Spectrophotometric determination of nickel(II) in aqueous medium using 1-phenyl-1,2-propanedione-2-oxime

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The reagent 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone (PPDOT) gives brownish yellow coloured complex with nickel(II) in sodium acetate-acetic acid buffer solution. The molar absorptivity and Sandell's sensitivity of Ni^{II}-PPDOT complex are 1.2×10^4 dm^3 mol^{-1} cm^{-1} at 395 nm and 0.0050 μg cm^{-2}, respectively. PPDOT has been used for the spectrophotometric determination of nickel(II) in hydrogenated vegetable oil and chocolate.

Oximes[1] and thiosemicarbazones[2] are the two classes of reagents widely employed for the spectrophotometric determination of metal ions. However, reagents containing both functional groups are not exploited much in the analysis of nickel. In continuation of our previous work[3], herein we report the spectrophotometric determination of nickel(II) using 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone (PPDOT) in aqueous medium. The method is applied for the determination of nickel(II) in hydrogenated oil and chocolate.

Results and discussion

The reagent PPDOT was prepared by condensing 1-phenyl-1,2-propanedione-2-oxime with thiosemicarbazide in 1% HCl-ethanol medium.
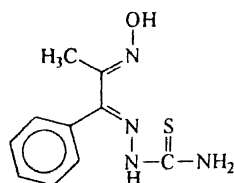
PPDOT

The values of the deprotonation of PPDOT were found to be 6.53 (pK_1) and 8.55 (pK_2). The pK_1 may be assigned to the deprotonation of imine (NH) through enolization while pK_2 is assigned to deprotonation of oxime hydrogen (=N-OH).

Important physico-chemical and analytical characteristics of Ni-PPDOT complex are summarized in Table 1.

The colour reaction between Ni^{II} and PPDOT was in-

Table 1. Physico-chemical and analytical characteristics of complex

Characteristic	Ni-PPDOT complex
Absorbance maximum (λ_{max}, nm)	395
Optimum pH range	3–6
Mole of reagent required per mole of metal ion for full colour development	10
Molar absorptivity (dm^3 mol^{-1} cm^{-1})	1.2×10^4
Sandell's sensitivity (μg cm^{-2})	0.005
Beer's law validity range (ppm)	0.47–4.70
Optimum concentration range (ppm)	0.92–3.76
Specific absorptivity (ml g^{-1} cm^{-1})	0.2045
Standard deviation*	0.0048
Relative standard deviation (%)	1.08
Composition of the complex (Job's and molar ratio methods)	1 : 2
Stability constant of the complex (Job's method)	5.15×10^9

*In the determination of 2.35 ppm of nickel.

stantaneous at RT. The absorbance of the complex was found to be constant for more than 24 h. The order of addition of buffer, nickel(II) and reagent has no adverse effect on the absorbance.

Interferences :

The effect of various diverse ions on the determination of nickel(II) was studied to find out the tolerance limits of foreign ions in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of ±2% in the absorbance. The tolerance limit (μg ml^{-1}) values of diverse ions in the determination of 1.88 μg ml^{-1} nickel are as follows : citrate (2270), tar-

trate (1775), iodide (1525), thiosulphate (1345), sulphate (1155), phosphate (1140), oxalate (1055), bromide (960), thiourea (915), iodate (765), nitrate (745), urea (700), thiocyanate (700), ascorbate (700), cyanate (505), W^{VI} (2205), Ba^{II} (1650), Sr^{II} (1050), Ca^{II} (480), Al^{III} (325), Mg^{II} (290), Pb^{II} (250), Zr^{IV} (110), Cd^{II} (70), Mn^{II} (65), Sn^{II} (14), Pd^{II} (9), Cr^{III} (4), Cu^{II} (25). Interference of Fe^{III} (26.8), Co^{II} (0.5) is masked with fluoride (200) and thiocyanate (600), respectively.

Applications :

Nickel(II) was determined in hydrogenated vegetable oil and chocolate. The results are presented in Table 2.

Conclusion :

A novel heterofunctional two-in-one reagent (PPDOT) has been synthesized and characterized for the first time.

Table 2. Analysis and recovery of nickel(II) in edible oils, oil seeds and chocolate

Sl. no.	Name of the edible sample	Amount of nickel found* ($\mu g\ g^{-1}$)	Amount of nickel recovered* ($\mu g\ g^{-1}$)		Percentage of recovery**	
		AAS method	PPDOT	AAS	PPDOT	AAS
1.	Hydrogenated vegetable oil (HVO)	0.129	1.106	1.137	97.7	100.8
2.	Chocolate (Eclairs)	0.176	1.160	1.189	98.4	101.3

*Average of three determinations. In recovery studies 1 μg of nickel/ gram of the sample was added.

**Nickel found by AAS method is used in the calculation of percentage of recovery.

Convensional methods using dimethylglyoxime[4], salicylaldoxime[5], resacetophenone oxime[6] and 2-hydroxy-5-methyl propiophenone oxime[7] involve extraction procedures which are expensive, time consuming and laborious. The present method is simple and offers the advantage of determining nickel in aqueous medium without the need for extraction. Thus, PPDOT is found to be potential reagent for the spectrophotometric determination of nickel(II), The present method is applied for the determination of nickel in hydrogenated oil and chocolate. PPDOT method compares favourably (Table 3) with other methods[8-13] using oxime-thiosemicarbazones and heterofunctional ligands.

Experimental

Preparation of PPDOT :

The reagent PPDOT was prepared by refluxing a mixture of 1-phenyl-1,2-propanedione-2-oxime (1 mol) and thiosemicarbazide (1 mol) in 1% HCl-ethanol (100 ml) for 3 h and the resulting solid was washed with hot water, cold methanol and dried under reduced pressure (yield 70%), m.p. 189°. IR spectrum of PPDOT shows ν_{max} (KBr) 3419 (OH), 3348 (NH asym), 3249 (NH sym), 1609 (C=N) and 1199 cm^{-1} (C=S); δ_H (DMSO-d_6) signals corresponding to -CH_3, C_6H_5, NH_2, NH and OH at 2.1 (3H, s, CH_3), 7.2–7.5 (5H, m, C_6H_5), 8.4 (2H, d, NH_2), 10.7 (1H, s, NH) and 11.7 (1H, s, OH); m/z 236 (molecular weight), 178, 104, 84, 57 and 43. The pK_a values were determined by recording UV-visible spectra of micromolar (8 × 10^{-5} M) solution of PPDOT at various pH values and by taking the arithmetic mean of the values obtained from the measurement at four

Table 3. Comparison of spectrophotometric methods for the determination of Ni^{II} using oxime thiosemicarbazone and related ligands

Sl. no.	Name of the reagent	Molar absorptivity (ε) dm^3 mol^{-1} cm^{-1}	λ_{max} nm	Beer's law range ppm	Medium (pH)	M : L		Ref.
1.	Diacetylmonoxime thiosemicarbazone	0.88 × 10^4	356	–	Buffer (9.5)	1 : 2		8
		0.56 × 10^4	355	0.508	Buffer (2–6)			9
2.	Diacetylmono-thiosemicarbazone	–	400	1.0–3.5	Buffer	1 : 2		10
3.	Salicylaldehyde thiosemicarbazone	1.1 × 10^4	370	0.5–3.0	n-Butanol (6.5)	–		11
4.	Quinoline-2-aldehyde thiosemicarbazone	1.58 × 10^4	460	0.5–2.5	CHCl$_3$ (6–7)	1 : 2		12
5.	Diacetylmonoxime 4-phenyl-3-thiosemicarbazone	1.70 × 10^4 1.75 × 10^4	375 355	– 0.47–2.35	Buffer (5.2–10.0)	–		12
					Buffer (5.7)	1 : 1 1 : 2	and	9
6.	1-Phenyl-1,2-propanedione-2-oxime thiosemicarbazone	1.20 × 10^4	395	0.47–4.70	Buffer (3–6)	1 : 2		Present study

different wavelengths.

Reagent solutions (0.01 M) were prepared by dissolving 236 mg of PPDOT in dimethylformamide : HCl ($1M$)-NaOAc ($1M$) (pH 0.5–3.5); 0.2 M NaOAc-0.2 M AcOH (pH 3.5–7.0) and $2M$ NH$_4$Cl-$2M$ NH$_4$OH (pH 8–11) buffer solutions were used in the determination of pK_a values of reagents. The standard Ni^{II} solution (1 × 10^{-2} M) was prepared using A.R. grade ammonium nickel sulphate and standardized gravimetrically.

Procedure :

A mixture of an aliquot of the solution containing 0.47–4.70 μg ml^{-1} of Ni^{II}, buffer solution (pH 4.0), and 0.01 M PPDOT solution (1 ml) was diluted to 25 ml with distilled water. The absorbance of the solution was measured at 395 nm against corresponding reagent blank and the Ni content computed.

Sample solutions of hydrogenated oil and chocolate were prepared by following the literature procedure[14]. A 50 g of the sample was heated in a 500 ml conical flask with 40 ml of concentrated HNO$_3$ on a steam bath and shaken vigorously until a fine emulsion was formed. The heating was continued with gradual addition of 40 ml of 6% H$_2$O$_2$. The extraction was repeated twice with further addition of 20 ml of conc. HNO$_3$ and 20 ml of 6% H$_2$O$_2$. The combined extracts were evaporated to dryness. The residue was dissolved in minimum amount of HCl and transferred into a 50-ml standard flask quantitatively. The contents were diluted to the mark with distilled water.

To 10 ml of buffer (pH 4.0) solution, 1 ml of 0.1 M NaF (to mask Fe^{III}), the sample solution, 2.5 ml of DMF and 1 ml of 0.01 M reagent solution were added. The solution was diluted to volume 25 ml with distilled water and the absorbance was measured at 395 nm against the reagent blank. The absorbance of sample solution was referred to the calibration plot and the amount of nickel was determined. The results including recovery data are given in Table 2. The results of PPDOT method are compared with AAS data.

A Schimadzu 160 A spectrophotometer equipped with 1.0 cm quartz cells and an ELICO LI-120 pH meter were

used. IR spectra were recorded on a Bruker IFS 66v FT IR spectrometer in KBr disc. ^{1}H NMR spectra (DMSO-d_6) on a Varian XL-300 MHz spectrometer, mass spectra on VG 7070 H spectrometer and AAS on Solar 939 Atomic absorption spectrophotometer (wavelength 232 mm, slit width 0.2 nm).

Acknowledgement

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