Synthesis and sequential separation of Co (II), Mn (II) and Cu (II) metal complexes using diazepam (7-Chloro-1-methyl -5- phenyl -3H -1,4- benzodiapine-2-one) on high performance liquid chromatography

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ABSTRACT

Present work describe the synthesis, characterization and sequential separation of metal complexes have been characterised by elemental analysis & IR spectral data. *Diazepam* forms stable anionic complexes with a wide range of metal ions. These ions can be separated qualitatively by reverse phase chromatography converting C_{18} stationary phase coloumn to ion exchange one with an eluent containing acetonitrile water & appropriate amount of Diazepam. In this system 0.05 mol L^{-1} Diazepam is prepared by dissolving 0.0142 gm in the mobile phase & the pH is adjusted to 8 by NH_3 buffer . Because of the intense UV absorption in the low UV range, detection at 254 nm is recommended for *Diazepam* complexes. The developed method simultaneously separated the above Co, Mn and Cu Diazepam complexes.

Key words: Complexes, Co, Mn, Cu and HPLC.

INTRODUCTION

Diazepam drug a benzodiazepine is a commercially available with myorelaxant and anxiolytic activity[1]. The benzodiazepine have wide applications in the pharmaceutical industries[2] and in some cases they have carcinostatic activity[3-4]. The significance of Co, Mn, and Cu as essential transition metals lie in their wide spectrum of industrial applications, especially in steel, catalyst, alloy, electroplatins, fungicide, ceramic & petrochemical industries, apart from the utility of their compounds as potential medicinal agents. Thus owing to the increasing commercial importance of these metals the literature survey reveals, that a wide variety of reagents have been employed for their spectrophotometric and extractive spectrophotometric determination, but most of them are found to be unsatisfactory for various reasons & not useful for the simultaneous determination & separation of Co^{+2}, Mn^{+2} & Cu^{+2}.

Thus the HPLC technique is employed for the simultaneous separation of above metal complexes.

EXPERIMENTAL

All the chemicals used were of AB (BDH) grade & their solutions were prepared in double distilled water. The complexes were prepared by mixing molar solutions of metal nitrate dissolve (in double distilled water) & ligand *Diazepam* dissolved (in ethanol) in 1:1 ratio.

Standard metal ion solution (mg ml^{-1}) were prepared by dissolving an accurately weighted amount of anhydrous metal nitrate in 100 ml doubled distilled water with few drops of concentrated HCl and standardized by a known method[5]. It was further diluted & used as required. Alliance 2690 waters separation HPCL model was used for the separation. The pH measurement were made with an ELICO LI 120.

Experimental parameters for HPCL

Instrument	:	Alliance 2690 water·s HPCL
Coloumn	:	Lichrosphere C_{18} reverse phase coloulmn
Eluent	:	Acetonitril, 70 ml water, 30 m l
		Diazepam ligand (0.05 mol lt⁻¹)
Detector	:	2487 dual wave length
Pump	:	Alliance in built
2λmax	:	254 nm 0.08 AUFS
Injection	:	20 µl
PH	:	8
Guard coloum	:	water·s C_{18} guard – pack™
Flow rate	:	2.0 ml min-1

All the solvents used for the separation were of HPCL grade . The purity of complexes were confirmed by TLC carried out on silica gel – G plate using ethanol : benzene (80 : 20) mixture. The complexes were analysed for metal & chlorine content by standard procedure [6]. IR spectra of metal complexes was recorded as (KBr) matrix on Perkin Elemer 842- spectrophotometer. Elemental analysis

of C,H,N were carried out at NCL Pune.

RESULTS AND DISCUSSION

Analytical & physical data are given below in table. Complexes are insoluble in common organic solvent while moderately soluble in DMF & DMSO. The analytical data & pH metry indicates 1:1 metal : ligand stoichiometry for all complexes. The coloured complexes are stable at room temperature . In IR spectra of metal complexes of Diazepam the bands at 1690cm⁻¹, 1683cm⁻¹ & 1695 cm⁻¹ attributed to ν (C =O) group shows small positive shift as compare to free ligand 1680cm⁻¹ . The band at 1608 cm⁻¹ at the free ligand due to ν(C =N) [7-8] but in complexes show lowering of shifting of band around 1565 cm⁻¹ , indicating the participation of azomethine N (4) nitrogen atom in complexation. The moderately strong band of 1428 cm⁻¹ assigned to (N-CH₃) in the free ligand undergoes blue shift in complexes , indicating the involvement of N (1) atom in coordination. The bands at about 500cm⁻¹ in IR spectrum of complexes indicates to ν (M-N) linkage[9].

Compound	Colour	Mol.Wt.	m. p. °C	pH	Elemental analysis (calcd.) Found				
					C	H	N	Cl	metal
Diazepam ($C_{16}H_{13}ClN_2O$)	white	284.7	135		67.62 (67.41)	4.24 (4.56)	9.43 (9.83)	12. 14 (12.46)	
CuDZ(NO₃)	skyblue	472	290	8	40.73 (40.21)	2.92 (2.21)	11.40 (10.98)	7.21 (7.42)	13.05 (13.98)
CoDZ(NO₃)	Greybrown	467	>360	8	40.98 (40.39)	2.81 (2.42)	11.31 (11.01)	7.32 (6.98)	12.98 (12.01)
MnDZ(NO₃)	brownish	463	>360	8	41.29 (41.02)	2.98 (2.39)	12.84 (12.04)	7.19 (7.84)	13.89 (13.08)

Water,s C_{18} Guard -Pak™ pre column insert is conditioned with a mobile phase containing Diazepam 20 µl of sample was then injected through the Guard Pak insert & the precious metal were trapped on the packing material of the column. The precious metal are then eluted on to a merk C_{18} lichrosphere column for separation of the desired species. This method has been used to simultaneously determine the Diazepam complexes of Co (II) , Mn (II), Cu (II) , as shown in fig. The

minimum detection limit for these metals is 500 ppm.

The over all results obtained that the method offers simple & simultaneous isolation of the desired components in the absence of RDM (Reagent Delivery Model), conductivity detectors & pic reagent, as required by most of the reported methods. In this method, acid is avoided which prevents the corrosion of the solvent wetted stainless steel parts in ion chromatography.

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