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α-Benzoin Oxime as the complexing agent for the estimation of small amount of Nickel (II) without extraction

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Abstract

A selective and sensitive complexing reagent, α-benzoin oxime gives orange colour complex with ammoniacal Nickel(Ni(II)) at pH 9 in the existence of non-ionic surfactant Triton-X-100 in an aqueous medium. Detection of Ni(II) in distinct water samples and in alloys can be done using this highly selective complexing agent with low cost and with accurate results by spectrophotometric method. The spectrophotometric method of estimation of Ni(II) was carried out at pH 9. The maximum absorbance was found to be at 422nm. Ni(II)- α-benzoin oxime complex obeys Beer's law. The influence of various category of surfactants and the quantity of it is studied. The composition of the complex was found by Job's method and mole ratio method.

Keywords: Spectrophotometry, α-benzoin oxime, Nickel(II)ion, Triton X-100, Job's method, Mole ratio method.

Introduction

Nickel is a silvery-white metal with a minor golden tinge that acquires a huge polish. Nickel(II) forms complexes with most of the common anions, in addition to sulfide, carbonate, hydroxide, carboxylates, and halides. Ni(II) sulfate is obtained in huge amount by solubalising Nickel metal or oxides in sulfuric acid, results in the formation of the two, a hexa and heptahydrates[1]. Nickel is used in several peculiar and detectable industrial and consumer commodities, along with stainless steel, rechargeable batteries, electric guitar strings, microphone capsules, plating on plumbing fixtures[2]. Since it is not undergoing corrosion, Nickel was sometimes used as a counterfeit for decorative silver. Raney Nickel is extensively used for hydrogenation of unsaturated oils, and substandard margarine and remaining oil may consist of Nickel as pollutant. Forte et al. estimated that type 2 diabetic patients have 0.89ng/ml of Nickel in the blood relative to 0.77ng/ml in the control subjects[3]. Various complexing agents like oximes[4], thiosemicarbazones[5,6], azodyes[7], imines[8] and carbamates[9,10] have been reported for the qualitative & quantitative estimation of Ni(II) using various other analytical equipments. Among the recorded complexing agents, isonicotinoylhydrazide and thiol analogous molecules contain stable binding capacity because of the existence of nucleophiles (N and S atoms)[5].

Various methods like flame atomic absorption spectrometry (AAS)[11], electrothermal AAS[12], Graphite furnace AAS[13], atomic fluorescence spectrometry[14], inductively coupled plasma optical emission spectrometry[15], energy dispersive-flourescence spectrometry[16], chromatography[17], voltammetry[10,18], colorimetry[19], spectrophotometry[7,20-33] and other methods[34-44] were already recorded to do the estimation of Ni(II) in natural samples. Energy Dispersive X-ray Flourescence Spectrometry and Inductively coupled plasma optical emission spectrometry high cost and refined techniques that needs committed scholar to operate. On the hand chromatographic techniques require more time while voltametry and colorimetry are not reproducible. Therefore these methods are not convenient for the daily analysis of huge sets of specimens where quick analysis is required. UV-Vis spectrophotometry is the most simple method applied for the Ni(II) estimation owing to its neutrality and low budget.

Accordingly, the current work includes a facile procedure to estimate the micro levels of Ni(II) in various water and alloy samples.

Materials and methods

Materials: Spectrophotometric measurements were done using Agilent Cary W in UV software based spectrophotometer, pH of the various different buffer solutions were measured using Systronics μ 361 pH meter. High purity reagents were used. Most of the chemicals such as compounds containing Nickel(II) and other cations were of the analytical grade purchased from Merck company. A 5% of all surfactant, was prepared by solubalising 5g of each surfactant in 100mL of double distilled water. All the surfactants were purchased from Merck company.

Stock solution of 0.02M Nickel(II) sulfate hexahydrate and 0.02M α-benzoin oxime was prepared. Different pH solutions from 1 to 12 were prepared using 0.2M KCl and 0.2M HCl (pH 1), 0.1M potassium hydrogen phthalate and varying amounts of

0.1M HCl (pH 2-5), 0.1M potassium dihydrogen phosphate and varying amounts of 0.1M NaOH (pH 6-8), 0.025M borax and 0.1M HCl (pH 9), 0.025M borax and 0.1M NaOH (pH 10), 0.05M disodium hydrogen phosphate and varying amounts of 0.1M NaOH (pH 11and pH 12)[45].

Procedure: Verification of Beer-Lambert's law: To each set of different 10mL standard flask, varying volumes of Ni(II) sulfate solution in microlitres, was added. Ni(II) solution was made ammoniacal by adding ammonium hydroxide to each standard flask. α-benzoinoxime was added in equal quantity to each standard flask which is followed by the addition of pH resistant solution (pH 9)[46-48]. Then added 5% Triton-X-100 to each standard flask and then made up to the mark by adding double distilled water. Absorbance was found at λ_{max}422nm against the blank. The calibration plot was prepared.

Analysis of different samples of water: Different Water samples were taken in a separate beaker, it is concentrated to half its volume with stirring. After attaining the desired pH value by adding suitable pH resistant solution, the spectrophotometric measurements were done based on the normal specified procedure.

Analysis of standard alloy samples: Alloy sample of 0.2g each was dried in an oven and solubalised in aquaregia. The solution was dried by heating and nitrate was removed from the remnant, using 5ml of conc HCl. Extraction of the each remnant was carried out separately in 100mL standard flask by using double distilled water.

Result and discussion

Absorption spectra of α-benzoin oxime and Nickel(II)- α-benzoin oxime complex: Absorption spectra of α-benzoin oxime and Ni(II)-α-benzoin oxime complex was measured using a UV-visible spectrophotometer. Maximum absorbance of the complex was found to be at 422nm (Figure-1) and at this wavelength reagent blank and Ni(II) solution did not show any absorbance. Therefore at this λ_{max} (422nm), detailed study of the complex was done.

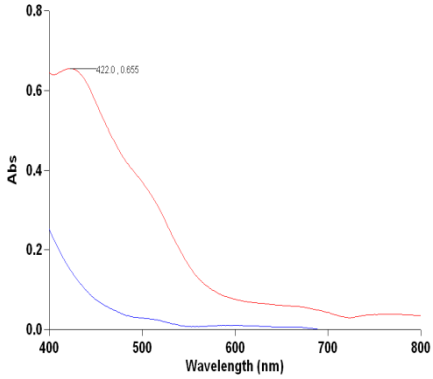

Figure-1: UV-Visible spectra of Nickel compex against reagent blank.

Impact of pH on the absorbance of the complex: Measurement of complex absorbance at 422nm using different pH solutions showed that maximum colour intensity was produced by the use of pH9 solution (Figure-2). Therefore the further analytical study of the complex was done by maintaining the solution pH9.

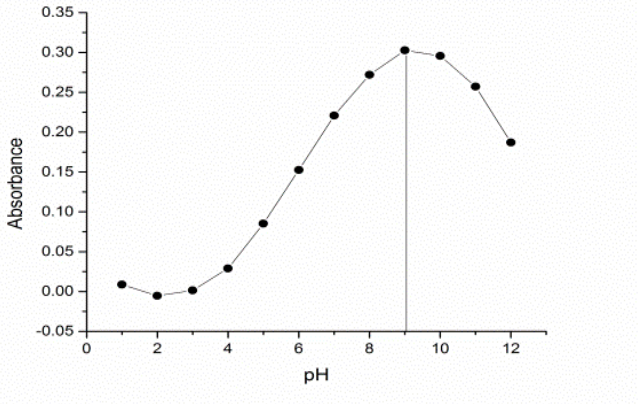

Figure-2: Impact of pH on the absorbance.

Consequences of different surfactants on sensitivity: To determine the suitable surfactant for the dissolution of sparingly soluble Ni(II)-α-benzoin oxime complex, the absorbance of the complex in different category of surfactants, for example Triton X-100, Brij 58, sodium dodecylsulfate (SDS), cetyltrimethyl ammonium bromide (CTMAB) and n-dodecyltrimethyl ammonium bromide (DTMAB) were studied. The results are shown in the below Table-1. As it is clear from Table-1, that for a 5mM Triton X-100 solution, the spectra with intense sensitivity could be obtained and its slope was found to be about two times greater than the one without Triton X-100. Therefore, Triton X-100 could be considered as better surfactant for further analysis.

Table-1: Influence of different kind of surfactant on absorbance and spectra-12µg/mL Ni(II) ion,7mM α-Benzoin oxime, pH 9.0, 5mM surfactant.

Surfactant	Absorbance	Maximum wavelength(nm)
Triton X-100	1.02	442
Briji 58	0.98	440
CTMAB	0.75	439
DTMAB	0.88	436

Influence of Triton X-100 of different concentrations: To raise the sensitivity and to stabilize the Ni(II)-α-Benzoinoxime complex formed, the varying concentrations of Triton X-100 was taken at optimum condition and absorbance was measured. Results are displayed below in Figure-3.

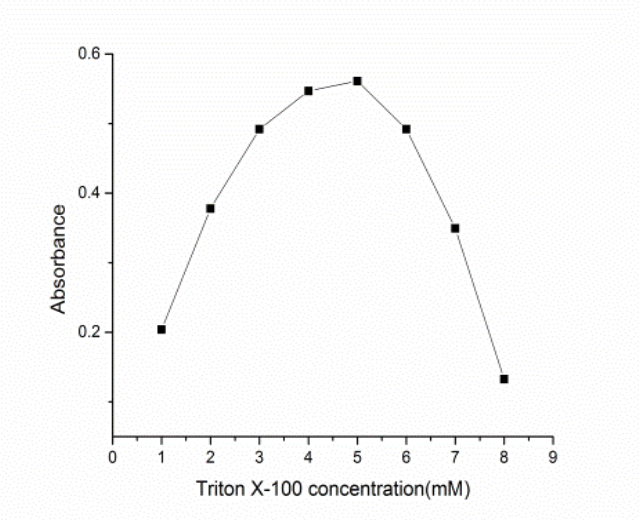

Figure-3: Influence of Triton X-100 concentration.

According to Figure-3, the maximum absorbance for the Nickel(II)-α-Benzoin oxime complex was obtained at 5mM concentration of Triton X 100. The assumption was made that the concentration of the Triton X-100 was quite less than the critical micelles concentration complex. Therefore 5mM concentrated Triton X-100 was found to be more suitable for further studies.

Influence of complexing agent concentration on absorbance of the complex: Amount of complexing agent required for the complete formation of the complex was studied by taking 500µL of 0.02M Ni(II) and adding varying volumes of α-benzoin oxime solution. It was found that at 1mL there was a maximum absorbance and after 1mL there is no much effect on further addition of alpha benzoin oxime (Figure-4).

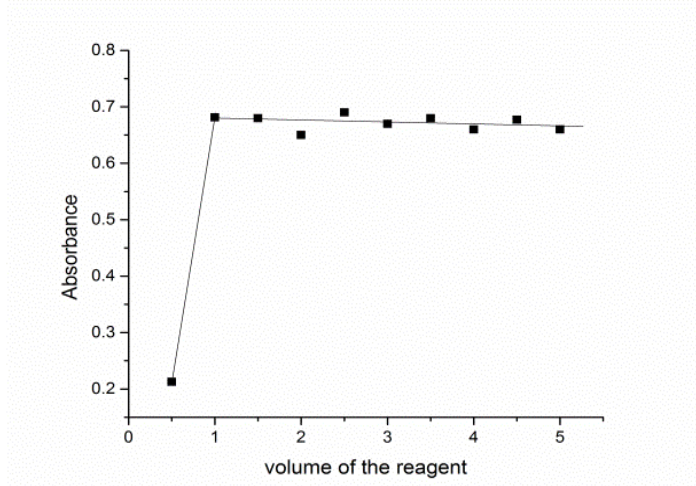

Figure-4: Influence of α-Benzoin oxime concentration on the absorbance of Nickel(II)- α-Benzoin oxime complex.

Beer's law sensitivity and calibration plot: Determination of Ni(II) at the microlevel was done by taking a different amount of Ni(II) and measuring the absorbance at 422nm under the most favorable condition. And then the calibration plot was set up (Figure-5), which shows that from 10.564-93.908µg/cm^3 of Ni(II) can be estimated accurately.

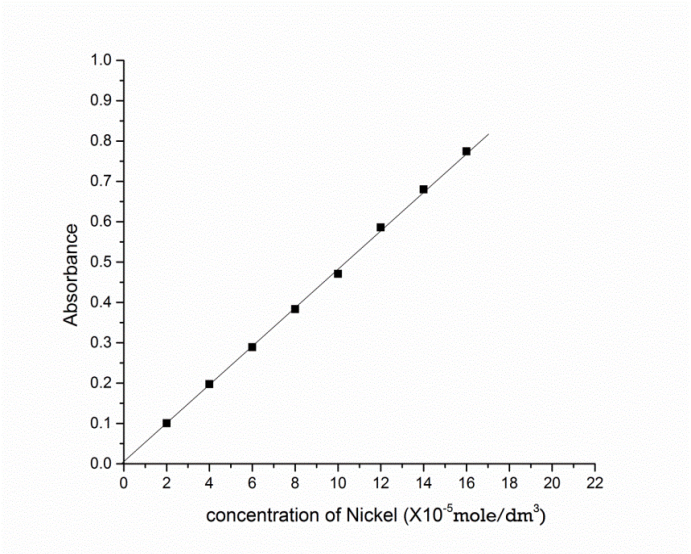

Figure-5: Beer's law plot for Nickel(II) α-benzoin oxime complex.

The stoichiometry and nature of the complex: The α-Benzoin oxime binds to the Nickel to form complexin the ratio 1:2 (M:L), which was determined by mole ratio method (Figure-6) and Job's continuous variation method (Figure-7). Stability constant of the complex was found to be 3.069X10^4 (Figure-8) which was determined by Turner Anderson method.

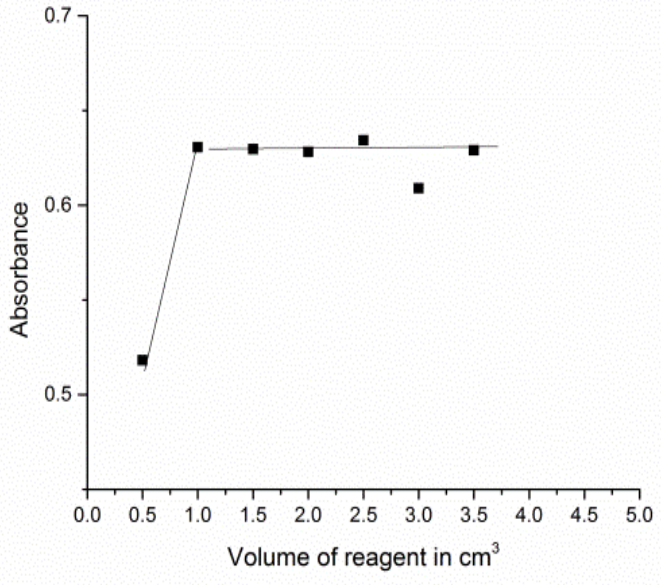

Figure-6: Mole ratio plot for Nickel(II)-α-Benzoin oxime complex.

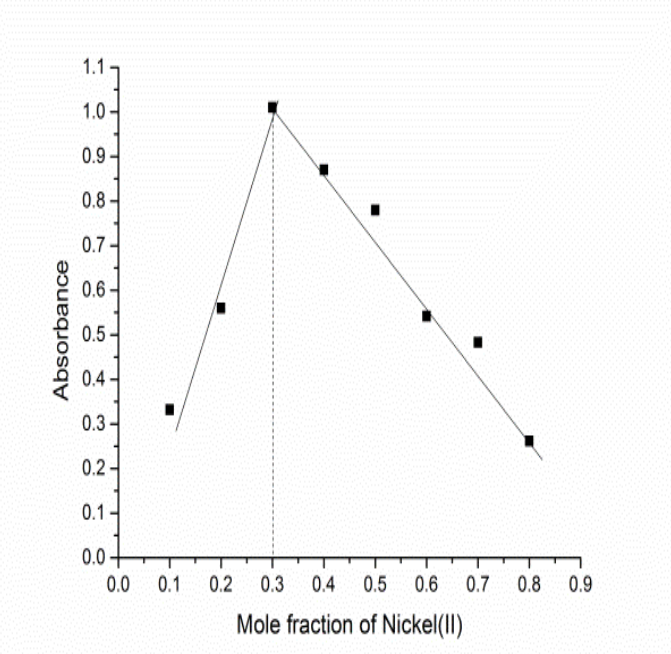

Figure-7: Job's continuous variation plot for Nickel(II)-alpha-Benzoin Oxime complex.

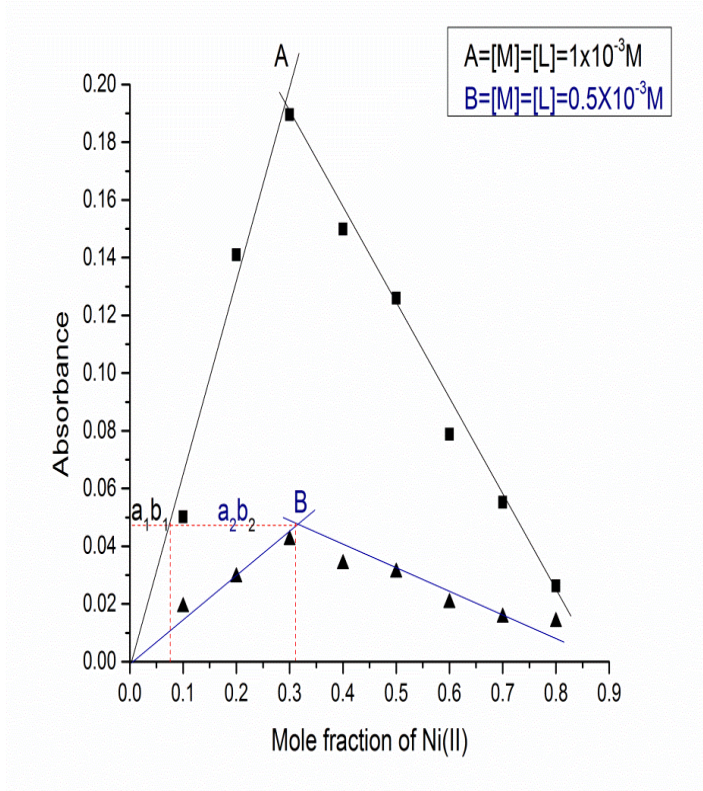

Figure-8: Stability constant of Nickel(II)-α-Benzoin Oxime complex-By Turner and Anderson method.

Influence of distinct ions: In the existence of distinct ions, the absorbance value of the complex Ni(II)-α-Benzoin Oxime containing 10µg/mL of Ni(II) was studied. The experimental outcomes are summarised in Table-2.

Results of Table-2 shows that proposed technique has good preference even in the existence of Copper, Cobalt and Chromium, that this uniqueness is due to high pH. The selectivity was also determined by seeing the concentration of interfering ion in which there is less than 3% effect on sensitivity in the existence and in the absence of diverse ions which so called tolerance limit.

Precision and accuracy: To evaluate the precision and accuracy of the proposed method, the amount of Nickel(II) was estimated in four different samples of alloy and 3 different samples of water under the reliable experimental conditions. The experimental outcomes are mentioned in Table-3 and Table-4. The relative standard deviations of alloy and water samples are not exceeding 0.1% and 0.08% respectively. Therefore the method is found to be more precise and accurate.

Table-2: Study of tolerance limit of distinct ions on proposed method.

Ions added	Tolerance limit(µg/cm^3)
Cd(II)	600
Cu(II) ♦	40
Pb(II)	1000
Co(II)	400
Zn(II)	1000
Ba(II)	1000
Mg(II)	1000
K(I)	1000
Cr(VI) ♦	40
Fe(II)	1000
Hg(II)	600
Ag(I)	600
Br^-	1000
SCN^-	1000
Tartarate	600
Citrate	600
EDTA	1000

Note: ♦ Masked by masking agents

Table-3: Analysis of Nickel(II) in various samples of alloy.

Samples of Alloy	Quantity of Ni(II) present	Quantity of Ni(II) estimated		Standard deviation		Relative standard deviation (%)	
		AAS process	Current process	AAS process	Current process	AAS process	Current process
Nickel base super alloy (CM 247 LC)	61.91	61.89	61.91	0.005	0.009	0.009	0.01
Nickel base super alloy (IN 718)	54.9	54.87	54.89	0.005	0.008	0.009	0.07
Steel (BCS 233)	11.22	11.17	11.19	0.0009	0.008	0.008	0.09
Steel (BCS 266)	13.3	13.25	13.29	0.004	0.012	0.037	0.04

Table-4: Analysis Ni(II) in various samples of water.

Various water samples containing Ni(II) (µg/mL)	Added Ni (µg)	Current method (µg)	RSD (%)	Found with AAS±RSD (%)
Tap water	0.0	0.249	----	0.25
	1.0	1.229	0.04	1.188±0.008
Waste water	0.0	0.868	-----	0.869
	0.5	1.346	0.07	1.367±0.006
River water	0.0	0.364	----	0.37
	2.0	2.342	0.04	2.362±0.004

Table-5: Physico chemical properties of Ni(II)- α-Benzoin Oxime complex.

Characteristics	Results
λ_{max}	422
Optimum pH range	9
Beer's law validity range	10.564-93.908µg/cm^3
Composition of the complex	1:2
Stability constant	3.069×10^4
Molar absorptivity	0.2580×10^4
Sandell's sensitivity	4.395×10^4

Conclusion

The current method is advantageous with high accuracy, reproducibility, sensitivity and selectivity. It does not require heating and extraction. And also the reagent is readily available.

The low value of RSD of actual sample analysis is a proof of methods versatility for actual sample analysis. These qualities and functions presented in this paper, make the current method suitable for estimating the Nickel content in a vast variety of samples.

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