

Spectrophotometric determination of nickel(II) using 5-Br-PADAP and *N*-hydroxy-*N,N'*-diphenylbenzamidine

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A sensitive and simple spectrophotometric method for determination of Ni^{II} with 2-[(5-bromo-2-pyridylazo)]-5-diethylaminophenol (5-Br-PADAP) and *N*-hydroxy-*N,N'*-diphenylbenzamidine (HDPBA) is described. The Ni^{II} -2-[(5-bromo-2-pyridylazo)]-5-diethylaminophenol (5-Br-PADAP) complex is extracted with *N*-hydroxy-*N,N'*-diphenylbenzamidine (HDPBA) in chloroform at pH range 4.0–6.0 to give red colour complex. Extracted complex shows λ_{max} at 530 nm. Procedure is checked by finding relative standard deviation (RSD, $n = 10$) value for solutions each containing $2.0 \mu\text{g ml}^{-1}$ Ni^{II} and the RSD value of the procedure is found to be 1.6%. The system obeyed Beer's law up to $0.5 \mu\text{g ml}^{-1}$ of nickel and the identification limit of the method is $7.4 \times 10^{-10} \text{ g ml}^{-1}$ on a three times the standard deviation of the blank absorbance basis. The Sandell's sensitivity and molar absorptivity of the complex are $0.00056 \mu\text{g ml}^{-1}$ and $1.04 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ respectively. The effect of foreign ions and other experimental variables are studied.

The present paper deals with a simple and highly sensitive ($\epsilon = 1.04 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) spectrophotometric method for nickel in steel samples using 2-[(5-bromo-2-pyridylazo)]-5-diethylaminophenol (5-Br-PADAP) and *N*-

hydroxy-*N,N'*-diphenylbenzamidine (HDPBA). The characteristic features of some spectrophotometric methods reported earlier for determining nickel are presented in Table 1.

Table 1. Comparison with other spectrophotometric method

Reagent	pH	Solvent	λ_{max} nm	$\epsilon =$ $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	Remarks
1-(2-Pyridylazo)-2-naphthol ^a	4.6	CHCl_3	580	5.1×10^4	Critical pH, Co and Fe interfere
1-(2-Pyridylazo)-2-naphthol + Tx-100 ^b	6.0–10.0	–	590	5.6×10^4	Sulphydryl acetic acid was used as accelerator
Diacetylmonoxime isonicotinoyl hydrazone ^c	8.0–9.0	Water	366	1.75×10^4	Al and Cu interfere
2-(2-Pyridylazo)-5-methoxyphenol ^d	7.5–10.0	CHCl_3	520	1.1×10^4	Sensitivity is poor
2-(2-Thiazolylazo)- <i>p</i> -cresol ^e	5.9	Water	580	2.6×10^4	Cu, Bi, Sn, Cd, etc. interfere
Diacetyl monoxime glycinimine ^f	8.5–11.0	Aqueous ethanol	450	1.7×10^4	Cr, V and Mn precipitated
5-Mercapto-3-methyl-4-(2-pyridylideneamino)-1,2,4-triazole ^g	7.0–10.0	Water	400	8.51×10^3	Poor sensitivity
<i>N</i> -Hydroxy- <i>N,N'</i> -diphenylbenzamidine + 2-[(5-bromo-2-pyridylazo)]-5-diethylamino phenol	4.0–6.0	CHCl_3	530	1.04×10^5	Metal ions interfere but it could be removed by using masking agent Present method

^aRef. 4. ^bRef. 5. ^cRef. 6. ^dRef. 7. ^eRef. 8. ^fRef. 9. ^gRef. 10.

Results and discussion

The method for determination of Ni^{II} has been done by extraction of Ni^{II} -5-Br-PADAP-HDPBA complex into chloroform at pH 5.0.

The complex Ni^{II} -5-Br-PADAP-HDPBA formed in chloroform, exhibits maximum absorbance at around 530 nm against the reagent blank at an extraction pH 5.0.

The effect of various organic solvents for the extraction of Ni^{II} -5-Br-PADAP-HDPBA complex was studied. The values of molar absorptivity at wavelength of maximum absorption of the complex in different solvents are as follows: benzene ($\epsilon = 1.02 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; λ_{max} 530 nm), ethyl acetate ($\epsilon = 0.80 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; λ_{max} 530 nm), toluene ($\epsilon = 1.00 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; λ_{max} 530 nm), CCl_4 ($\epsilon = 1.02 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; λ_{max} 520 nm), chloroform ($\epsilon = 1.04 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; λ_{max} 530 nm). Complete extraction (>99%) and maximum absorbance of the complex is observed with chloroform as compared to the other solvents therefore chloroform was chosen for further studies.

The maximum absorption of the Ni complex at different pH values was plotted and all the curves were found similar and exhibited maximum absorption at 530 nm (Fig. 1). Maximum and constant absorbance was observed at pH range 4.0–6.0 for nickel complex. Therefore, buffer solution of $\text{pH } 5.0 \pm 0.2$ was kept throughout the experiment (Fig. 2).

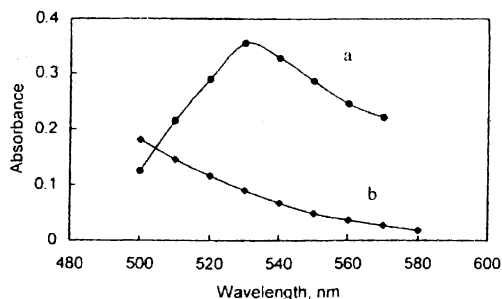


Fig. 1. Absorption spectra of Ni^{II} - (5-Br-PADAP)-HDPBA complex: (a) in chloroform against reagent blank, (b) at pH 5.0.

The stable colour of the complex was achieved, when the concentration of 5-Br-PADAP in the final aqueous solution was varied between $2.3\text{--}3.7 \times 10^4 \text{ mol dm}^{-3}$. Hence, the present investigation was carried out at $3.1 \times 10^4 \text{ mol dm}^{-3}$ of 5-Br-PADAP throughout the experiment.

The result obtained indicated that at least $0.86\text{--}1.70 \times 10^{-2} \text{ mol dm}^{-3}$ HDPBA in chloroform was adequate for the complete extraction of the Ni^{II} complex. Therefore, a $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ HDPBA was employed throughout

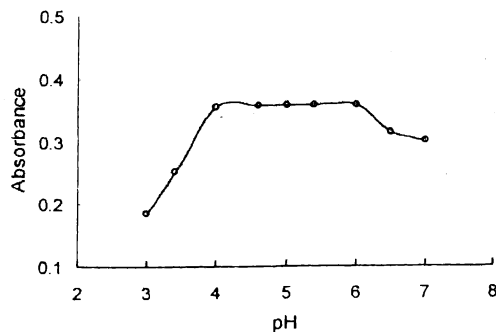
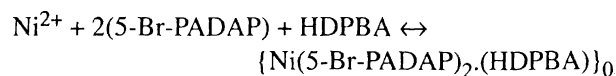


Fig. 2. Effect of pH on the absorbance of the Ni^{II} - (5-Br-PADAP)-HDPBA complex in chloroform.

the experiment.

The composition of the nickel complex was determined by the curve fitting method. The molar ratio of metal to 5-Br-PADAP and HDPBA was determined by logarithmic value of distribution ratio of metal [$\log \{A_{\text{eq}}/(A_{\text{max}} - A_{\text{eq}})\}$] (where, A_{max} = maximum absorbance of the complex at λ_{max} under optimum reagent concentration at a level of $2.0 \mu\text{g Ni}^{\text{II}}$ 10 ml^{-1} organic phase and A_{eq} = absorbance of Ni^{II} complex at equilibration with different known concentrations of reagents viz. 5-Br-PADAP/HDPBA) versus logarithmic values of varied known concentrations of 5-Br-PADAP/HDPBA in chloroform.

The inclinations of the curves for 5-Br-PADAP and HDPBA were found to be very close to integer 2 and 1 respectively. Thus, a 1 : 2 : 1 molar ratio complex of Ni^{II} : 5-Br-PADAP : HDPBA in chloroform was predicted. Fig. 3 indicates the metal-ligand ratio of the 5-Br-PADAP and HDPBA. The overall reaction can be expressed as follows:



Subscript 0 is organic phase.

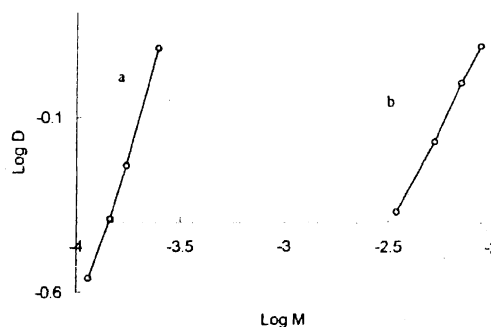


Fig. 3. Plot of curve fitting data for the determination of stoichiometry of the Ni^{II} -5-Br-PADAP-HDPBA complex in chloroform: (a) 5-Br-PADAP; (b) HDPBA.

The system obeyed Beer's law up to $0.5 \mu\text{g Ni}^{\text{II}} \text{ ml}^{-1}$ with an excellent linearity in terms of correlation coefficient¹ value of 0.99. The sensitivity of the Ni^{II} -5-Br-PADAP-HDPBA complex, calculated in terms of molar absorptivity, is $1.04 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 530 nm. The precision of the method in terms of relative standard deviation ($n = 10$) for the determination of $2.0 \mu\text{g Ni}^{\text{II}}$ is 1.6%. In this method the detection limit, defined as for photometry, the concentration of analyte causing more absorbance than twice the standard deviation of ten replicate measurements of blank absorbance at 95% probability is $7.4 \times 10^{-10} \text{ g Ni}^{\text{II}} \text{ ml}^{-1}$ in organic phase.

The effect of several metal ions was investigated. It was observed that at lower concentration there was no appreciable interference but at higher concentration they interfered. The tolerance limits (in μg given parenthesis) are as follow : It was observed that cation Zn^{II} , Hg^{II} , Pb^{II} , Cd^{II} , Cr^{VI} and Mn^{VII} ions 3.0, 6.0, 7.0, 8.0, 4.0, 7.0. It was observed that anions Cl^- , SO_4^{2-} , NO_3^- , EDTA, oxalate, I^- ions interfered at 30, 45, 50, 5, 1100, 1500 respectively. It was observed that Cr^{VI} , Mn^{VII} and V^{V} , which interfered in this method, might be masked by 0.01% EDT A solution.

Experimental

A standard stock solution ($100 \mu\text{g ml}^{-1} \text{ Ni}^{\text{II}}$) was prepared by dissolving nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) in distilled water and further diluted to get standard solution of $2.0 \mu\text{g ml}^{-1} \text{ Ni}^{\text{II}}$. A 0.01% solution of 2-[(5-bromo-2-pyridylazo)]-5-diethylaminophenol (5-Br-PADAP) was prepared in methanol. *N*-Hydroxy-*N*, *N'*-diphenylbenzamidine (HDPBA) was synthesized as according to the literature². A $3.5 \times 10^{-3} \text{ mol dm}^{-3}$ (0.1%, w/v) solution of HDPBA in chloroform was used for extraction. Potassium hydrogen phthalate buffer³ of pH 5.0 was used for pH adjustment.

All chemicals used were of analytical reagent grade B.D.H./E. Merck. A Carl-Zeiss Jena (Jena, Germany) spectrophotometer fitted with EK-5 unit and matched quartz cells of 1-cm path length was used for absorbance measurements. A Systronic 335 digital pH meter was employed for the measurement of pH of the solutions.

Procedure : To an aliquot containing 2 to $6 \mu\text{g ml}^{-1}$ nickel, 2 to 5 ml of potassium hydrogen phthalate buffer solution of pH 5.0 is added. To this 1 ml of 0.01% of 2-[(5-bromo-2-pyridylazo)]-5-diethylaminophenol is added and made up to 10 ml with distilled water. The mixture is shaken with 5 ml of *N*-hydroxy-*N*, *N'*-diphenylbenzamidine reagent in chloroform for 2 min. The two phases are allowed to separate. The organic phase is separated and dried over anhy-

drous sodium sulphate and its absorbance was measured at 530 nm against reagent blank.

Determination of nickel in steel sample : The method has been satisfactorily applied for the determination of Ni^{II} in steel samples. A steel sample weighing 0.1 g was dissolved in requisite amount of aquaregia. The volume of the solution was reduced to 5 ml by evaporation. To it, concentrated HCl was added and warmed. The volume of the resultant solution was made to 250 ml using distilled water. An aliquot of the solution was boiled for a few minutes, cooled and the pH adjusted to the optimum value. The results are shown in Table 2.

Table 2. Determination of Ni^{II} in steel sample

Sample composition, %	Nickel found %	Relative standard deviation ^c ±, %
Low alloy sample ^a (Si, 0.24; Cr, 0.20; Mn, 0.016; Ni, 4.10; Co, 0.040; Cu, 0.11; Mo, 0.007; Sn, 0.004)	4.05	1.6
Cr-Ni-Mo Alloy ^a (Si, 0.64; Cr, 0.80; Mn, 0.64; Ni, 2.45; Mo, Sn, 0.024)	2.40	1.4
3H Steel sample ^b (Cu, 0.22; S, 0.018; W, 0.19; Cr, 0.82; Mn, 0.82; Ni, 0.42; Mo, 0.20)	0.40	1.4

^aBritish Chemical Standards, No. 252. ^bObtained from Himmat Steel Foundry, Kumhari, Durg, India. ^cAverage of four determinations.

The reagent 2-[(5-bromo-2-pyridylazo)]-5-diethylaminophenol (5-Br-PADAP) provides a new, sensitive and accurate method for the spectrophotometric determination of nickel.

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References

1. G. D. Christian, "Analytical Chemistry", 4th ed., John Wiley & Sons, New York, 1986.
2. K. Satyanarayana and R. K. Mishra, *Anal. Chem.*, 1974, **47**, 1609.
3. Vogel, "A Textbook of Quantitative Inorganic Analysis", 5th. ed., ELBS, London, 1985.
4. Y. Zhu and L. Zhang, *Huaxue Shiji*, 1982, **23**, 77.
5. Y. Yuan, *Fenxi Ceshi Tonbuo*, 1985, **4**, 41.

6. K. B. Chandrasekhar and K. H. Reddy, *Indian J. Chem., Sect. A*, 2002, **41**, 1643.
7. K. Ohshita, H. Wada and G. Nakagawa, *Anal. Chim. Acta*, 1981, **124**, 193.
8. S. L. C. Ferreira, *Talanta*, 1988, **35**, 485.
9. P. Riyazaddin, *Analyst*, 1980, **105**, 1196.
10. R. A. Nazareth and B. Narayana, *Indian J. Chem., Sect. A*, 2003, **42**, 564.