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# Determination of vanadium in different environmental, Leafy vegetable and biological samples using 2-hydroxy-1-naphthaldehyde-p-hydroxy benzoichydrazone (HNHBH) spectrophotometrically

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**ABSTRACT**

*2-hydroxy-1-naphthaldehyde-p-hydroxy benzoic hydrazone (HNHBH)* ***is*** *used as a new analytical reagent for the direct and derivative spectrophotometric determination of vanadium (V). It reacts with vanadium in acidic medium (pH 4.0, sodium acetate and acetic acid buffer) to form deep yellow colored (λ max, 430 nm) 2:3 (V- HNHBH) complexes. The colour reaction is instantaneous and the absorbance remains constant for about 72h. The molar absorptivity and Sandall's sensitivity were found to be 2.30 x $10^4$ L $mol^{-1}cm^{-1}$ and 0.0025 µg $cm^{-2}$ respectively. The system obeys Beer's law in the range of 0.101-1.121 µg $mL^{-1}$ of V (V). Tolerance limits of various foreign ions were also studied. The complex was fairly stable (stability constant 4.73 x $10^{19}$) and Second and third order derivative spectrophotometric methods were also developed for the determination of vanadium (V) which showed greater sensitivity and selectivity. The proposed method was applied for the determination of vanadium (V) in Different Environmental, Leafy vegetable, and Biological Samples. The method has high sensitivity, selectivity, and precision and accuracy.*

**Keywords**: Vanadium (V), HNHBH, Direct and derivative spectrophotometry, Environmental, Leafy vegetable, and Biological Samples

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## INTRODUCTION

Vanadium is an important constituent of many industrially important alloys. It is widely distributed in various minerals and is a common constituent of coals, asphalts, bitumens and oil. Vanadium occurs in +2, +3, +4 and +5 oxidation states in its compounds, vanadium (V) compounds being the most stable.

Vanadium is essential for the growth of certain bacteria and algae. It is essential to ascidians (Sea squirts). Vanadium has long been recognized as an essential element in biological systems. It is apparently essential for chlorophyll and porphyrin biosynthesis in some higher plants. The presence of 30 to 40% vanadium in ferrovanadium steels imparts tensile strength, elasticity and toughness. Vanadium is an important component of ferrous alloys used in jet-aircraft engines and in turbine blades where high temperature creep resistance is a basic requirement. Vanadium compounds are used as catalysts in colouring glass and ceramics and as driers in paints and inks.

Vanadium compounds are toxic to human beings and animals. They inhibit biosynthesis of cholesterol in mammals. It is found to be present in many tissues and the concentrations in human blood and plasma are reported [1] to be in the range 0.005-8.4 µM. Vanadium poisoning is an industrial hazard [2]. Vanadium has also been reported as the index element in urban environmental pollution, especially air pollution,[3] Fossil fuels such as crude petroleum, fuels, oils, some coals and lignite contain high amounts of vanadium. Burning of these fuels releases vanadium into the air which then settles on the soil. There are cases of vanadium poisoning, the symptoms of which are nervous depression, vomiting, coughing, anemia, diarrhea and increased risk of lung cancer, that are sometimes fatal. [4-5]

The most widely used reagent for vanadium (V) determination is pyridyl resorcinol (PAR). Most of the reported methods suffer from limitations such as serious interference from U (VI), Ti (IV), Zr (IV) and Nb (V) ions, the delay in colour development and also significant absorbance for the reagent blank solution. [8-10]

Though several organic reagents are used for the determination of trace amounts of vanadium, only a few of these regents are useful for the spectrophotometric determination of the metal ion in aqueous medium. Majority of the reported methods are extraction methods using harmful organic solvents. An attempt has been made for simple, sensitive and non- extractive methods for the determination of vanadium in microgram quantities using HNHBH as chromogenic agent.

## MATERIALS AND METHODS

Schimadzu 160A UV-visible spectrophotometer (PerkinElmer Singapore Private Limited, Singapore) equipped with 1.0 cm quartz cell and an ELICO model LI - 610 pH meter (M/s ELICO private limited, Hyderabad, India) were used in the present study.

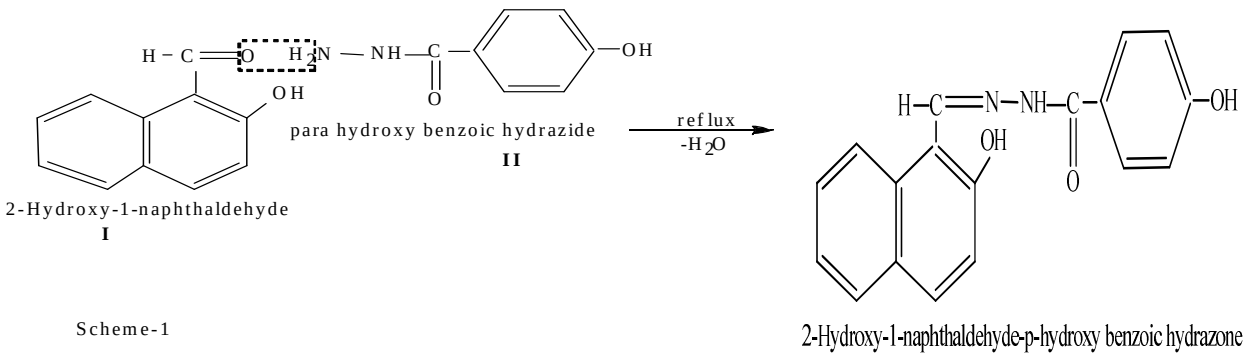
**Reagent and solutions**

All chemicals used were of analytical-reagent grade of the highest purity available procured from Merck. Doubly distilled de-ionized water was used throughout the experiment. Glass vessels were cleaned soaking in acidified solutions of $K_2Cr_2O_7$ followed by washing with con. $HNO_3$ and were rinsed several times with high purity deionized water.

**2.1 Preparation of 2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone (HNHBH):**

The reagent (HNHBH) was prepared by simple condensation of 1 mol of 2-hydroxy-1-naphthaldehyde and 1 mol of p-hydroxybenzoichydrazide. In a 2

50-ml Erlenmeyer flask, a hot ethanolic solution of 2-hydroxy-1-naphthaldehyde (5ml, 0.0438mol in 5ml of ethanol), thiosemicarbazide (4g, 0.0438 mol, dissolved in10 ml of hot water) were taken in 250-ml round bottom flask. Suitable quantity (~ 2ml) of glacial acetic acid was added to the reaction mixture and refluxed for 3 hours.[10] On cooling the reaction mixture, the reddish brown coloured solid obtained was then separated by filtration, washed and dried. The product was recrystallized from aqueous ethanol in the presence of norit and dried in *vaccuo*, yield 4.2 g; m.p.273$^0$c as shown in Scheme 1.




Scheme-1

**2.2. Characterization**:
The compound was characterized by IR and 1H-NMR spectral data. Infrared spectrum of HNHBH shows bands at [3467(m) and 3185(m,br)], 3292(m), 3207(m), 1735(s), merged peaks at 1635 and 1608(m),1466(s), 1383(w), 1455 to 1591, 1256(δ) and 1280(δ) 746, 764 cm-1 respectively corresponding to υ OH stretching, υ (N-H) stretch, υ (C-H ) bond, υ (C=N) stretching, υ (C-C) aromatic ring, δ phenolic (>C=O) stretching and naphthalic( >C=O) stretching vibrations respectively, δ (C-H)-oop bend (aromatic) vibrations.1H-NMR spectrum of HNBH (CDCl3+ DMSO-d6) showed signals at 12.10 (2H,s), 10.50 (1H, s), δ9.49 (1H,s), 7.91(4H, s), 6.93-7.65 (5H, m), 8.20(1H, d) due to –OH( phonolic and naphthalic),–NH, –CH, phenyl, naphthyl, naphthyl (influenced by the adjacent –CH proton of azomethine group).

**2.3 HNHBH solution**
The reagent solution (0.01M) was prepared by dissolving 31 mg of the compound in dimethylformamide (DMF) in 25-ml standard flask. The reagent solution is stable for at least 12h.

**2.4 Vanadium (V) solution**
0.1219 g of ammonium meta vanadate ($NH_4VO_3$) (AR Qualigens) was dissolved in hot distilled water and the solution was made up to 100 ml in a volumetric flask after cooling with distilled water. The stock solution was standardized titrimetrically[6,7].

**2.5 Buffer Solution**
Buffer solutions of various pH values were prepared by mixing 1 M hydrochloric acid and 1 M of sodium acetate (pH 1.0-3.0), 0.2 M acetic acid and 0.2 M sodium acetate (pH 3.5-7.0), 0.2 M acetic acid and 1 M sodium acetate (pH 7.0) and 2M ammonium chloride and 2 M ammonium hydroxide (pH 8.0-10.0) solutions in appropriate ratios. The pH of the solutions was checked with pH meter. Suitable portions of these solutions are mixed to get the desired pH.

**2.6 Preparation of Sample solutions:**
**Preparation of Biological Sample solutions**
**Cabbage leaves and Goat liver**
The cabbage leaves and goat liver were washed with distilled water thoroughly to remove the adhered impurities. They were dried with filter paper and suitable weight of the sample was weighed. Known amounts of vanadium were added as the real samples do not contain any measurable amounts of vanadium. The samples were dried, ashed and brought into solution by acid treatment as per the recommended procedures. [11,12] The contents were neutralized with dilute $NH_4OH$ solution and diluted to known volume with distilled water. The amounts of vanadium present in biological samples were determined by the proposed method and the results obtained are presented in the table 3.

**Human blood, urine [13]**
Human blood or urine (50 ml) samples were taken into 100 ml micro Kjeldhal flask. 5 ml concentrated $HNO_3$ were added and gently heated. When the initial brief reaction was over, the solution was removed and cooled. 1 ml of concentrated $H_2SO_4$ was added followed by 1 ml of 70% $HClO_4$. The solution was again heated to dense white fumes, repeating $HNO_3$ addition. The heating was continued for 30 minutes and then cooled. The contents were filtered and neutralized with dilute $NH_4OH$ in the presence of 1-2 ml of 0.01% tartrate solution. The solution was transferred into 10 ml volumetric flask and diluted to the volume with distilled water. Suitable aliquots were taken and analyzed for vanadium and the results are presented in table 3. Preparation of environmental water samples [14]

One liter of each filtered environmental water sample was evaporated almost to dryness with a 1: 5 mixture of $H_2SO_4$ : $HNO_3$. This was then dissolved in 10 ml of distilled water by heating, then cooled and neutralized with dilute $NH_4OH$. The resulting solution was quantitatively transferred into a 25 ml volumetric flask and made upto the mark with distilled water. Known volumes of the prepared samples were analyzed by the proposed method and the amounts of vanadium present were evaluated. Known amounts of vanadium were also added and the total recovery percentages were calculated. Results obtained in these analyses are given in table 3.

**Preparation of rice sample solution [15]**
The sample was dried at 110$^{o}$C until constant weight was obtained. One gram of the sample was heated with 10 ml of 5 M $HNO_3$ on a sand bath. 5 ml of $HClO_4$ (70% W/W) were added and the solution was evaporated to near

dryness. The residue was dissolved in 10 ml of 0.1 M HCl and the mixture was heated to boiling, cooled and filtered. The filtrate obtained was transferred into a 100 ml volumetric flask and diluted to the mark with distilled water.

**Preparation of human hair solution**
The sample solution of human hair was prepared using the procedure described in 2.6.

The amount of vanadium present in rice and human hair samples were determined by the proposed method and the results obtained are presented in table 3.

**Preparation of soil samples**
The soil sample solutions were prepared using the procedure described in 2.6. Vanadium present in these samples was determined by the present method as well as by atomic absorption spectrophotometric method. Results obtained in these analyses are given in table 3.

**2.7 Absorption spectrum**
The absorption spectrum was recorded between differential absorbance (ΔA) and the wavelength and shown in fig.1. As the absorption was maximum at 430 nm, the analysis of V (V) was carried out by measuring the absorbance at 430 nm against the reagent blank.

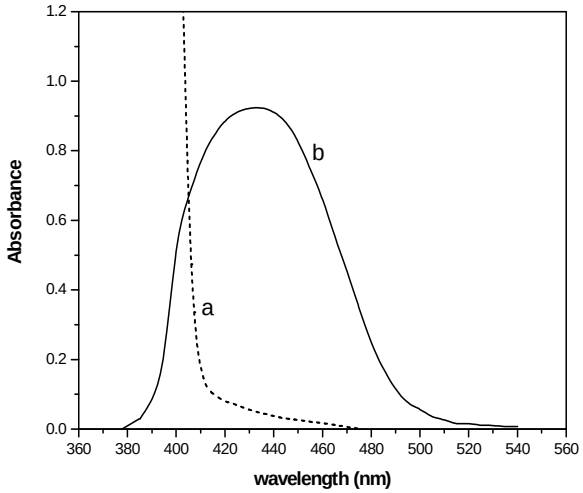



**Fig.1. Absorption spectra of (a) HNAHBH Vs buffer blank**

**(b) V(V) – HNAHBH Vs reagent blank**
[V(V)] = $4 \times 10^{-5}$ M
[HNAHBH] = $1 \times 10^{-3}$ M
pH = 4.0

## RESULTS AND DISCUSSION

The reagent, HNHBH is easily obtained by the condensation of 2-hydroxy-1-naphthaldehyde and p-hydroxybenzoichydrazide. A 0.01M solution of this reagent is stable for 72h. The absorbance data measured for experimental solutions containing different known amounts of Vanadium (V) fitted into a straight line equation $A_{430}$=0.346C +0.0028. Beer's law was obeyed in the concentration range 0.101-1.121 µg $mL^{-1}$ of Vanadium (Fig.2.) The molar absorptivity, Sandell's sensitivity, detection limit, determination limit, relative standard deviation, correlation coefficient and other statistical data of the direct method were evaluated and presented in table 1.

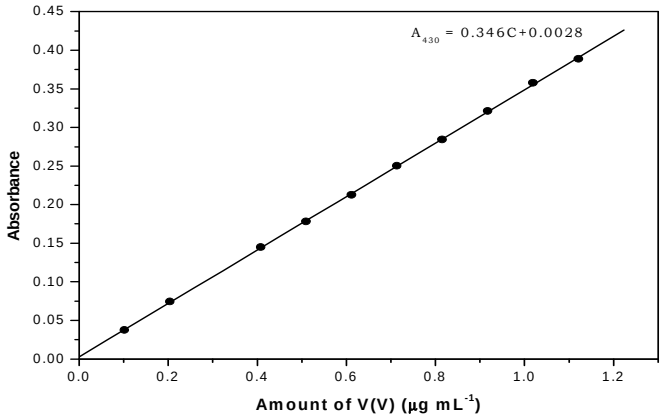



**Fig.2. Applicability of Beer's law**

[HNAHBH] = 5 x $10^{-4}$M
Wavelength = 430 nm
pH = 4.0

**Table.1.Analytical characteristics of [V(V)- HNAHBH]**

| Parameter | V(V)- HNAHBH method 430 nm |
|---|---|
| Beer' law range (µg $mL^{-1}$) | 0.101-1.121 |
| Molar absorptivity, ε (L $mol^{-1}$ $cm^{-1}$) | 2.30 x $10^4$ |
| Sandell's sensitivity (µg $cm^{-2}$) | 0.0025 |
| Angular coefficient (m) | 0.3460 |
| Y-intercept (b) | +0.0020 |
| Correlation coefficient (r) | 0.9999 |
| RSD (%) | 0.67 |
| Detection limit (µg $mL^{-1}$) | 0.013 |
| Determination limit (µg $mL^{-1}$) | 0.039 |
| Composition | 2 : 3 |
| Stability constant | 4.73 x $10^{19}$ |

The anions EDTA, citrate, tartrate, phosphate, iodide, thiosulphate, thiocyanate, sulphate, bromide and chloride did not interfere even when present in more than 1000 fold excess. Thiourea and carbonate were tolerable in more than 800 fold excess. Tolerance limits of oxalate and fluoride were 560 and 520 folds respectively. The cations Na (I), Mg(II), Ca(II), K(I), Sr(II), Ba(II), did not interfere even in more than 1000 fold excess. Pb(II), Te(IV) were tolerable in 200 fold excess. Numbers of transition and lanthanide metal ions were tolerable between 20 – 80 fold excess. Many cations which showed serious interference were masked with suitable masking agents except Fe (II) and presented in table 2.

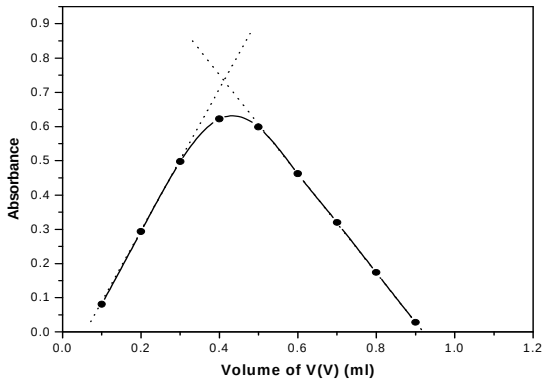



**Fig.3. Job's curve**

[V(V)] = [HNAHBH] = 1x $10^{-3}$M
Wavelength = 430 nm : pH = 4.0

### 4.1. Determination of Vanadium (V)

Vanadium (V) reacts with HNHBH in acidic pH to give coloured complexes. The colour reaction is instantaneous at room temperature. The order of addition of metal ion, reagent, and buffer has no effect on the absorbance of complex. Various physico-chemical and analytical characteristics of the complex are summarized in Table 1. The stoichiometry of the complex (M: L=2:3), was determined by Job's continuous variation [16], molar ratio methods. The data obtained in Job's method were used in the calculation of stability constant of the complex, it is found to be 4.73 x $10^{19}$. Acetic acid (2M) –Sodium acetate (2M) buffer solution (pH 4.0 μ, 0.2 and T=300K) and equimolar (5 x$10^{-4}$M) solution of V (V) and HNHBH were used in these methods.

### 4.2. Interference

The effect of various cations and anions which are generally associated with the metal ion on the determination of Vanadium (V) was studied by measuring the absorbance of the Vanadium (V) complex containing 0.5 μg/ml of Vanadium (V) in solution. An error of ± 2% in the absorbance or amplitude reading in the case of derivative methods considered tolerable.

**Table.2. Tolerance limits of foreign ions**

Amount of V(V) taken = 0.51μg $mL^{-1}$ pH =4.0

| Foreign ion | Tolerance limit (folds) | Foreign ion | Tolerance limit (folds) |
|---|---|---|---|
| EDTA | 10950 | $Na^{I}$, $Mg^{II}$, $Ca^{II}$, $K^{I}$ | 3700 |
| Citrate | 6305 | $Sr^{II}$, $Ba^{II}$ | 2855 |
| Tartrate | 4352 | $Pb^{II}$, $Te^{IV}$ | 210 |
| Iodide, Thiosulphate | 3640 | $Cd^{II}$ | 130 |
| Bromide | 2350 | $Se^{IV}$, $Cr^{VI}$, $Au^{III}$, $Ce^{IV}$ | 84 |
| Thiocyanate, Sulphate | 1705 | $Th^{IV}$ | 46 |
| Phosphate | 1550 | $Zr^{IV}$, $Ag^{I}$ | 38 |
| Nitrate | 1370 | $Ir^{III}$, $Bi^{III}$ | 24 |
| Chloride | 1050 | $Fe^{II}$ | 8 |
| Thiourea | 905 | $Zn^{II}$ | 6 |
| Carbonate | 850 | $Mn^{II}$, $U^{VI}$, $In^{III}$, $Tl^{III}$ | 4 |
| Oxalate | 560 | $Mo^{VI}$ | 1.5 |
| Fluoride | 520 | $Cu^{II}$, $Al^{III}$, $Co^{II}$, $Ni^{II}$ | <1 |

### 4.3 Applications:

To substantiate the validity of the proposed direct method, it was applied for the determination of Vanadium (V). The results obtained were compared with certified values and presented in tables 3.

**Table.3. Determination of Vanadium in Environmental, Leafy vegetable, and Biological Samples**

| Name of the sample | Amount of Vanadium found (µg/L) | | | | |
|---|---|---|---|---|---|
| | V(V)added (µg $mL^{-1}$) | Proposed method* | Reference Method* | Recovery (%) | RSD (%) |
| Sea water [a] | 100 | 144.0 | Dithizone Method 140.1 | 102.7 | 1.18 |
| Tap water [b] | 100 | 125.05 | 123.32 | 99.1 | 1.15 |
| Well water [c] | 100 | 137.40 | 138.3 | 101.3 | 0.80 |
| Drain water [d] | 100 | 150.00 | 149.62 | 102.7 | 0.65 |
| Cabbage (5g) [e] | 12.0 | 11.54 ± 0.08 | 12.2± 0.04 | 101.6 | 0.66 |
| Goat liver | 7.0 | 7.42 ± 0.06 | 7.12± 0.02 | 101.7 | 0.69 |
| Rice | 1.00 | 0.138 ±0.002 | | 97.4 | |
| Human hair | 1.00 | 0.198 ±0.006 | | 101.5 | |
| Blood Sample-1 [f] | | 10.5 ± 0.9 | 12.0 ± 1.4 | | |
| Urine sample-1 [g] | | 2.8 ± 0.5 | 2.5 ± 0.6 | | |
| Blood Sample-2 [h] | | 428 ± 1.8 | 420 ± 2.1 | | |
| Urine Sample-2 [i] | | 120 ± 1.2 | 125 ± 1.5 | | |
| Soil sample-1 [j] | | 0.0385 ± 0.002 | AAS Method 0.0388 ± 0.001 | | |
| Soil sample-2 [k] | | 0.0240 ± 0.008 | 0.0250 ± 0.003 | | |
| Soil sample-3 [l] | | 0.0486 ± 0.018 | 0.0502 ± 0.005 | | |

*Average of five determinations ± SD
a = collected from Bay of Bengal near Nellore, A.P.
[b=] Anantapur Municipality, Tap water
[d=]collected from discharges of J.K.Steel industry; Tadipatri,A.P.
f =Normal Adult Male
g=Normal Adult Male
h= Lung cancer patient(male)
i=Lung cancer patient(male)
j=Bellary iron mines, Bellary
k=Agriculture land, Anantapur
l=Ultratech cement industries, Tadipatri
f to i= By the courtesy of Nizam institute of medical sciences, Hyderabad

**Table.4.Comparison of determination of V(V) with different methods**

| Reagent | λmax(nm) | pH/ medium | Aqueous/ Extraction | Beer's law range(µg $mL^{-1}$) | ε x $10^4$ (L $mol^{-1}cm^{-1}$) | Interference | Ref |
|---|---|---|---|---|---|---|---|
| 6-Chloro-3-hydroxy-2[2'-(5'-methylfuryl)]-4H-chromen-4-one | 432 | - | Extraction | 0.2-1.4 | 3.98 | - | 17 |
| Diantipyryl-p-methylphenylmethane | 480 | - | Aqueous | 0.002-0.06 | 80.5 | Oxalic acid and thiourea | 18 |
| Trioctylamine | 605 | - | Extraction | 0-0.34 | 4.22 | - | 19 |
| Pyridine and dibenzoylmethane | 405 | - | Extraction | Up to 5 | - | - | 20 |
| Phenothiazine derivatives | 513 | - | Aqueous | 0.25-5.0, 0.2-4.0 | 1.05,7.18 | Cr(VI) and Ce(IV) | 21 |
| 2-(2-Quinolylazo)-5-diethylaminophenol | 590 | - | Aqueous | 0.01-0.6 | 12.3 | Pt(IV), Ag(I), Ir(IV), Rh(III), Ru(III), U(VI) and Th(IV) | 22 |
| 2,4-Dihydroxyacetophenone benzoylhydrazone and pyridine | 363 | - | Extraction | 0-1.5 | 2.83 | - | 23 |
| N-Hydroxy-N-o-tolyl-N'-(2-methyl)-phenyl-benzamidine HCl and 4-hydroxy benzaldehyde | 580-590 | - | Extraction | - | 0.828 | - | 24 |
| Pyridylazo resorcinol and iodonitro-tetrazoliumchloride | 560 | - | Aqueous | upto 15.0 | - | - | 25 |
| 2,3-dichloro-6(3-carboxy-2-hydroxy naphthylazo)quinoxaline | 606 & 800 | - | Aqueous | - | - | - | 26 |
| Thionin | 600 | - | Aqueous | 0.2-10.0 | 2.298 | - | 27 |
| 2-Pyrrole aldehyde phenyl semicarbazone | - | - | Extraction | - | - | - | 28 |
| 2-Hydroxy-1-naphthaldehide-p-hydroxybenzoichydrazone | 430 | 4.0 | Aqueous | 0.101-1.121 | 2.3 | Mn(II),Tl(III), U(VI),Mo(VI), In(III), Al(III), Cu(II), Zn(II), Co(II), Ni(II) interference eliminated by masking agents. | Present (direct) method |

## CONCLUSION

The present method is simple, rapid, and sensitive without any type of extraction and various samples have been studied which gave encouraging results. The results of the present method were compared with those of some of the already reported methods and presented in table 3. The comparison shows that both the direct and derivative methods proposed are more sensitive than majority of the reported methods. Some of the recent methods were presented in table.4. for comparison.

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## REFERENCES

[1] J.Versieck, and R.Cornelis, *Anal. Chim. Acta***, 1980**, 116**,** 217.
[2] G.D. Clayton and F.E.Calyton, Patty's Industrial Hygiene and Toxicology, vol. 2A, 3rd Ed., Wiley New York, **1981**, P. 2013.
[3] S.Langard, T. Norseth, L. Friberg, G.R.Nerberg, and V.B. Vouk, (Eds.), Hand Book on toxicology of metals**,** Elsevier, Amserdam, **1986**.
[4] B.Venugopal and T.D Luckey, Metal Toxicity in Mammals 2**,** plenum press, New York, **1979**, P. 220.
[5] A.Safavi, M.R. Hormozi Nezhad, and E.Shams, *Anal Chim. Acta***, 2000**, 409, 283.
[6] A.Ali Ensafi, M.K. Amini, and M. Mazloum, *Anal. Lett***, 1999**, 32**,** 1927.
[7] K.Gavazov and A.Alexandrov, *Talanta***, 2000**, 52**,** 539.
[8] M.N.Abbas, A.M. Homoda and C.A. E.Mostafa, *Anal. Chim. Acta***, 2001**, 436**,** 223.
[9] G.Chakrapani, D.S.R.Murthy, B.K. Balaji and R. Rangaswamy, *Talanta***, 1993**, 40**,** 541.
[10] S.A.Abbasi, *Anal.lett*, **1987**, 20, 1347.
[11] D.Glick(Ed), Methods of biochemical analysis, Johnwiley, **1973**, 21, 39.
[12] M.L.Jockson, Soil chemical analysis, Prentice-Hall Englewood Cliffs, **1987**, 326.
[13] M.J.Ahmed, S.Banoo, *Talanta*, **1999**, 48, 1085-1094.
[14] J.Gao et al, *Talanta*, **2000**, 51**,** 447-453.
[15] A.U.Bielvonwu, *Afr. J. Sci. Technol***, 1996**, 8, 32..
[16] A.K.Chakrabarti, *Proc. Natl. Acad. Sci***,** *India section A***, 1989**, 59, 31.
[17] Y.K. Agarwal and K.T.John, *Anal. Lett***, 1986**, 19**,** 1177.
[18] N.Agnihotri, R.Dass and J.R.Mehta, *J. Indian Chem. Soc***, 2000**, 77**,** 264.
[19] W.Huang, Q.Xie, Q.Luo and Q. Xu, *Yejin Fenxi***, 2000**, 20, 44.
[20] M.B.Melwanki, J.Seetharamappa and S.P.Masti, *Anal. Sci***, 2001**, 17, 979.
[21] Q.Hu, X.Wu, G.Yang, Z.Huang and J.Yin, *S. Afr. J. Chem***, 2004**, 57, 15.
[22] N.Agnihotri, R.Dass and J.R.Mehta, *Chem. Anal. (Warsaw)***, 2003**, 48, 853.
[23] A.Mishra, S.Khan and M.Hemlata, *Asian J. Chem***, 2001**, 13, 1199
[24] K.Gavazov, Z.Simeonova and A.Alexandrov, *Talanta***, 2000**, 52**,** 539-544.
[25] S.Amin Alaa, *Spectrochimica Acta Part A:* Molecular and Bimolecular spectroscopy**, 2003**, 59, 1025 – 1033.
[26] B.Cherian, Tom, Narayana, *ulletin of the Chem. Soc. of Ethiopia*, **2005**, 19(7)**,** 155 -161.
[27] G.M.Mastoi, M.Y.Khunawar and R.B.Bozdar, *Journal of Quantitative Spectroscopy and Radiative Transfer*, accepted 6 February **2006**.
[28] T.M..Kiran Kumarand H.D.Revanasiddappa, *Journal of Iranian chemical society*, **2005**, 2, 161-167.