Extractive- Spectrophotometric Determination of Fe(II), Fe(III), Mn(II) and Cr(III) through complexation with 2,2^I-ethylenebis (nitrilomethylidene) diphenol (H$_2$EBNMDP)

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Abstract

Solvent extraction using 2,2^1-ethylenebis(nitrilomethylidene)diphenol as ligand has been investigated for the spectrophotometric determination of Fe(II), Fe(III), Mn(II) and Cr(III). The complex formed by H$_2$EBNMDP with the Fe(II), Fe(III), Mn(II) and Cr(III) ions were stable in water for pH 8, 4, 6 and 6 respectively with a maximum of absorption at 366nm, 383nm, 415nm 405nm and molar absorptivity (Epsilon) 1.84 x 10^4, 2.29 x 10^4, 2.96 x 10^4 and 3.85 x 10^4 respectively. The combination ratio has been established using the logarithmic method to be 1:2, 1:1, 1:2 and 1:1 for Fe(II), Fe(III), Mn(II) and Cr(III) respectively. The proposed method was applied successfully in the determination of Fe(II), Fe(III), Mn(II) and Cr(III) from tap water and synthetic samples.

Keywords: H$_2$EBNMDP, spectrophotometric determination, metal ions, solvent extraction.

Introduction

Since Dubsky, Sokol and Pfeiffer et al works on the isolation and structural elucidation of N,N^1-bis(salicylidine) ethylenediamine complexes of Cu(II) and Ni(II), a considerable literature has appeared on the subject[1-2]. Much of it concerns the synthesis and structural studies of various metal ions with the Schiff base as well as catalytic applications of the complexes in epoxidation, aziridination, cyclopropanations, epoxide ring opening, selective hydrogenation, carbonyl cyanosilylation, imine addition, reaction centre's of metalloenzymes and in some analytical applications[3-15]. Although, these compounds have not found much use either as metal extractants or as spectrophotometric reagents they have been noted as promising for the purpose[16-18].

We have found 2,2^1-ethylenebis(nitrilomethylidene)diphenol to be suitable and promising for the extractive - spectrophotometric determination of iron, manganese and chromium.

Material and Methods

Analytical grade reagents were used without further purification unless otherwise stated. All aqueous solutions were prepared in distilled demineralized water. Working solutions were prepared by dilution as required.

The standard stock solution of Fe(II), Fe(III), Mn(II) and Cr(III) (1000mgL^{-1}) was prepared as follow. Requisite amounts of ammonium ferrous sulphate hexahydrate and ammonium ferric sulphate dodecahydrate (Merc, Germany) were dissolved in dilute H$_2$SO$_4$ and were standardized by the permanganate method[19]. Manganese acetate tetrahydrate (Merc, Germany) and Chromium nitrate nonahydrate (Merc, Germany) were dissolved in distilled deionized water.

8610 UV-vis grating spectrophotometer (Barloworld, England) was used to measure the absorbance of the analytes while the pH of solutions was measured using pH meter (Hanna, Italy).

Synthesis of 2,2^I-ethylenebis(nitrilomethylidene) diphenol: Ethylenediamine (22.475g) was gradually added with stirring to 91.336g of salicylaldehyde in a 500mL beaker. Initially, a yellow hot mixture resulted and stirring continued until crystallization started leading to formation of golden yellow cake. The product was recrystallized twice from carbon tetrachloride to give golden yellow crystal. The reagent is used as a freshly prepared 5mgmL^{-1} H$_2$EBNMDP ethanol solution.

Buffer solutions: pH 1-12 were prepared using Clark and Lube's method and as described elsewhere [20-21].

Experimental procedure: Transfer aliquots equivalent to 4μg of metal (Fe(II), Fe(III), Mn(II) and Cr(III)) into a series of 20mL calibrated extraction bottle and add 4mL of buffer of pH 8,4,6 and 6 respectively. Add 0.6mL of H$_2$EBNMDP in each bottle and make up the volume to 5mL with buffer solution allow the time for maximum color development as determined and add 5mL of chloroform. Agitate the phases for 5mins, 10mins, 10mins and 10mins respectively for Fe(II), Fe(III), Mn(II) and Cr(III).Addition of H$_2$EBNMDP to the solution resulted in the formation of reddish-brown, light-yellow, light pink coloured Fe(II), Fe(III), Mn(II) and Cr(III)respectively.

Allow to settle, centrifuge and separate and the absorbance of the solutions was read at 366nm,383nm,405nm and 415nm for Fe(II), Fe(III), Mn(II) and Cr(III) respectively against the reagent blank.

Measurement of distribution ratios: Equal volumes (5mL) of the aqueous and organic phases were shaken mechanically 5 min for Fe(11), 10 min for Fe(III), Mn(II) and Cr(III) in glass-stoppered bottles at 27 ± 1^0C. The phases were centrifuged, separated, and analysed spectrophotmetrically as described in Mirza and Nwabue[22].

Recommended procedures for iron, manganese and chromium: Iron: Adjust 0.1mL of a freshly prepared sample solution containing 4µg of Fe(II) to pH 8 with dilute ammonia solution and buffer. Add 0.6mL of 0.5% H_2EBNMDP solution, make up to 5mL with the buffer solution, let stand for 5min, shake with 5mL portions of chloroform for 5 min. measure the absorbance of the reddish-brown extract at 383nm against reagent blank. For Fe(III), adjust to pH 4 of 0.1mL of sample solution containing 4µg of Fe(III) with dilute HCI and buffer, add 0.5mL of KCN to mask Fe(II)[23]. Then add 0.6mL of 0.5% H_2EBNMDP, make up to 5mL with buffer allow standing for 5min shake with 5mL portion of chloroform for 5min and measure the absorbance of the light green extract at 366nm against a reagent blank.

Manganese: Adjust 0.1mL of sample solution containing 4µg of manganese (II) to pH 6 with dilute HCl and buffer. Add 0.6mL of H_2BMPDE solution, make up to about 5mL with same buffer, let stand for 10 minutes, shake with 5mL portions of chloroform for 10min and measure the absorbance of the light yellow extract at 405nm against reagent blank.

Chromium: Adjust 0.1mL of sample solution containing 4µg of Cr(III) to pH 6 with dilute HCI and buffer. Add 0.6mL of H_2EBNMDP solution, make up to about 5mL with same buffer, let stand for 15 minutes, shake with 5mL portions of chloroform for 10 min and measure the absorbance of the light pink extract at 415nm against a reagent blank.

Method development and validation: Linearity: The linearity of the suggested method was determined by analyzing the solution of aliquots of metal and treated using the procedure in the range of 0.1-0.4µg. By plotting the concentration versus absorbance, the calibration curves were constructed.

Limit of detection (LOD) and limit of quantification (LOQ): Limit of detection (LOD) the lowest detectable signal for a given analytical process and limit of quantification (LOQ) the minimum level at which the solution of the analyte can easily be quantified with accuracy. These parameters were calculated according to the method employing 3.3 $^{\delta}/s$ and 10 $^{\delta}/s$ respectively where s is the slope of the corresponding calibration curve and $^{\delta}$ is the standard deviation of the intercept of regression equation[24-29].

Precision: The precision of the method was evaluated by calculating the intra-day and inter-day variations of the method in 3 replicates and by measuring the absorbance of the solutions at the determined wavelength. This is a measure of concordance, reproducibility and repeatability of the method when done the same day (within run/intra-day) and on different days (between run/inter-day).

Accuracy: Recovery studies were done to determine the accuracy of the method by the method of standard addition using water samples.

Robustness: The ability of the analytical procedure to remain unaltered by small though deliberate variation in analytical parameter was investigated by temperature, volume of reagent (ligand) and time variation of same sample. This is important as it helps to determine whether the method can be for routine laboratory and on the field use.

Sensitivity parameters: Molar absorptivity and Sandells sensitivity are sensitivity parameters and are calculated using their formula[24].

Molar absorptivity=Slope x molecular weight x 10^3I/molcm

Sandells sensitivity=molecular weight/molar absorptivity

Results and Discussion

Effect of pH: The effect of pH on the absorption spectra of each metal complex was studied over the range of 1-10 in the presence of H_2EBNMDP adjusted using NH_3 and HCl solutions against the reagent blank. Illustrated in figure-1 is the relationship between percentage extraction and pH. As observed, Fe(III) absorbs maximally at pHs 4 and 8 and hardly at pH 10. Iron(II) aborbs at pH 8 while Mn(II) and Cr(III) absorbs maximally at pH 6. In more acidic solutions, there is a monotonous decrease in the percentage extraction due to hydrolysis of the complexes and incomplete complexes formation. The competitive complexation between the complexes of Fe(II) and Fe(III) at pH 10 and Fe(II) and Cr(III) at pH below 5 due to the precipitation of their hydroxides may be the reason behind their near zero extraction. Similar observation was made in the simultaneous determination and complexation study of Fe(III), Al(III) and V(V) with morin in micellar media[29].

Spectral studies: The absorption spectra of H_2EBNMDP and of chloroform extracts of its Fe(II), Fe(III), Mn (II) and Cr(III) complexes, measured against a reagent blank, are shown in figure-2. The spectra of the reddish-brown Fe(II) complexes have maxima at 366nm while the light green Fe(III) have maxima at 383nm. The light yellow Mn(II) complex and light pink Cr(III) complex have similar spectra with maxima at 405nm and 415nm respectively.
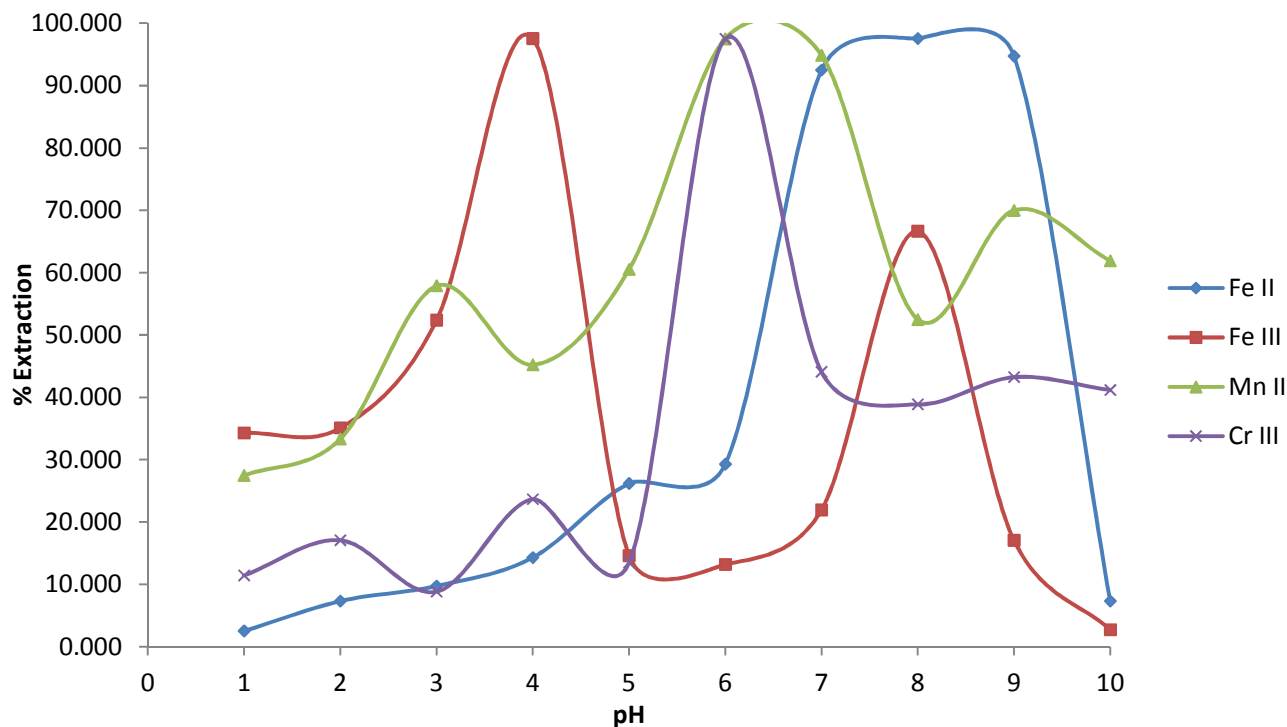
Figure-1
Percentage Extraction of Fe(II), Fe(III), Mn(II) and Cr(III) From 0.5% H$_2$EBNMDP /CHCl$_3$ and Aqueous pH Buffer at 25±1°C
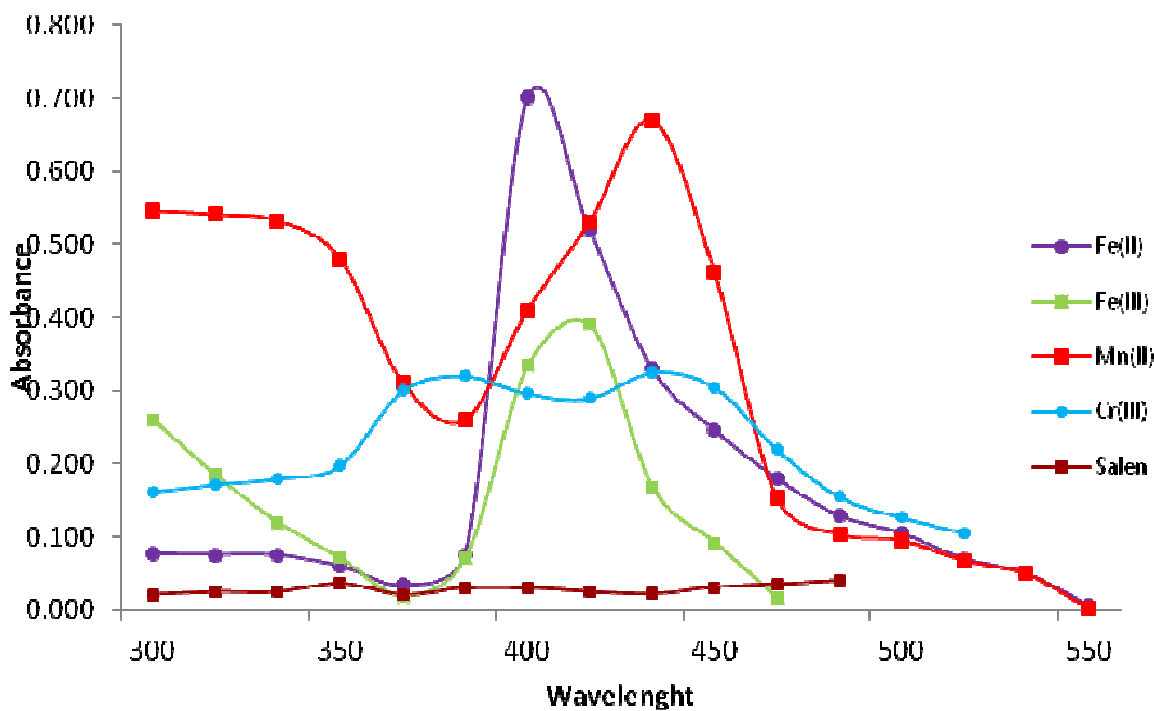

Figure-2
Absorption Spectra of 0.5% H$_2$EBNMDP and chloroform extracts of Fe(II), Fe(III), Cr(III) and Mn(II), complexes from Buffer Solution

Method development and validation: H$_2$EBNMDP (5mgmL^{-1}) was used to develop suitable UV-vis spectrophotometric method for the determination of metal ions; Fe(II), Fe(III), Cr(III), Mn(II). UV spectroscopic scanning run(300-550nm) was carried out to select the best UV wavelength (λ_{max} = 366 nm for Fe(II), 383nm for Fe(III), 405 nm for Mn(III) and 415nm for Cr(III) for the detection of these ions in solution. The analyses was carried out using a blank and absorbance of the solutions determined as well the molar absorptivity and Sandell sensitivity calculated according to the standard formula. Various concentrations of the metal ions (0.1-0.4µgmL^{-1}) were treated with 5mgmL^{-1} H$_2$EBNMDP at the various pH of their complexation and method development is carried out at such pHs.

Method validation: Under the optimized laboratory conditions, calibration curves were plotted between absorbance versus concentrations. Optimized statistical parameters were given in regression equation calculated from calibration graphs. The results of the analytical performance are given in table-1. In all the cases studied, Beers law plot (n=5) were linear with very small intercept and good correlation coefficients in the general concentration range of 0.1-0.4µgmL^{-1}. Standard formula based on standard deviation of the responses and slope approach as defined in International Conference on Harmonization (ICH) guidelines was used for the determination of LOD and LOQ[30]. The values of Sandell sensitivity, limit of detection (LOD) and limit of quantification (LOQ) are listed in table-1. Also, the sensitivity parameter; molar absorptivity was calculated from the formula and presented in table-1.

Accuracy and Precision: Recovery experiment was performed to evaluate the accuracy of the method. Recovery and RSD (%) were found between 98-101% and 0.09-0.1%. The intra- day precision shows no significant variation in the absorbance of the solution of the complexes at triplicate determination. However, inter- day (up to 5days) precision shows significant variation in the absorbance of the solutions. This may be as a result of complex degradation or competitive complexation. In all the analysis, there is excellent repeatability and good precision of the method.

Robustness: Changes in experimental variables were used in estimating the robustness of the method. It was observed that variation in reagent volume (H$_2$EBNMDP), temperature and reaction time did not significantly affect the method. The method is useful being robust for routine analysis.

Selectivity: Varying concentrations of each ion with fixed concentrations of Fe(II), Fe(III), Mn(II) and Cr(III) were taken and absorbance was recorded to determine the concentration of Fe(II), Fe(III), Mn (II) and Cr(III). Tolerated amounts of each ion being the concentration that caused less than±2% absorbance variation was used whereas when the deviation is more interference is said to occur. Consequently, chloride, sulphate, perchlorate, nitrate, alkali and alkaline earth metals up to 1000 fold amount (w/w) and Ag(I), Zn(II), Pb(II) up to 500 fold amount relative to iron(II), iron(III), Mn(II) and Cr(III) do not interfere significantly.

Stoichiometry: Stoichiometry of reaction between iron(II), iron(III), Mn(II), Cr(III) and H$_2$EBNMDP was evaluated by limiting logarithmic method[26-27]. Stoichiometries were postulated from the log – log plots of distribution ratio vs ligand concentration at constant ionic strength for the metal ions and or for the ligand. In the first set of the experiment, the concentration of the metal ions were varied keeping the concentration of the ligand constant whereas in the second set, the concentration of the metal ions were kept constant and ligand concentration varied. Jobs method of continuous variation indicated a mole ratio of 1:2 and 1:1 for iron (II) and iron (III) complexes respectively while for manganese (II) and chromium (III) complexes, a 1: 2 and 1:1 mole ratio is observed.

Applications: The method was applied for the determination of trace Fe(II), Fe(III), Mn (II) and Cr(III) from tap water. Known water samples were analysed using the same methods described for iron(II), iron(III), Mn(II) and Cr (III) determination and recovery test was performed to evaluate the reliability of the proposed method. 1mg/ml of iron(II), iron(III), Mn(II) and Cr(III) was added to each sample and the spiked samples were analysed by the given procedure. Reproducible results of less than 0.1% RSD and the recoveries of 98-101% were obtained for the analysis of trace Fe, Mn(II) and Cr(III).

Table-1
Spectra data and analytical performance of the complexes of H$_2$EBNMDP

Parameter	Fe(II)	Fe(III)	Mn(II)	Cr(III)
λ_{max} ,nm	366	383	405	415
ε, 10^4 LMol^{-1}cm^{-1}	1.84	2.29	2.96	3.85
Linear range, µgL^{-1}	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4
Sandell Sens,mgcm^{-2}	0.003	0.002	0.0018	0.0014
LOD, µgmL^{-1}	0.4	0.38	0.54	0.45
LOQ, µgmL^{-1}	1.30	1.28	1.8	1.5

Conclusion

The method is simple, sensitive, cost effective, and easy and can be applied on the field. It does not require sample pretreatment; and data obtained in the analysis shows that the method is precise and accurate. UV-spectrophotometry provides quick and accurate result especially when interferents are prevented and as such plays germane role in method development.

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