synthetic mixtures, alloys samples, and in drinking water samples.*

Keywords: *Ni (II) Complex, Pyridine-2, 6-dimethanol, Solid Phase Spectrophotometric (SPS), Spectral analyses.*

I. Introduction

Nickel is one of the most common transition metals which belongs to platinum metals family with relative abundance of 0.008 %. Wide spread applications of Ni (II) covering many areas of study. It can be considered is one of the frontier elements in the alloys industries for stainless steels, cast iron, german silver and monel metal and also found in many heat resistant alloys [1-3]. This metal also has great application in the field of electroplating, ink, varnishes, pigments and ceramics industries. Nickel plays important roles in the biology of micro-organisms, plants and is an essential element in human diet. It has been reported that normal human plasma contains 0.012-0.085 ppm of nickel (II) ions. The plant enzyme urease contains nickel which is required for the hydrolysis of urea. Nickel can have an impact on human health through infections diseases arising from nickel-dependent bacteria. Though it can be considered non-toxic, but its compounds are carcinogenic, allergic, dermatitis and pompholyx [4-5].

The Nickel (II) ion forms many stable complexes with different reagents. Several reported reagents for the complexation of Ni (II) are dimethylglyoxime, 1-(2- pryidylazo)-5-diethylaminophenol, 2-[2-(3, 5-dibromopyridyl) azo]-5-dimethylamino benzoic acid, 5-bromo-2-hydroxy-3-methoxybenzaldehyde-4-hydroxybenzoichydrazone, 2-hydroxy-3-methoxy benzaldehydethiosemicarbazone and tributylphosphate. Some of the reagents were used for extractive determination of nickel (II) in acidic or basic mediums. Pyridine-2, 6-dimethanol is found to be suitable ligand as it is well known versatile N, O-donor chelator in coordination chemistry [6-7]. The Complex formation studies of large number of cations are reported of the proposed ligand [8]. The Complexes of Cu (II), Cobalt (II), nickel (II), rhodium (II) and rhodium (III) have been synthesised and spectral, magnetic properties and crystal structure have been reported [9-11]. According to all of these above literatures encouraged us for the complexometric determination of nickel (II). The reported methods for the metal ions speciation and pre-concentration are liquid-liquid extraction and solid phase extraction (SPE), but SPE is simpler, sensitive, selective and more convenient [12-15]. Based on the advantages of SPE, we report here solid phase spectrophotometric (SPS) technique for the determination of nickel (II) by Pyridine-2, 6-dimethanol modified with alumina [16-20]. It is simple, sensitive and selective spectrophotometric method for the micro determination of Ni (II) ion. This method is also effective for the removal of interferences in a simpler way. The chelating agent is modified with alumina for the complexation with Ni (II) ion from methanol. The optimum conditions for complexation and determination of Ni (II) such as pH, equilibrium time, effect of temperature, concentration of metal ions, photometric studies, effect of interfering ions, elution studies, electronic spectra , IR spectra, magnetic properties, molar conductance of the adsorbent matrix were studied.

II. Experimental

Instrumentation

The absorbance measurements were recorded using Shimadzu UV-Vis spectrophotometer (UV-1800) fitted with 1 cm quartz cells. The IR spectrum was recorded in KBr pellets with Shimadzo Corporation (Class-1 Laser Product, 220V/230/240V, V50-60Hz, 240V). A mechanical shaker was used throughout the experiments. The pH measurements were carried out by a labtronic pH meter (Model No-23) equipped with a combined glass-calomel electrode.

Reagents and Solutions

Extra pure methanol, hydrochloric acid, ammonia solution, acetic acid, all from Sisco Research Lab., Mumbai, India was used. Nickel chloride hexahydrate (BDH, India) was of analytical grade reagent. Pyridine-2, 6-dimethanol (Alfa Aeser, A Johnson Matthey Company, England) and a neutral solid alumina was of analytical grade reagent for the determination of Ni (II) from Oxford Lab., Mumbai, India. A stock of 0.001 M solution of nickel (II) was prepared by dissolving 0.2377 g of $NiCl_2.6H_2O$ in doubly distilled water with adding 3 ml of 1 (M) HCl and standardized gravimetrically. The working solutions were prepared by diluting the stock solution with bi-distilled water. The solution of the complexing agent was prepared in methanol. The other reagents were (0.1 M) CH_3COOH and (0.1 M) CH_3COONa and solutions of interfering ions were prepared in double distilled water.

General Procedure

The reagent Pyridine-2, 6-dimethanol was modified on the surface of 3.0 g of alumina at the 1:2 ratios in methanol solvent and stirred for 40 minutes at room temperature. The resulting composition was left in an oven at 60^0 C for one day. After drying, the sorbent was ground into powdered for metal ion extraction.

For the batch method of extraction 300 mg of sorbents were used in each of 100 ml flasks with 25 ml of $1x10^{-4}$ M of Ni (II) ion and the pH was adjusted to 4.5 using dil. HCl and dil. NaOH solutions. The mixture of the sorbent matrix and Ni (II) solutions were shaken by a mechanical at about 400-500 rpm at room temperature for 30 minutes. After the extraction, the filtrates and unextracted Ni (II) were determined by spectrophotometer at λ_{max} 390 nm. The amount of Ni (II) absorbed on the sorbent materials was calculated by standard calibration curve.

III. Results And Discussion

The modified reagent was used for the spectrophotometric method for determination of Ni (II). The metal ion forms coloured complex which is stable and its extraction could be quantitative at pH 4.5. All the absorbance measurements were carried out at 390 nm against the reagent blank [Fig.1]. The calibration curve was constructed by plotting absorbance against the amount of Ni (II) in the concentration range of 0.01 to 60 µg/ ml. The formula of the complex was ascertained by Job's and molar ratios methods as 1:2. The stability constant of the complex is ($2.37x10^6$) measured by Job's method. The analytical characteristics of the complex are given in [Table 1]. The proposed structure of the complex can be confirmed by the spectrophotometric characteristics and it is shown below.

Influence of pH

The pH for the extraction of Ni (II) was adjusted in the range of 2.03 to 7.5 by adding hydrochloric acid and NaOH solution or a suitable buffer such as sodium acetate and acetic acid. According to the results shown in [Fig.2] upto pH 4.0-4.5, maximum recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to fact that in less acidic solution the protonation of the reagent occurs and consequently, there is a weak tendency for retention of Ni (II) by the reagent takes place. Therefore, sodium acetate-acetic acid buffer with pH 4.0-4.5 was used for the extraction of Ni (II) ions. However, at lower pH (< 4.0) nitrogen atoms of the reagent could be protonated and the stability of the complex would be reduced. Hence, pH 4.5 was chosen for further extraction studies of Ni (II) ion.

Influence of Temperature and Equilibrium time

The effect of temperature on the percentage of extraction of 10 µg/ml of Ni (II) was studied in the range of 25-60^0 C at pH 4.5. The percentage of sorption of the metal ion increases with temperature and the results shown in [Fig.3]. Maximum percentage of sorption of the metal ion has been found in the temperature range of 30-60^0 C. Hence, the Ni (II) complex is stable in the above range of temperature.

The study of the percentage of extraction of Ni (II) with variation in equilibrium time shown in [Fig.4], the maximum quantitative extraction has been found within 100 min. Increase of equilibrium time, sorption of the metal ions reached after the maximum quantity of sorption. Therefore, 100 min extraction time was chosen for further studies.

Effect of the Reagent Concentration (PDM) on the Complex

The effect of the reagent concentration immobilized with alumina on the extraction efficiency towards Ni^{2+} ions was studied in the concentration range of $0.1x10^{-3}$ to $1x10^{-3}$ M. It was found that the blank sorbent matrix had no extraction efficiency to the metal ion. Accordingly, the extraction efficiency was carried out by the reagent on the surface of the sorbent matrix. Results show that the extraction of the sorbent was enhanced on the addition of the reagent. The best result is at $1x10^{-3}$ M, where more than 87% of the Ni^{2+} ions are extracted [Fig.5]. There is slight decrease in the extraction was found beyond this concentration.

Effect of Ni (II) ions concentration

The percentage extraction efficiency of Ni (II) ions concentration was studied at a fix PDM concentration ($1x10^{-3}$ M) on the solid matrix. The effect of Ni (II) ions concentration on the extraction efficiency was tested by shaking different concentration of Ni (II) ions [21-23]. A linear calibration graph is constructed between absorbance and metal ion concentration predicts that Ni (II) may be determined in the range of 0.01 to 60 µg /ml. The calibration graph is shown [Fig.6]. The effect of the concentration on the extraction efficiency was investigated by the different concentrations of Ni (II) ion with 300 mg of the sorbent matrix at pH 4.5. Almost 85% of Ni (II) was extracted by the sorbent [Table 2].

Stoichiometry of the Ni (II)-PDM Complex

The stoichiometry of the complex was determined by Job's method of continuous variation and by Mole-Ratio method [24-26]. It was found that metal-ligand ratio of the complex would be 1:2. The molar absorptivity was $1.597x10^4$ L $mol^{-1}cm^{-1}$. This is shown by [Fig.7].

Effect of Foreign ions

The effect of foreign ions was studied for their effect on the determination of Ni (II) ions. The tolerance limit (in µg) of these ions in the determination of 10 µg/ml of nickel. The results are given in [Table 3]. It can be calculated from the interference studies that the anions do not interfere even when present in more than 100 fold excess. Most of the cations also do not interfere, but Cu (II) was tolerated upto 40 fold excess.

Desorption studies of Ni (II) ions

The selection of a suitable eluent for desorption of Ni (II) ions is one of the important factors to obtain the extraction efficiency of the resin and recovery of the metal ions [27-29]. The experiments were performed by using different eluants. It can be seen from [Table 4], the best results were obtained by using 2N HNO_3 (20 ml). This eluent desorbed Ni (II) of about 89%. So, 2N HNO_3 is the selective eluent of desorption of the Ni (II) ions.

Electronic Spectra of Ni (II)-Complex

Nickel (II) is a $3d^8$-system. In octahedral geometry the ground state is $3A_{2g}$ and the following spin-allowed but Laporte forbidden transitions are possible.

$^3A_{2g} \rightarrow {}^3T_{2g}$ (F) ; $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) ; $^3A_{2g} \rightarrow {}^3A_{2g}$ (P)

The three spin-allowed transitions for nickel (II) complex in octahedral geometry occur at 11.2, 18.35 and 29.0 kK.

IR Spectra

The IR spectrum of PDM loaded alumina was recorded in KBr and shown in [Fig.8]. The peaks observed at 3360 cm^{-1} and 3096 cm^{-1} may be assigned to the stretching frequency of alcoholic –OH group and to the stretching of Ar-H stretching of aromatic portion. The peaks observed in the range of 1600.94 cm^{-1} to 977.84 cm^{-1} was characteristics of aromatic ring stretching frequency. Another IR spectrum of PDM loaded alumina and Ni (II) complex is also in [Fig.9].

Magnetic Moment Measurement

The effective magnetic moment (μ_{eff}) was measured by Gouy method [30-31]. The complex shows magnetic moment value is 2.81 BM, which is in accordance with two unpaired electron indicating that the complex is monomeric. This is in agreement with the magnetic moment value of the $3d^8$-system of octahedral geometry of the complex.

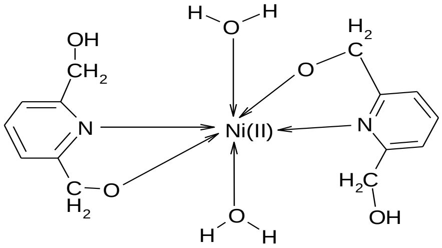
Molar Conductance

Molar conductivity (Λ_M) value of the PDM-Ni (II) complex was measured by our reported method [32]. The molar conductivity of this PDM-Ni (II) complex was measured in methanol. The molar conductance value is 3.9 Ohm^{-1} cm^2 mol^{-1} indicating its non-electronic nature.

Application for the determination of Ni (II) ions

The present method was applied for the determination of Ni (II) ions in various synthetic mixtures, alloys samples, and in drinking water samples. The results are shown in [Table 5].

The proposed structure of PDM-Ni (II) Complex



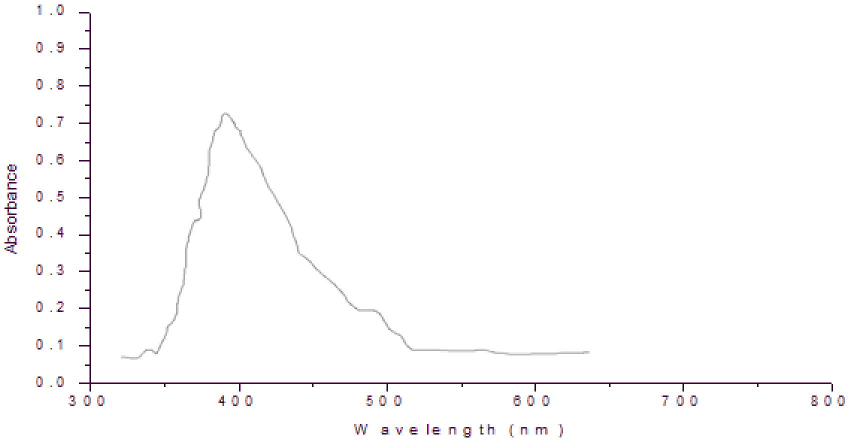


Fig.1: Absorbance Spectra of PDM-Ni (II) Complex.

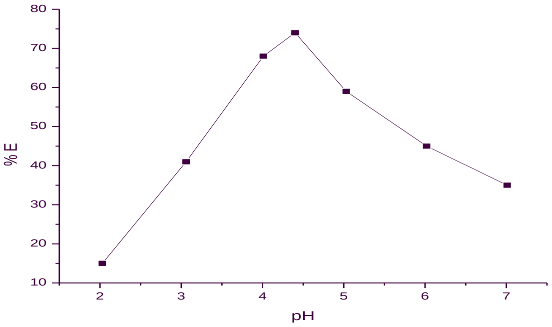


Fig.2: Influence of pH on the extraction of Ni (II) ions.

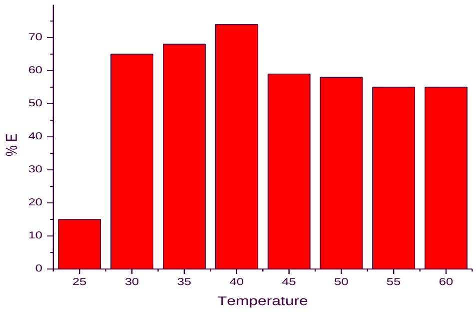


Fig.3: Effect of temperature on the extraction of Ni(II) ions.

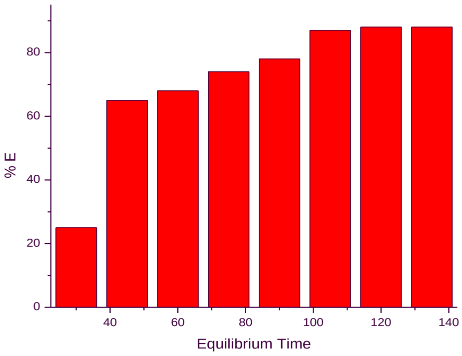


Fig.4: Effect of Equilibrium Time.

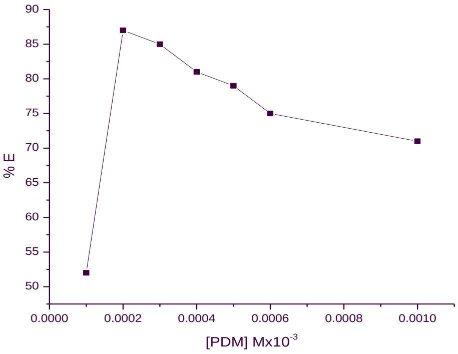


Fig.5: Effect of the Reagent Concentration on the extraction of 10 µg/ ml of Ni (II) ions.

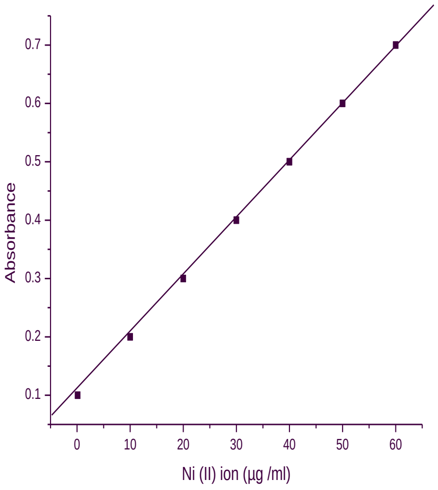


Fig.6: Effect of Ni (II) ions concentration (µg/ ml).

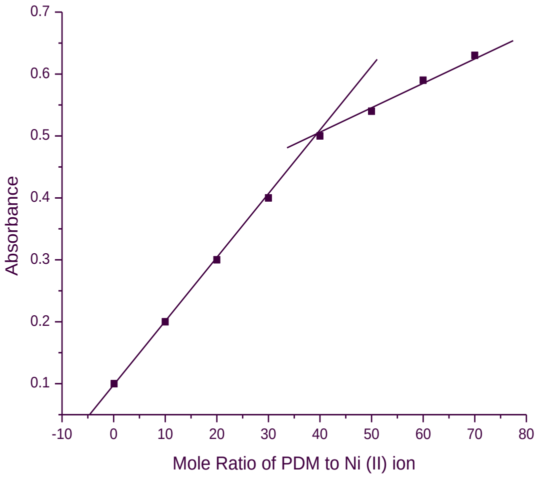


Fig.7: Mole-Ratio of PDM concentration to Ni (II) ions.

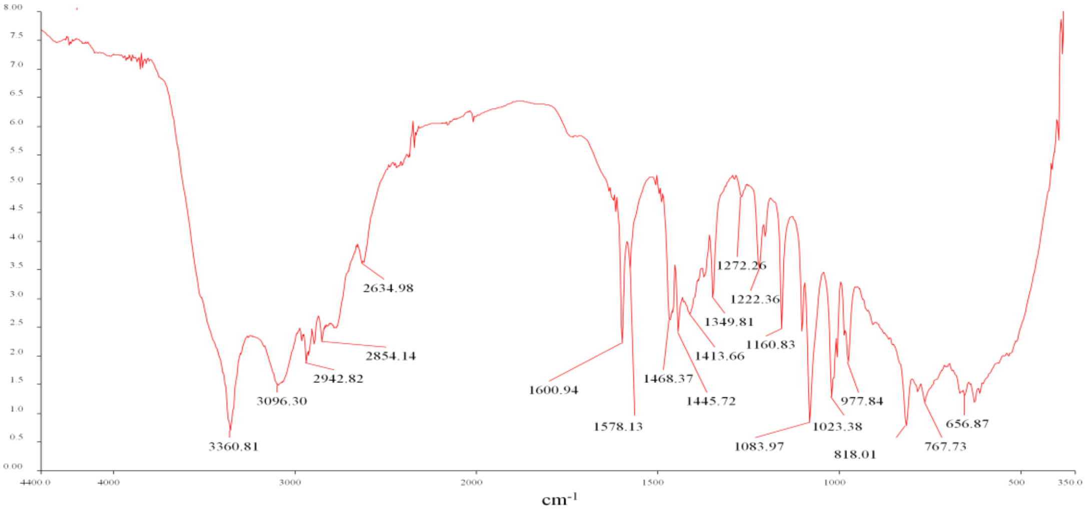


Fig.8: IR Spectrum of PDM impregnated on alumina.

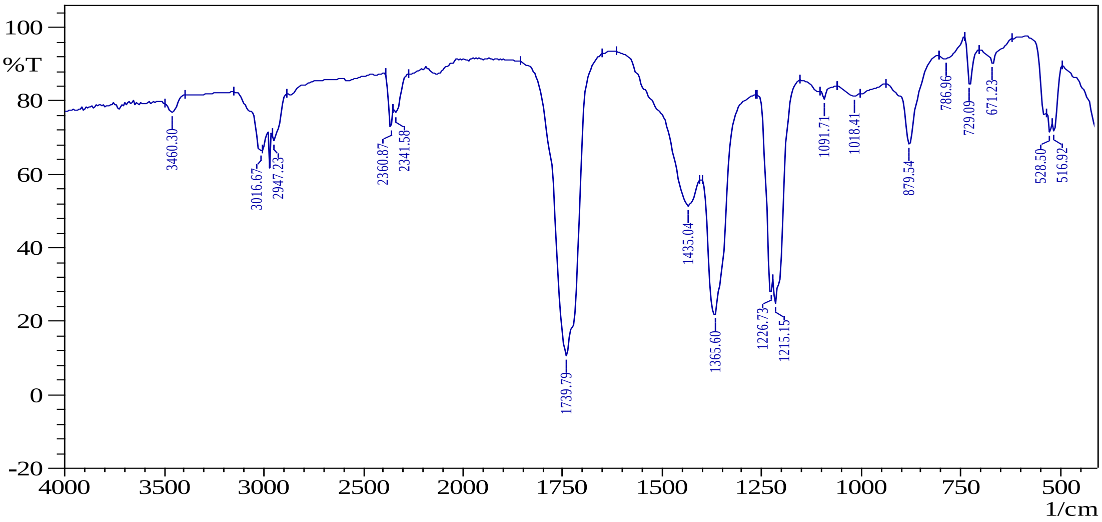


Fig.9: IR Spectrum Ni (II)-PDM Complex impregnated on alumina.

Table-1

Physical and Analytical Characteristics of Ni (II)-PDM Complex.

Parameters	Value
Limit Of Detection (µg/ Ml)	0.0225
Beer's Law Range	0.01-60 µg/ Ml
Molar Absorptivity	1.597x10^{-4} L Mol^{-1} Cm^{-1}
Stability Constant (B)	2.37x10^{6}
Correlation Coefficient (ϒ)	0.9921
Standard Deviation	0.025
Composition (Metal : Ligand)	1:2
Maximum Absorbance (Λ_{Max})	390 Nm
Molar Conductance (Λ_M)	3.9 Ohm^{-1} Cm^{2} Mol^{-1}
Magnetic Moment (μ_{eff})	2.81 BM

Table-2

Effect of Ni (II) ions concentration on the extraction efficiency of the sorbent matrix at pH 4.5.

Used (µg/ ml)	Extracted (µg/ ml)	% E	Capacity of the sorbent (m mol g^{-1})	% RSD
0.01	0.0074	74	3.78x10^{-8}	0.021
0.1	0.074	74	3.78x10^{-7}	0.01
10	1.24	87.6	6.33x10^{-6}	0.09
20	2.85	85.75	1.45x10^{-5}	0.023
30	3.86	87.1	1.97x10^{-5}	0.045
40	4.89	87.7	2.499x10^{-5}	0.037
50	6.1	87.8	3.0x10^{-5}	0.017
60	7.56	87.4	3.84x10^{-5}	0.06

Table-3

Tolerance Limits of Foreigns ions. Amount of Ni (II) ions is 10 µg/ ml.

Anions	Tolerance limit (µg/ ml)	Cations	Tolerance limit (µg/ ml)
Cl^{-1}	345	Cd (II)	240
Br^{-1}	900	Mn (II)	350
F^{-1}	210	Al (III)	150
BrO_3^-	1500	Ca (II)	250
IO_3^-	340	Ba (II)	300
I^-	589	Zn (II)	275
ClO_3^-	340	K (I)	300
NO_3^-	625	Cr (III)	250
HSO_4^-	2000	Na (I)	158
SO_4^{2-}	975	Cu (II)	40
CH_3COO^-	1720	Pb (II)	172
$Cr_2O_7^-$	340	Fe (II)	305

Table-4

Desorption Studies of Nickel (II) ions by different eluents.

Eluents Composition	5 ml	10 ml	20 ml	% RSD
HNO_3 (1N)	67	74	82	±1.3
HNO_3 (2N)	71	79.2	89.3	±1.4
HNO_3 (3N)	65.2	72.1	73.3	±1.4
HCI (1N)	57.7	61.1	64.3	±1.6
HCI (2N)	61.2	63.4	67.1	±1.3
HCI (3N)	63.2	66.6	69.9	±1.8
CH_3COOH (1M)	51	52.1	54.3	±1.8
$H_2C_2O_4$	53.3	56	59.7	±1.5
EDTA	56.2	57	63.2	±1.2
Thiourea	45	48.2	48.5	±2.1

Table-5
Application for the determination of Ni (II) ions.

Name of the Samples		Amount found	Referred Value	Standard deviation
Synthetic Mixtures	$Ni^{2+}(10) + Zn^{2+}(10)$	9.92	_	0.078
	$Ni^{2+}(10) + Mg^{2+}(10)$	9.95	_	0.07
	$Ni^{2+}(10) + Sn^{2+}(10)$	9.99	_	0.05
	$Ni^{2+}(10) + Pb^{2+}(10)$	9.92	_	0.03
Alloys Samples	Stainless Steel	8.52	8.5	0.06
	Cupronickel	53.99	54.1	0.03
	Ni-Al powder	50.01	50	0.05
Drinking Water	Sample-1	1.09	_	0.045
	Sample-2	2.05	_	0.07
	Sample-3	2.15	_	0.061

IV. Conclusion

This study demonstrated the successful determination of nickel (II) ions by pyridine-2, 6 dimethanol as an analytical reagent which impregnated with alumina. The proposed is simple, highly sensitive and selective than other reported methods for the micro level spectrophotometric determination of nickel. The results presented in this report predicts the well referred value for the determination of nickel in synthetic mixtures, alloys samples and natural drinking water. The proposed method showed minimum interferences compared to the other conventional procedures for the determination of nickel.

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