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Journal of Chemical and Pharmaceutical Research

ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(2):34-38

Analytical application of m-chlorophenylazo-bis-acetoxime (m-CPABA) in the spectrophotometric determination of Nickel (II)

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ABSTRACT

m-Chlorophenylazo-bis-acetoxime has been used for spectrophotometric determination of nickel (II) at 376 nm and a pH of 7.0-8.0. Beer's law is obeyed in the range of (2.0-16.0) × 10^{-5} M. The molar absorptivity and Sandell's sensitivity values are 3,691 L mol^{-1} cm^{-1} and 15.90 ng cm^{-2} respectively. Log β is determined by two different method i.e. Harvey and Manning's method and Purohit's method and the values of it are 12.93 and 13.23 respectively. Hydroxytriazenes have been used as analytical reagents for a number of transition metals. Similar compounds arylazo-bis-acetoximes developed by Bamberger and subsequently used by Sogani & Bhattacharaya as spectrophotometric reagents for determination of various transition metals such as cobalt, iron and copper. In the present paper m-chlorophenylazo-bis-acetoxime (m-CPABA) has besen used for spectrophotometric determination of nickel (II).

Keywords: m-Chlorophenylazo-bis-acetoxime, Spectrophotometric determination of nickel (II), m-CPABA, Acetoximes,

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INTRODUCTION

Arylazo-bis-acetoximes are well established analytical reagents for both complexometric and spectrophotometric determination of transition elements. Bamberger[1-5] proved that they possess the same skeleton as hydroxytriazenes and thus their preparative methods as reported by Mai[6-7] involve coupling of diazonium salt with aldoximes or ketoximes. The application of this class of compounds as analytical reagents is shown by various reviews[8-12] as well as papers[12-14] appearing in last many years. In the present communication a new reagent, m-chlorophenylazo-bis-acetoxime (m-CPABA) has been used first time for the spectrophotometric determination of nickel (II). The reagent (m-CPABA) has been synthesized by using standard methods, duly characterized by IR, elemental analysis (CHN) and m.p. determination etc. proving that compound was obtained in pure form. It was used for the spectrophotometric determination of nickel (II). The studies indicate that the method developed is reasonably sensitive with advantage that it can be applied to nickel samples in presence of 27 different anions/cations with a standard deviation of 0.0832 i.e. 0.71% . Thus the compound is a new addition to reagents available for nickel determination.

EXPERIMENTAL SECTION

Synthesis of m-chlorophenylazo-bis-acetoxime (m-CPABA*)*

m-chlorophenylazo-bis-acetoxime (m-CPABA) was synthesized per standard method. The general method is described below. The synthesis was done in three steps.

Step: 1 Preparation of acetoximes

In the preparation of m-chlorophenylazo-bis-acetoxime (m-CPABA) 0.1 moles of hydroxylamine hydrochloride was dissolved in minimum quantity of water and to it an aqueous solution of 8 gm. of NaOH was added. After cooling the solution in an ice water bath, acetone (14.7ml) was added slowly followed by shaking for few minutes. This resulted in the separation of acetoxime soon as a crystalline solid. The reaction mixture was filtered and directly used for coupling.

Step: 2 Preparation of aryldiazonium salts

m-toludine (0.1 moles) was dissolved in mixture containing 24.7ml of HCl and 25 ml of water. In another beaker 7.0 gm. of sodium nitrite was dissolved in minimum quantity of water. The temperature of the aryl amine hydrochloride solution was maintained between 0-5^0 C. To this solution, sodium nitrite solution was added drop by drop with stirring. The diazotised product so obtained was directly used for coupling.

Step: 3 Coupling

Freshly prepared acetoxime obtained in step-1 was dissolved in 10% sodium hydroxide solution (150ml) and cooled below 5°C. The temperature of diazotised product obtained from step-2 was maintained between 0-5°C. Then step-2 solution was added dropwise to the solution obtained in step-1 and pH of solution was maintained close to 10 and the temperature during the entire course of the reaction was kept below 5°C. The resultant product was filtered, washed with petroleum ether (40-60°C) and dried.The crude compounds was purified and recrystallized. The purity of the compound was checked by I.R. studies and physical characteristics. The compositions were verified by elemental analysis. All these data have been given in table 1.

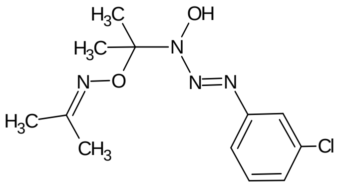
m-chlorophenylazo-bis-acetoxime(m-CPABA) was subjected to four spot tests as described by Purohit and this reagent gave positive test with all the four testing methods, proving the purity of the compound.

(a) α-naphthylamine test
(b) Picric acid test
(c) Sulfuric acid test
(d) N, N-Dimethylaniline test

Table 1. Physical Characteristics, M.P., CHN values of the Reagent

Molecular formula	Colour and shape of the crystals	Solvent used	Elemental analysis				M.P. (°C)
				% Carbon	% Hydrogen	% Nitrogen	
$C_{12}H_{17}N_4O_2Cl$	Red micro crystals	Ethanol	Th. Exp.	50.61 50.44	5.98 5.99	19.68 19.48	109

Table 2. Characteristic IR Bands Obtained for m-CPABA

Structure of the Compound	IRBands Obtained(cm^{-1})		
	ν_{N-H}	δ_{N-OH}	δ_{N-H}
	3195	1075	1511

Various peaks given in the Table-2 clearly confirms the presence of all these bands thus proving purity of the compound.

Preparation of solutions:

I. **Reagent solution**: A fresh stock solution of 1.0 × 10^{-2} M of the reagent(M-CPABA) was prepared by dissolving requisite quantity of the reagent in ethanol .Dilute solution was prepared from this stock solution and when required.

II. **Standard solution of nickel (II):** A 1.0 × 10^{-2} M stock solution of Ni (II) was prepared by dissolving the requisite quantity of Ni (II) sulphate heptahydrate(A.R. grade) in double distilled water. It was standardized with standard EDTA solution using xylenol orange as an indicator. Weaker solutions were prepared by appropriate dilution of the stock solution with double distilled water.

III. **Solutions for pH adjustment:** Tris-buffer solution: An aqueous solution of 2% (w/v) tris buffer was prepared by dissolving it in double distilled water.

IV. **Instruments:**The spectrophotometric study was carried out on Systronic- 108UV-VIS spectrophotometer Systronic pH meter-324 was used for pH measurement.

V. **Procedure:** Following set of experiments were carried out for the spectrophotometric determination of Ni (II).

Selection of suitable working wavelength: One ml of 5.0×10^{-4} M Ni (II) and 5ml of 2.5×10^{-3} M reagent solution were taken in 10 ml volumetric flask and then made up with acetone. Absorbance of solution against its reagent blank was measured in the wavelength region 360-420nm. The working wavelength was selected in a region where the absorption of Ni (II) complex was maximum and absorption due to reagent was minimum. For working wavelength and maximum absorbance wavelength were selected at 376 nm.

a. Effect of pH on absorbance: Absorbance of the solutions at various pH values containing Ni (II) and reagent solutions in the ratio of 1:5 were taken at working wavelength 376 nm against reagent blank. The optimum pH range for constant maximum absorption was selected.

b. Composition of the nickel (II) complex: The composition of the Ni (II) complex with was determined using Job's method, mole ratio method of Yoe and Jone’s and slope ratio method.

d. Job's method: The composition of Ni (II) complex with m-CPABA was determined at two different concentrations with Job's method[12]. For each concentration, set of solutions was prepared by varying the volume of equimolar Ni (II) and reagent solution from 0 to 6 ml. After pH adjustment, the solutions were marked (10 ml.) with ethanol. The absorbance of solution was measured at suitable working wavelength against reagent blank. The second set of this method differed from the first set only in the concentration used. By this method the composition was found to be 1:3 [Ni: R].

e. Mole ratio method of Yoe and Jone's [13]: In this method Ni (II) concentration was kept constant and reagent concentration was varied. A series of solutions having Ni (II) to reagent ratio 1:0.4 to 1:10 were prepared with maintaining the pH of constant absorbance. Absorbance of each solution of a set was measured at working wavelength against the reagent blank. By this method the composition was found to be 1:3 [Ni: R].

f. Beer's Law: A set of solution having metal to ligand ratio 1:5 was prepared. The studies were performed under optimum condition of pH, concentration and solvent at corresponding working wave length. The absorbance was measured for the complex against the reagent blank. The straight line shows that the Beer's law is valid in the entire concentration range studied.

g. Precision Studies: Taking appropriate concentration of Ni (II) and a Ni:R (1:5), a set of ten solutions was prepared under optimum conditions of complex formation. Absorbance of each complex was measured against reagent blank. The results of precision studies reveal that by using this method Ni (II) can be determined at ppm level with good precision.

Table: 3 Result of precision studies

Name of the reagent	Nickel (II) taken in ppm	Nickel (II) found in ppm
m – CPABA	11.74	11.74 ± 0.083

h. Interference studies: Interference of various cations and anions in the determination of nickel was studied at 5, 10 and 100 ppm level. Interference was studied using following 27 cations and anions, viz. NH_4^+, Na^+, K^+, Mn^{2+}, Ba^{2+}, Pb^{2+}, Hg^{2+}, Sn^{2+}, Th^{2+}, Cd^{2+}, Co^{2+}, Mg^{2+}, CH_3COO^-, Br^-, Cl^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, $C_2O_4^{2-}$, $S_2O_3^{2-}$, NO_2^-, SO_3^{2-}, S^{2-}, HPO_4^{2-}, F^-, NO_3^-, and WO_4^{2-}. It was found that following ions did not interfere even at 100 ppm levels: NH_4^+, Na^+, K^+, Ba^{2+}, Cd^{2+}, Mg^{2+}, CH_3COO^-, Br^-, Cl^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, NO_2^-, S^{2-}, and NO_3^- Whereas HPO_4^{2-}, Ni^{2+}, Co^{2+}, could be tolerated only upto 5 ppm and $C_2O_4^{2-}$, WO_4^{2-}, Pb^{2+} upto 10 ppm. However, tolerance of still high concentration was not studied. Thus it can be seen that nickel (II) can be determined in presence of a number of interfering species present even at 100 ppm level. It may be concluded that m-chlorophenylazo-bis-acetoxime can be used successfully for spectrophotometric determination of Ni (II).

i. Sandell's sensitivity: The molar absorptivity of the Ni (II) complex was calculated from the Beer's law graph and it was found to be ε=9,071 L/mol.cm. The value thus obtained was used for determining Sandell's sensitivity of the complex that was 7.207ng/cm^2.This value shows that the method is quite sensitive and satisfactory for the determination of Ni (II).

Table 4a: Spectrophotometric Determination of Ni (II) with m-CPABA

Ni(II)complex with reagent	Composition of the complex [Ni(II):R]	Working Wavelength or $\lambda_{max\ (nm)}$	Optimum pH range	Beer's Law range (M)	Molar absorptivity [mol^{-1} cm^{-1}]
m-CPABA	1:3	376	7.0-8.0	2.0 x 10^{-5} to 16.0x10^{-4}	3,691

Table 4b: Spectrophotometric Determination of Ni (II) with m-CPABA

Sandell's Sensitivity ng cm^{-2}	Ni(II) taken in ppm	Standard Deviation in ppm	% error	Logβ from Harvey and Manning's method	Logβ from Purohit's method
15.90	11.74	0.0832	0.71	12.9286	13.2215

Table -5: Values of log β and ΔG by two different methods

Name of method	Reagents	Composition of complex	Conc. Of complex × 10^{-4} M	Em	Es	α	$K_{inst} \times 10^{-13}$	$\beta \times 10^{12}$	log β	ΔG *Kcal mol^{-1}
Harvey and Manning's method	m-chloro phenyl azo-bis-acetoxime (m-CPABA)	1 : 3	1	0.374	0.284	0.24	1.18	8.48	12.93	-17.74
Purohit's method	m-chloro phenyl azo-bis-acetoxime (m-CPABA)	1 : 3	3	1.01	0.89	0.11	1.65	6.07	12.78	-17.55
		1 : 3	1.5	0.506	0.44	0.12	2.15	4.66	13.67	-18.76

RESULTS AND DISCUSSION

As described in the table no. 5, the reagent forms 1:3 complex with m-CPABA. The conditional stability constants have also been given in the table, determined using two different methods. The results agree well as seen from the log β values from both the methods. Precision studies further validate the applicability of method using the reagent.

Further, the results of interference studies indicate that the method can be successfully applied in presence of number of cations as well as anions. Hydroxytriazenes as well as acetoximes act as bidentate ligands and in the present case the reagent has been found to form a 1:3complex with m-CPABA which indicates a tetracoordinated nickel (II) complex with a probable geometry being square-planar.

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