Comparative study of Synthetic dyes and Natural product extract for heavy metal ions chelation

Yogini Bambardekar
Department of Chemistry, CHM College,Ulhasnagar,India

***Abstract*—Synthetic organic derivatives have been widely used as complexing agents for transition metal ions. Increasing use of those reagents has certainly created threat to the environment by accumulation of waste deposits in soil and water. Development of natural complexing agents has been primarily driven by a desire to minimize the use of synthetic reagents. *Garcinia Indica* (Kokum) fruit extract is highly selective for Cd^{2+}ions forming coloured complex at pH 9.5. Use of *Garcinia indica* extract as an indicator in complexometric titrations exhibits a sharp colour change. Further, the comparative study with standard synthetic indicator also led to the conclusion that *Garcinia indica* as a natural complexometric indicator for Cd^{2+} ions impart the same degree of precision as obtained with synthetic indicators.**

Keywords - Cd^{2+}ions, complexometric. Extract, Garcinia indica

I. INTRODUCTION

Use of natural extract isolated from different parts of the plant as pH indicator has been studied extensively[1]. Capacity of it to bind with certain metal ion at a specific pH imparting coloured complex is of equal interest[2]. Number of synthetic derivatives are available as ligands for metal complex formation[3].Since 'benign chemistry' is the prime aspect of Green technology, tapping the use of natural extract as complexing agents becomes point of concern4. Garcinia Indica is commonly known as Kokum in India, abundant in southern part of India has been in use as an essential ingredient of food delicacies and medicines. Its dark red colour is attributed to Anthocyanine family [5-6] which is reviewed and established in literature survey [7--8]

Metal chelation also involves a chemical reaction, but it is between the anthocyanins and metal atoms or ions.[9] Pigments and metal ions interaction result in alteration of the final colour of the chelate. Metal ions can affect stability of final colour by altering vacuolar pH and activity of enzymes involved in biosynthesis, destruction, accumulation and transition of pigments[10-].[12] Anthocyanin chelation can produce colours ranging from intense violet to blue at acidic pH values.[13-14] Sigurdson and Giusti (2014) reported that co-pigmentation with metals ions can be a viable approach as desired color and stability of anthocyanin extract can be imparted by proper metal complexation. Pigment when isolated in methanol showed sharp coloured complex formation with transition metal ion Pigment when isolated in methanol showed sharp coloured complex formation with transition metal ion Cd^{+2} at pH9.5. The specific binding capacity of Garcinia Indica extract with copper ions at particular pH can be practically employed in complexometric titration.

Standard complexometric titrations make use of organic dyes as indicator that form complex with copper ions. Substitution of organic dyes with present natural extract also imparts sharp colour changes with same degree of accuracy and precision.

Experimental:

Material and Methodology: The peels of Garcinia Indica were procured from the Konkan region, Maharashtra. All AR grade chemicals (Thomas Baker) were obtained from Smt. CHM College, Ulhasnagar. Solutions of required Molarity were prepared as per standard procedures.

Calibrated glassware (Corning / Borosil) were used for all experimental procedures. Analytical Balance of 0.001gm sensitivity was used.

Extraction of natural product: The dry peels of kokum were cleaned by distilled water and cut into small pieces and macerated for four hours and anthocyanins were extracted at 300cc, Exaction was carried out by 60% acetone and 40% 0.1% HCl acidified water for few minutes The solution was vacuumed and passed through a 70mm Whatman No.4 filter paper, then collected by a Buchner Funnel (Fisher Scientific, Fair

Lawn, NJ). The extract was preserved in tightly closed container and stored in dark. The pigments in the extract separated by Thin Layer Chromatography – a technique similar to paper chromatography. The buffer system in pH range 1-14 was prepared using potassium dihydrogen phthalate.

Procedure: Complexometric titrations of 0.02 M solutions of $CdCl_2$ were conducted against 0.02M EDTA (Disodium salt) as per established procedures, using *Garcinia Indica* extracts as indicator. The results were compared with those obtained using synthetic Metallochromic indicators. Control experiments were conducted, varying the concentration of salts and also of EDTA, to verify the accuracy and reproducibility of the results.

Results and Discussion: Characterrization of uncomplexed cadmium ions and cadmium-EDTA complex

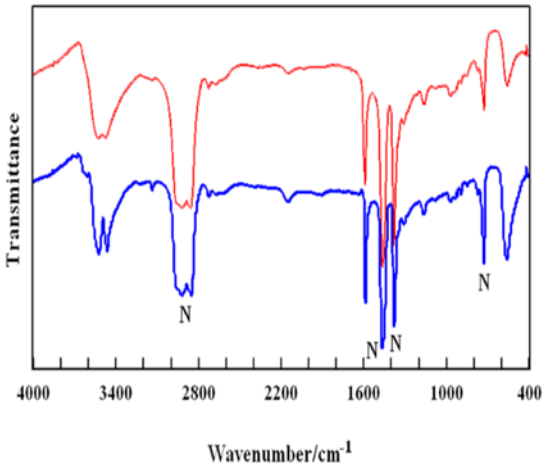
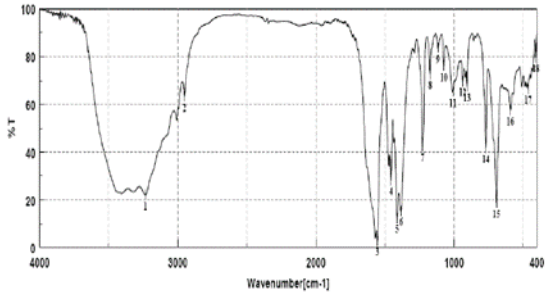


Fig.1 IR spectrum of $CdCl_2.H_2O$



Result of Peak Picking

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1:	3233.07	22.0440	2:	2952.48	63.2777	3:	1555.31	2.7366	4:	1456.96	28.1796
5:	1412.60	12.3976	6:	1383.68	15.2590	7:	1228.43	42.2745	8:	1173.47	72.6955
9:	1116.58	83.7008	10:	1074.16	76.0707	11:	1007.62	65.1848	12:	938.20	69.7320
13:	905.42	67.5760	14:	769.46	41.6810	15:	693.28	18.7685	16:	692.04	57.6884
17:	463.80	66.3895	18:	407.87	79.6775						

Fig.2 IR spectrum of Cd-EDTA

In IR spectrum of bivalent cadmium ions, two intensive bands, at 3525 cm^{-1} and 3470 cm^{-1}, appear in the region of the OH stretching vibrations (Fig. 1, upper curve). In the same region, four intensive bands are observed at 3540 cm^{-1}, 3475 cm^{-1} (lower curve) as a result of correlation splitting of the antisymmetric and symmetric stretching HOH modes. In the same region of the IR spectrum, one low intensity band is observed at 3133cm^{-1} what might be attributed to a second order transition of the bending HOH modes. In the difference IR spectrum of the complex with low deuterium content (≈ 4 % D) recorded at RT, one broad band is observed at around 2590 cm^{-1}, and two bands (at 2584 cm^{-1}and2575 cm^{-1}) appear in the LNT spectrum which are due to the uncoupled O–D stretching modes of isotopically isolated HDO molecules (Fig. 3). The presence of these two bands in the LNT spectrum is in accordance with the structural data of this compound [3]i.e. with the existence of two non-equivalent hydrogen bonds. The slight frequency difference between these two bands indicates that the force field for these two OD stretching vibrations is almost identical. 4000-2000cm^{-1}spectral range is relevant for the characterization of the OH and CH groups and CH groups. The presence of crystallization water in the metal complexes (2,3) generates complex, broad bands for ν(H_2O) in the 2500-3500 cm^{-1} region of the IR spectra, for chelated compounds. On the other hand, the characteristic band for the carboxylic OH group (IR of 1a: 3620 cm^{-1}) disappears in the IR spectra

The 4000 – 2000 cm On the other hand, the characteristic band for the carboxylic OH group (IR of 1a: 3620 cm $^{-1}$) disappears in the IR spectra of 2,3, sustaining the formation of a coordination compound with carboxylate anion.

Complex broad band at 2500-3500cm^{-1} clearly indicated formation of a chelate compound.

Sr. No.	Initial	Final	Difference	C.B.R.
1.	0.0cm^3	10.0 cm^3	10.0 cm^3	10.0 cm^3
2.	0.0 cm^3	10.1 cm^3	10.1 cm^3	
3.	0.0 cm^3	10.0 cm^3	10.0 cm^3	

Selectivity of extract: comparative study

Extract was studied for its selectivity towards transition metal ion copper in bivalent oxidation state.

Estimation of Cd with EDTA by complexometric titrations:

- Titration of 0.02M EDTA with 0.02M $CdCl_2$ solution using solochrome black T indicator in presence of buffer of PH9.5. (Table1) Colour change: Yellow to blue violet
- Titration of 0.02M EDTA with 0.02M $CdCl_2$ solution using *Garcinia Indica* extract as an indicator in presence of buffer of pH9.5. (Table2)

Colour change: yellow to purple

Sr. No.	Initial	Final	Difference	C.B.R.
1.	0.0cm^3	10.1 cm^3	10.1 cm^3	10.1ml
2.	0.0 cm^3	10.1 cm^3	10.1 cm^3	
3.	0.0 cm^3	10.1 cm^3	1010 cm^3	

CONCLUSION

The results indicate that the ethanol extract of *Garcinia Indica* peel can replace synthetic metallochromic indicators for the Complexometric estimation of Cadmium. High degree of accuracy and sharp, intense colour change at the end-point was observed.

It is particularly beneficial as it can be locally extracted with no energy input, is easily available and being a natural pigment, is Environment friendly.

FUTURE SCOPE FOR STUDY

As the present fruit extract proves its efficiency in complexometric titrations and its selectivity for copper ions. Thus, interference study with other metal ions can be studied in future.

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Department of Chemistry, Smt. Chandibai Himathmal Mansukhani College, Ulhasnagar.

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