A Novel Aqueous Spectrophotometric Method for the Determination of Trace Amounts of Nickel in Aluminum Alloys, Stainless Steel, Manganese Nodule and other Geological Samples with 5- (2' – Carboxyphenl) Azoxine in presence of Triton X-100, a Non- ionic Surfactant

R. Saran[a,*] and N.K. Baishaya[b]
[a]Ramdeobaba College of Engineering and Management,
(An autonomous college of RTM university, Nagpur)
[a]82 Swamy Colony, Phase II, Katol Road, Nagpur- 440013, Maharashtra, India.
[b]Department of Chemistry, Gauhati University
Gopinath Bardoloi Nagar, Gauhati – 781014, Indian

Abstract:- A novel micellar sensitized spectrophotometric method has been developed in the present work for the determination of nickel in varying geological matrices such as aluminum alloys, stainless steel, manganese nodule and others. The method utilizes the reaction of 5- (2'– carboxyphenyl) azoxine with nickel in aqueous medium at pH 5.2-6.1 to form a wine-red colored complex. The reaction is sensitized by Triton X-100, a non-ionic surfactant. Triton X-100, micellar sensitization of the reaction results in five times enhanced molar absorptivity enabling the determination of an amount as low as 1 ppm of nickel in rock samples within a relative standard deviation of ±1.2% and enhanced stability of the complex from 4 hours to at least 40 hours. Extraction of the complex is avoided making the procedure simple, rapid and easy in operation. The molar absorptivity and Sandell's sensitivity of the complex are $1.15.10^5$ $1.mol^{-1}.cm^{-1}$ and 0.51 $ng.cm^{-2}$ at λ_{max} 557nm, respectively. The limit of determination 5 ppb in solution is far better than the detection limit by ICP-OES (10 ppb) at the most favored nickel line 231.60 nm. The method was applied to the determination of nickel in aluminum alloys, stainless steel, manganese nodule and other geological materials.

Keywords:- Spectrophotometry, nickel, triton X-100, 5- (2' – carboxyphenyl) azoxine, micellar sensitization, aluminum alloys, stainless steel, manganese nodule, geological samples, ICP-OES, determination limit.

I. INTRODUCTION

Although ICP-MS is in use since almost last twenty years or more but major analytical load in developing country is shared by UV- Vis spectrophotometry, a technique with relatively low power of detection. It was, therefore, considered worthwhile to develop sensitized spectrophotometric methods with improved determination limits comparable or better with analytical techniques like flame AAS, Graphite furnace – AAS, ICP-OES suitable in varying matrices.

The dioximes, because of their selective reactions with nickel were the preferred reagents for the spectrophotometric determination of nickel[1]. Among the various dioximes such as dimethyglyoxime (DMG), α - furildioxime, heptoxime, nioxime, bezil α dioxime, oxamidoxime, 1, 2-cycloheptnedione dioxime and 1,2-cyclohexanedione dioxime , DMG enjoys special position partly because of its ability to form complexes with Ni (II) as well as Ni (III) and serves multiple purpose. The DMG complex with Ni (II) in presence of suitable oxidizing agent [Ni (III)] leads to greater sensitivity while extractability of the complex with Ni (II) alone into a suitable organic solvent provides selective extraction of nickel (II) and is more commonly a step, in separation of bivalent nickel from interfering ions in spectrophotometric determination of nickel[2] with several reagents[3-14].

As a part of our interest in analytical work [15-21] using 5-Azoxine derivatives, we had previously reported an extractive spectrophotometric method for the estimation of nickel with 5 – (2' – carboxyphenyl) azo – 8- quinolinol (R), a 5 – azoxine derivative. Further investigation showed that use of triton – X –100 (TX), a non – ionic surfactant, increased the molar absorptivity, the range over which Beer's law followed, stability of the nickel complex with R and did not require a solvent extraction step avoiding use of toxic organic solvents like iso- amyl alcohol, CCl_4 or $CHCl_3$ for the determination of nickel. We present, herein, a method for the determination of nickel. We present, here in, a method for the determination of nickel in geological samples with R in presence of TX. The method is simple, easy in operation, highly reliable and rapid with sensitivity

better than many of the reported methods employing reagents such as with 5 – (4 – diethylaminophenylazo) quinolin – 8– ol [22], 5 –Br – PADAP 2 – (5 Bromo –2– pyridylazo –5– diethyl amino phenol) and Triton X-100[23], 1-(2–Pridylazo)–2–napthol[24], hydroxynapthol blue[25], p–acetylarsenazo[26], 2– (2–pyrrolyazo) benzoic acid[27], 2– (6– nitro–2–benzo– thiazolylazo) –5– dimethylaminobenzoic acid[28], Sodium diethyldithiocarbamate and dodecylsulfate salts[29], 1–phenyl-1–hydrazony1–2–oximino–1,2– ethanedione[30], diethyldithiocarbamate after collection on an organic solvent soluble membrane[31], disulphonated benzimidazo l –2–yl phenyl ketone 5–nitro–2– pyridylhydrazone[32]. The extremely high sensitivity and excellent reproducibility of the method enables determination of an amount as low as 1 ppm of nickel in rock samples with relative standard deviation of ± 1.2%. The limit of determination[33] was found to be 5 ppb in solution which is far better than the detection limit by ICP-OES (10 ppb)[34] at the most favored nickel line 231.60nm.

II. EXPERIMENTAL

Apparatus

An Elico pH meter model Li –120 equipped with combined electrode was used for pH measurement. A Hitachi U–2000 double beam spectrophotometer was used with 10 mm matched quartz cuvettes for recording spectra and for individual absorbance measurements.

Reagents

All reagents used were of analytical grade. 5-(2-carboxyphenyl) azoxine (R) was synthesized as described in literature[35]. A 1.10^{-3} M solution of the reagent (R) was prepared by dissolving 0.029 g of R in distilled water containing NaOH (0.007g) and diluting with water to 100 ml. The solution is stable for 1 week. A standard Ni (II) stock solution 1.10^{-3} M solution was prepared by dissolving suitable amount of metallic nickel in 10 ml of 1:1 hydrochloric acid and evaporating to dryness. It was further dissolved in water with warming and finally was made up to 250 ml, further dilutions were made accordingly.

Procedure

To a solution (pH 5.2-6.1) containing 0-8.75µg of nickel in a 25 ml volumetric flask, 0.5ml of 1% sodium potassium tartrate, 2.0 ml of 1% TX and 0.8 ml of R solution were added, mixture was diluted to 25 ml final volume with water. Absorbance of the solution was measured at 557 nm against the reagent blank.

Sample preparation for geological samples

1.0 g of the samples (-100 mesh) was treated with 10 ml of hydrofluoric acid and 2-3 ml of nitric acid in a platinum dish. The samples containing organic matter or sulfides in abundance were roasted on a burner flame for ½ h prior to the treatment. The residue was fumed with perchloric acid, digested in hydrochloric acid (1.0M), filtered and volume was finally made up to 100ml, after neutralization with hexamine. Any precipitate appeared during the course of neutralization was removed by filtration.

10% Citric acid was added to 25ml aliquot of the solution. The solution was made ammoniacal with excess ammonia (2ml). 5ml of 0.1% DMG in 50% aqueous ethanol solution (v/v) was added and extraction was carried with three portions of 5ml $CHCl_3$. Nickel was stripped from the combined extracts with 0.5 ml HCl. The solution was evaporated to dryness and the residue was finally dissolved by warming with distilled water. Nickel was estimated in the solution by the method described in the procedure.

Sample preparation for aluminum alloys, stainless steel and manganese nodule 0.1g of sample was evaporated to dryness by heating with 5-6 ml of aqua regia. To the residue about 3 ml of H_2SO_4 (18 N) was added and evaporated to fumes. The mass obtained was heated to boiling with distilled water to dissolve the salts, undisslosed silica was filtered off through ashless pulp pad and the pad was washed thoroughly with hot water collecting the washings in the filtrate. The solution was made up to suitable volume after neutralization with hexamine. Any precipitate appeared during the course of neutralization was removed by filtration. Nickel was estimated in the solution by the method described in the procedure.

III. RESULTS AND DISCUSSION

Color reaction between R and nickel in absence or presence of surfactant

The reaction between R and Ni (II) in homogeneous aqueous medium at pH 5.2 -6.1 results in an intense wine-red color which is stable for at least 4h. Table 1 shows the effect of introducing the surfactants on the color reaction.

The presence of non-ionic surfactant TX sensitizes the reaction and greatly enhances the magnitude of absorbance (about 5 times), stability and reproducibility of the colored metal complex formed. Fig.1shows the absorption spectra of R and the complex in presence of TX against water and of complex against reagent blank (RB). The formation of the complex does not shift absorption maxima (486 nm) for the reagent appreciably (a little blue shift of 3.5nm). The presence of TX leads to a red shift about 12 nm of the λ_{max} for the complex. The absorbance of the complex in presence of TX against reagent blank (RB) is maximum at 557nm. The presence of anionic surfactant (Sodium dodecylsulfate) and cationic surfactant (Cetyltrimethyl ammonium bromide) affected the absorbance of the complex at λ_{max} adversely (Table 1).

Effect of pH

A maximum and constant absorbance was obtained within the range of pH 5.2-6.1.

Effect of surfactant concentration

This was determined by measuring the absorbance at 557 nm of a set of solution containing increasing amount of TX ($1.6.10^{-2}$% to $1.2.10^{-1}$ %) and fixed amount of metal ion and R. The absorbance increased with increasing TX, became maximum at $7.2.10^{-2}$% and remained constant until $8.8.10^{-2}$%. The TX concentration higher than this resulted in

decrease in the absorbance (Fig.2). In subsequent studies the concentration of TX was kept at $8.0.10^{-2}$%.

Effect of Na-K-Tartrate concentration

The effect of Na-K-tartrate was studied in the range 4.10^{-3}%-4.10^{-2}% on the formation of nickel-R complex by measuring absorbance of the complex at λ_{max} (557nm) of the complex. The optimal concentration of Na-K-tartrate was found to be in the range 4.10^{-3}%-2.10^{-2}%, concentrations exceeding this range resulted in decrease in absorbance (Fig.3) of the R-Ni (II) complex at 557 nm. A 2.10^{-2}% concentration of Na-K-Tartrate was used in subsequent studies.

Effect of R concentration

The effect of R concentration was studied in the range 1.10^{-5} – 8.10^{-5} M. The optimum absorbance of the complex coupled with minimum blank absorbance was found with $3.2.10^{-5}$ M R. The higher concentration of R was abandoned because of the increased absorbance of the reagent blank. In subsequent studies, the optimum concentration of the reagent $3.2.10^{-5}$ M was used (Fig.4).

Beer's Law, Sensitivity and Reproducibility

Beer's Law is obeyed at 557 nm between 0-0.35μg per ml of nickel in the final solution. The molar absorptivity and Sandell's sensitivity at 557 nm are $1.15.10^{5}$ L mol^{-1} cm^{-1} and 0.51ng cm^{-2} of nickel respectively. The precision is shown in table 2.

Composition, Stability and nature of the complex

The molar ratio[36] and continuous variation[37] method show that 6:1 ligand to metal complex is formed in the presence of TX. R-Ni (II) complex formed in the presence of TX was found to be stable for at least 40 hours. The presence of non-ionic surfactant TX greatly enhances the absorbance and stability of the nickel complex with R and the ionic surfactants, anionic (SDS) and cationic (CTAB) adversely, indicate the non-ionic nature of the complex.

Effect of the temperature

The reaction between R and nickel in presence of TX to form the colored R-nickel complex was found to be independent of temperature in the range of 10-40 °C.

Effect of diverse ions and removal of interferants

The effect of various diverse ions was studied individually setting the criterion as a ±2% change in the absorbance for 0.02 ppm of nickel in solution. Table 3 shows effects of diverse ions on the determination of 0.02 ppm of nickel in the solution by the method.

Under the conditions used no interference was observed in the determination of 0.02 ppm of nickel in solution by excess of ions in folds, Ca(II) (2.10^{6}), Sr(II) ($0.5.10^{6}$), Li(I) (12500), Mn(II) (400), Al(III) (400 in presence of 5 mg of K_2HPO_4, otherwise 100), Cr(VI) (20), V(V) (40), Cu(II) (40) in presence of 0.1ml of 1% hydroxylamine hydrochloride and 0.1ml of 0.1% KCNS), Zn(II) (40)in presence of 0.1ml of 0.1% KCNS), Pb(II) (40), U(VI) (100), SO_4^{2-} (25000), CNS$^-$(120), $C_2O_4^{-2}$ (900), Cl$^-$(35000), F$^-$(4500), $S_2O_3^{2-}$(175), citrate(30), PO_4^{3-}(6500).

However, Co (II) interfered seriously under the conditions used. The colour due to cobalt (2.34ppm,115fold excess) when alone fades after 45 minutes but the presence of nickel synergizes it making color stable which causes positive error.

The use of hexamine, a weak base, minimizes formation of amino complex and avoids co-precipitation of nickel along with insoluble hydroxides ensuring recoveries of nickel more than 95% at 0.25μg level and 99% at a level of 2.00μg of nickel, respectively (Table 2). However, cobalt and part of copper accompany nickel in solution and need removal (in case their amount exceed tolerance levels) prior to estimation of nickel by the procedure described. The presence of sodium potassium tartrate besides masking the interference due to uranium, vanadium and zinc, also complexes traces of iron and aluminum escaped precipitation as insoluble hydroxide on neutralization of sample solution with hexamine. Furthermore, hexamine acts as a buffer and its use brings the pH of solution in the range 5.2-6.1

Practical application

The validity of the method was tested by the determination of nickel in alloys of aluminum and cast stainless steel without prior separation and in inhouse samples, manganese nodules and few international geo-standard rock samples after prior separation of nickel with DMG.

The results (Table 4 and 5) agreed very closely with the values obtained by the ICP-OES and reported values in international geo-standard rock samples.

IV. CONCLUSION

The proposed method is highly sensitive, reproducible, simple, and rapid for the determination of Ni (II). The high sensitivity of the method superior to many of the reported methods[22-32] enables determination of Ni (II) in geological samples containing nickel down to 1ppm level without preconcentration.

ACKNOWLEDGEMENT

Table 1. Effect of the surfactants on the molar absorptivity λ max, etc of the R-Ni (II) Complex

Surfactant	Nature	λmax (RB) nm	Molar- Absorptivity $1 \, mol^{-1}cm^{-1}$	Stability h
Nil		545	2.1×10^4	4
Triton X-100	Nonionic	557	1.15×10^5	40
Sodium dode-cylsulfate	anionic	563	2.0×10^4	-
Cetyltrimethyl ammonium bromide		570	1.8×10^4	-

- Not studied because of low molar absorptibity.

Table 2.   Precision of Ni (II) determination, n=10

Nickel added μg	Nickel found μg	Standard deviation μg	RSD %
0.25	0.24	0.003	1.20
2.40	2.41	0.003	0.75
2.00	2.01	0.001	0.05

Table 3   Effect of foreign ions on the determination of 0.02 ppm of Ni (II)

Ions	Permissible* concentration, ppm
Li (I)	250
Ca (II)	4000
Sr (II)	1000
Mn (II)	8
Al (III)	2,8[a]
Cr (VI)	0.4
V(V)	0.8
Pb (II)	0.8
O (VI)	2.0
SO_4^{2-}	500
Cl^-	700
CNS^-	2.4
F^-	90
$S_2O_3^-$	3.5
Citrate	0.6
PO_4^{3-}	130
Cu (II)	0.8[b]
Zn (II)	0.8[c]
C_2O_4	18

*amount of foreign ions causing an error of $< \pm 2\%$ in the determination.

[a] In presence of 1ml of 0.5% K_2HPO_4

[b] In presence of 0.1ml of 1% hydroxylamine hydrochloride and 0.1ml of 0.1% KCNS.

[c] In presence of 0.1ml of 0.1% KCNS.

Table 4. Determination of nickel in International Geo-standard samples, n=6

Sample	Ni (II) ppm			
	Found (ICP-OES)	Found (Proposed-method)	Recommended* Value	RSD% (proposed method)
SY-2	9.9	10.01	10	0.12
SY-2	11.3	11.19	11	0.10
G-2	5.9	5.81	6	0.18
ASK-3	34.8	35.14	35	0.07

*Geostan. Newslett. Spce. Issue, 8 (1984) 22, Appendix

Table 5. Determination of nickel in geological samples, aluminum alloys, stainless steel and manganese nodule, n=6

Sample	Ni (II)ppm	
	Found (ICP-OES)	Found (proposed method)
Soil-1	3.0	2.95±0.02
Rock-1	11.0	10.85±0.03
Stream sediment-1	5.0	5.01±0.03
Mn-1[a]	1.22	1.21±0.01
Mn-2[a]	0.80	0.79±0.01
Al Ni-90[b]	22.3	21.0±0.03
Cast stainless steel-1[c]	0.95	0.98±0.12

[a] Manganese nodule

[b] Aluminum alloys

[c] Stainless steel.
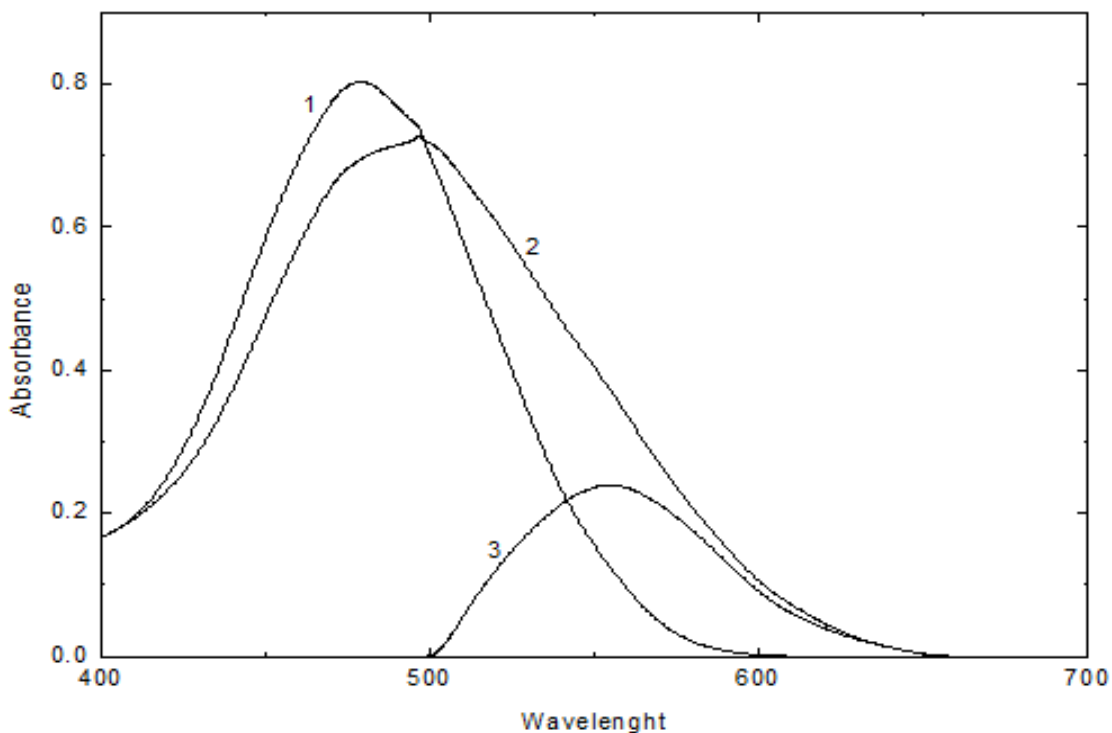
FIGURE 1. ADSORPTION SPECTRA OF NI (II)-5-(2'-CARBOXYPHENYL)AZOXINE-(R)-TRITON X (TX)-100 SYSTEM; [R] 3.2 x 10^{-5} M, [Ni (II)] 2.0 x 10^{-6} M, [TX] 8.0 x 10^{-2} %; (1) REAGENT AGAINST WATER; (2) COMPLEX AGAINST WATER; (3) COMPLEX AGAINST REAGENT BLANK
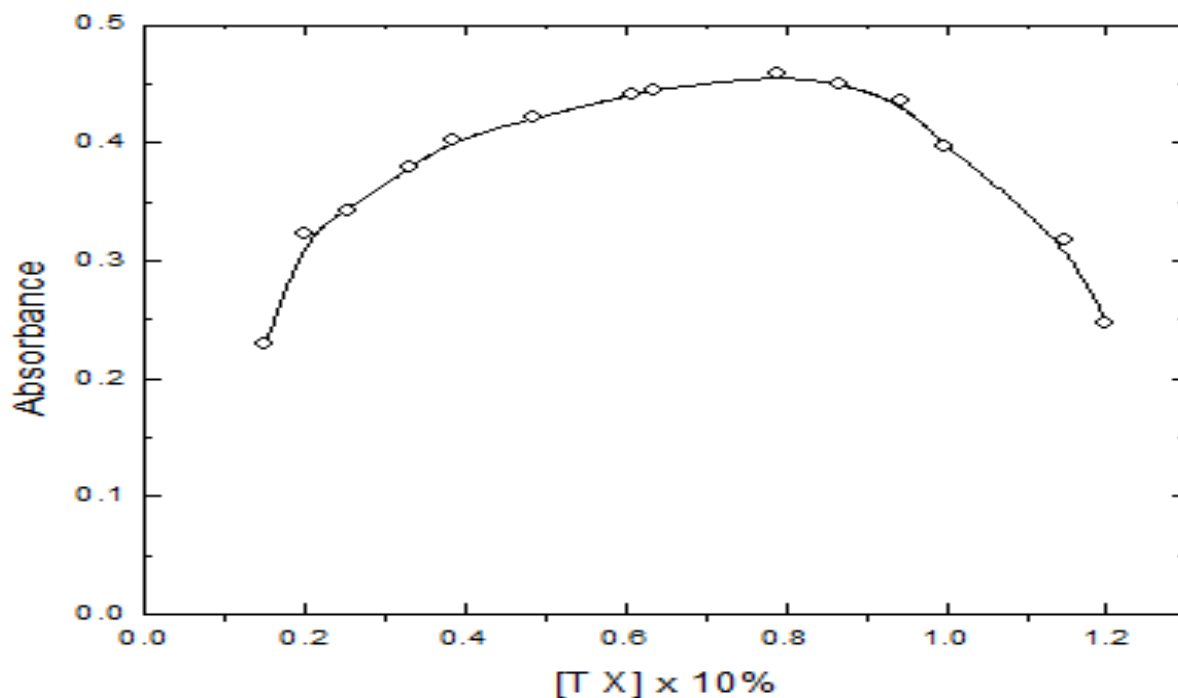

FIGURE 2. EFFECT OF TRITON X-100 (TX) CONCENTRATION ON Ni (II)-REAGENT-(R)-TX SYSTEM IN PRESENCE OF Na-K-TARTRATE AT pH 5.2-6.1; [Ni (II)] 4.0 x 10^{-6} M, [R] 3.2 x 10^{-5} M, [Na-K-TARTRATE] 2 x 10^{-2} %
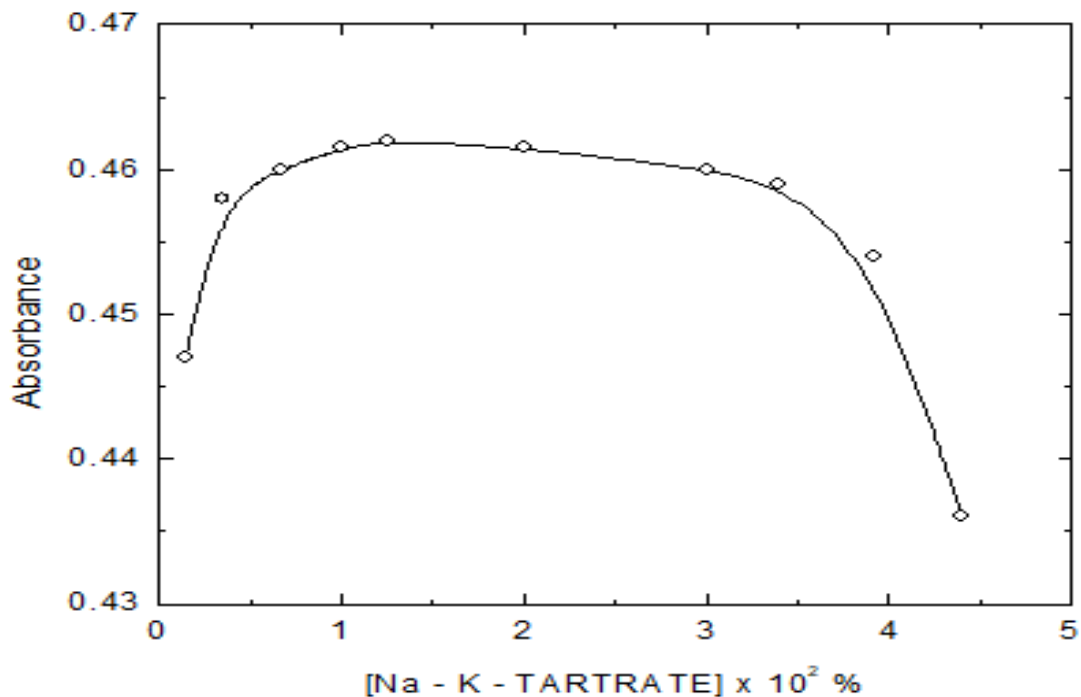
FIGURE 3. EFFECT OF Na-K-TARTRATE CONCENTRATION ON Ni (II)-REAGENT-(R)-TX SYSTEM AT pH 5.2-6.1 [Ni (II)] 4 x 10^{-6} M, [R] 3.2 x 10^{-5} M, [TX] 8.0 x 10^{-2} %

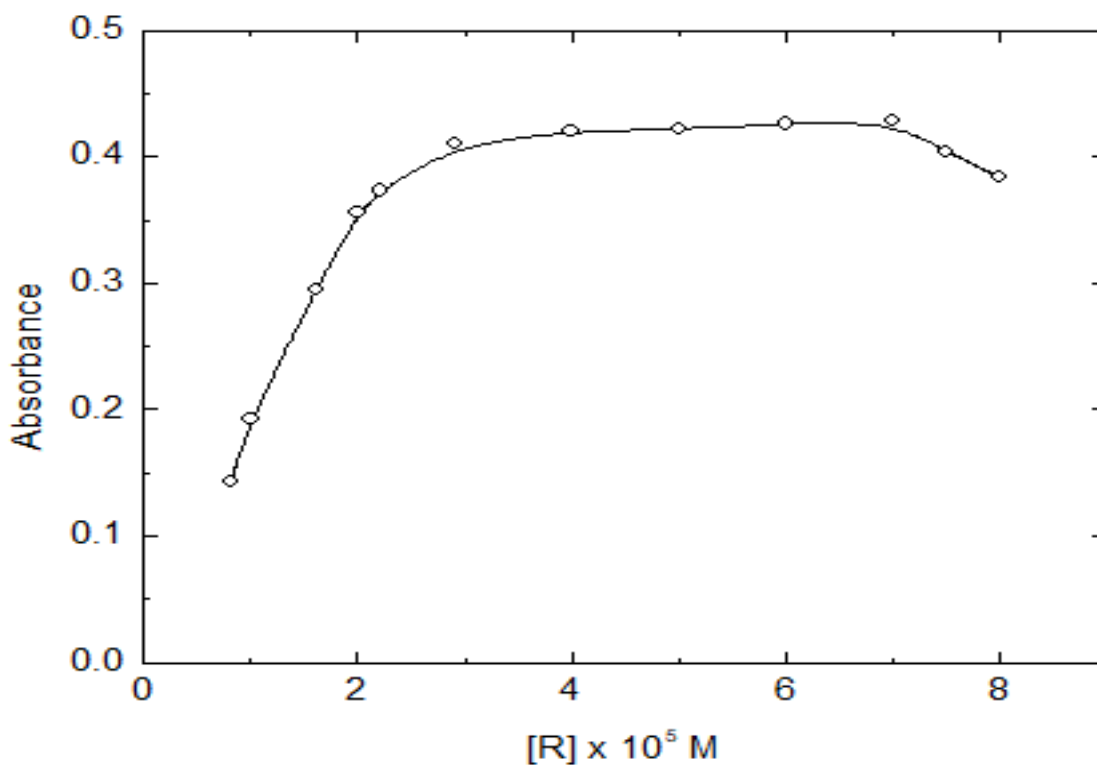FIGURE 4. EFFECT OF REAGENT CONCENTRATION [R] ON Ni (II)-R-TX SYSTEM IN PRESENCE OF NA-K-TARTRATE AT pH 5.2-6.1; [Ni (II)] 4 x 10^{-6} M, [TX] 8.0 x 10^{-2} %, [Na-K-TARTRATE] 2.0 x 10^{-2}%

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