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Journal of Chemical and Pharmaceutical Research, 2015, 7(11):30-40

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Bis(2-methylyidenephenol)diaminoethane (H_2BMPDE) as analytical reagent for solvent extraction studies of Fe(II), Fe(III), Mn(II) and Cr(III)

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ABSTRACT

The extraction of Fe(II), Fe(III), Mn(II), and Cr(III) with bis(2-methylylidene phenol) diaminoethane from various acid solutions have been studied. The light yellow Cr(III) and brown Mn(II) complexes have maximum absorption at 415nm and 405nm respectively while the reddish brown Fe(II) and light green Fe (III) complexes have maximum absorption at 445nm and 390nm respectively. Some effective parameters on extraction and complex formation, such as extraction solvent type and volume, equilibration time, effects of salt, diverse ions, temperature, masking agents, color stability, and acid concentrations have been optimized. Iron, manganese and chromium have been separated and determined in the presence of one another and of many other elements. The method was also successfully applied for the determination of Fe(II), Fe(III), Mn(II) and Cr(III) in the tap water and rain water with recoveries of 98-103% and RSD of less than 0.5%. The regression and ANOVA results shows that at 95% confidence level ($p<0.05$) the results as compared to other methods are statistically significant.

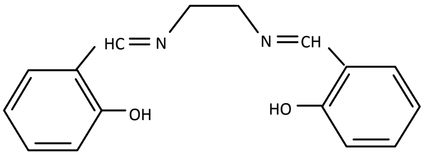
Keywords: liquid-liquid extraction, spectrophotometric technique, selective separation, H_2BMPDE, optimization.

INTRODUCTION

It is known [1-11] that bis(2-methylylidenephenol)diaminoethaane (H_2BMPDE) is a very effective extracting reagent for a number of metals which are extracted with high distribution coefficient at relative PH 4-8. H_2BMPDE metal complexes have been widely used as homogenous catalysts for epoxy resins and as catalysts for various organic syntheses [12-13]. Recently H_2BMPDE metal complexes have been applied in the determination of protein structures and DNA bas e sequences using the complexes site selective binding with a nucleic acid and DNA[14-15]. The capability of the immobilized N,N^1-bis (salicylidine) ethylenediamine as a complexing agent for online sorbent extraction/preconcentration of copper, lead and cyanide has been studied [16]

Solvent extraction also known as liquid liquid extraction is one of the most extensively studied and most widely used techniques for trace metal analysis as it offers advantages such as pre-concentration, matrix effect and interference elimination, convenience of subsequent analysis of the extracted species, and differentiation or separation of elements or chemical species[3,18]. In recent years, the technique has become more and increasingly useful due to the development of selective chelating agents such as bis(salicylidene)ethylenediamine (salen), bis(salicylidene)phenylenediamine (salophen) and bis(acetylacetanato)ethylenediamine (acacen) and conditions for trace metal determination[18]

In the present study, we synthesized (H_2BMPDE) bis(2-methyllidenephenol) diaminoethane and used it as an organic chelating agent to extract and determine Fe(II), Fe(III), Mn(II) and Cr(III) in aqueous solutions. The reliability of H_2BMPDE in solvent extraction as a rapid and sensitive method for separation of Fe(II), Fe(III, Mn(II), Cr(III) in various matrices followed by its determination by spectrophotometry has been developed. The method in comparison to other methods is better since co-precipitation is prevented, minimal reagent is used and the rigours of using colour developers such as 1,10-phenanthroline and dimethylglyoxime[19] is avoided.



Scheme 1. Structure of H_2BMPDE

EXPERIMENTAL SECTION

All reagents were of analytical grade (Merc, Germany) and used without further purification unless otherwise mentioned. All aqueous solutions were prepared in distilled demineralized water. Working solutions were prepared by dilution as required. Extraction was done using plastic stopper bottles of 50mL capacity and shaking effected with RF-12 multi-type rotary shaker. The agitation was done at a constant high speed such that no acceleration rate was observed on further increase in the agitation speed. Temperature variation was effected using ice and DK-420 electrical thermostatic water bath. UV-vis grating spectrophotometer model 8610 Barloworld, England was used for all absorbance measurement.

Metal stock solutions: The standard stock solution of Fe(II), Fe(III), Mn(II), and Cr(III) (100mgL^{-l}) was prepared as follow. Appropriate amount of Ammonium ferrous sulphate hexahydrate and ammonium ferric sulphate dodecahydrate (99%, Sigma Aldrich and 98.5%, Merc Germany respectively) were dissolved in distilled deionized water and were standardized by the permanganate method [19]. Manganese acetate tetrahydrate (99%,Merc Germany) was dissolved in distilled deionized water. Chromium nitrate nonahydrate (98%, Merc Germany) was dissolved in distilled deionized water.

Synthesis of bis(2-methylylidenephenol) diaminoethane.
Ethylenediamine (22.475g) was gradually added with stirring to 91.336g of salycyladehyde 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 the golden yellow crystals [64.45% yield, M.P 121± 1°C]. The reagent is used as a freshly prepared 5mgmL^{-l} H_2BMPDE- ethanol solution.

Acid solutions: 2M solutions of H_2SO_4, HNO_3, HCl and $HClO_4$ were prepared by dissolving requisite amount in distilled deionized water, volume made up to 1dm^3 and standardized using sodium trioxocarbonate(IV).

2.2 Experimental procedures

An aliquot of a sample solution containing 8µg of metal (Fe (II), Fe (III), Mn (II), Cr (III)) was transferred into a series of 20mL calibrated extraction bottle, 1mLof acid solution of concentration 0.0001-2M was added followed with addition of 0.2mL of ligand solution (H_2BMPDE), volume was made up to 5mL with acid solution and maximum time for color development as previously determined allowed and 5mL chloroform added. The phase was agitated and then allowed to settle, centrifuged and separated and the absorbance of the organic extract measured at 445, 390, 405 and 415nm for Fe (II), Fe (III), Mn (II)and Cr(III) respectively against reagent blank. The aqueous phase was treated according to the procedure and amount left determined by material balance[19].

2.3 Determination of Protonation and Acid Dissociation Constants of the reagent.

A 0.01M H_2BMPDE/ethanol solution gave a pH value of 8.2±0.10. The protonation constants were determined by titration of the reagent with 0.01M hydrochloric acid and 0.1M sodium chloride as $\log K_1 = 4.57\pm0.01$ and $\log K_2=3.82\pm0.01$ at 27±1°C. These values suggest stepwise protonation of the two nitrogen sites in the ligand, H_2BMPDE, to give H_3BMPDE^+ and H_4BMPDE^{2+} respectively. The acid dissociation constant were obtained by titration with 0.01M sodium hydroxide and 0.1M sodium chloride, and were found to be PK_{1d}=8.60±0.10 and PK_{2d}=10.36±0.10 at 27±1°C, corresponding to the formation of $HBMPDE^-$ and $BMPDE^{2-}$ respectively.

2.4 Measurement of Distribution Ratios

Equal volumes (5mL) of the aqueous and organic phase were shaken mechanically, 5min for Fe(II), 10min for Fe(III), 10min for Mn(II) and 10min for Cr(III) in glass stoppered bottles at 27±1°C. The phases were centrifuged, separated and analyzed spectrophotometrically [19].

2.5 Recommended Procedures for Iron, Manganese and Chromium

Iron: adjust 0.1mL of freshly prepared sample solution containing 100µg of Fe(II), to pH 4 with dilute HCl/HNO_3. Add 0.6mL of 0.5% H_2BMPDE solution, make up to 5mL with acid solution, let stand for 5 min, shake with 5mL portion of chloroform for 5 min. Measure the absorbance of the reddish-brown extract at 445nm against reagent blank. For Fe(III), adjust to pH 4 of 0.1mL of sample solution containing 100µg of Fe(III) with dilute HCl, HNO_3 or H_2SO_4 and add 0.05mL of 3.5% hydrogen peroxide to quantify total iron in solution[18] . Then add 0.6mL of 0.5% H_2BMPDE, make it up to 5mL with acid solution allow to stand for 10min shake with 5mL portion of chloroform for 5min and measure the absorbance of the light green extract at 390nm against the reagent blank.
Manganese: adjust 0.1mLof sample solution containing 100µg of Mn(11) to pH 4 with dilute HCl. Add 0.6mL of H_2BMPDE solution, make up to about 5mL with dilute acid, let stand for 15 min, shake with 5mL portion of chloroform for 10 min and measure the absorbance of the brown extract at 405nm against reagent blank.

Chromium: adjust 0.1mL of sample solution containing 100µg of Cr(III) to pH 4 with dilute HCl. Add 0.6ml of H_2BMPDE solution, make up to about 5mL with dilute acid, let stand for 15min , shake with 5mL portion of chloroform for 10min and measure the absorbance of the light yellow extract at 415nm against a reagent blank.

RESULTS AND DISCUSSION

3.1 Color Stability

The stability of the color of the complexes was studied at room temperature (27±1°C). Maximum absorbance of the chloroform extract was obtained after 5min standing of the aqueous phase before extraction for Fe(II) and 10min for Fe(III), Mn(II) and Cr(III). The absorbance of Fe(II) and Fe(III) complexes was constant for at least 3 days while that of Mn(II) and Cr(III) complexes was stable for up to 10min.This is illustrated in Fig.i.

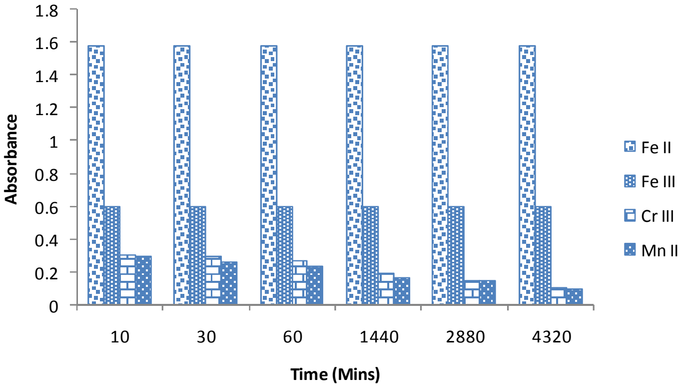


Fig. i: Effect of storage (color stability) on the absorbance of 0.2mg/mL Fe(II), Fe(III), Mn(II) and Cr(III) extracted from 10^{-4} HCl using equal volumes (5mL) of aqueous phase and 1.86mg/mL $H_2BMPDE/CHCl_3$ solution

3.2 Temperature Effect

The temperature was varied from 15 to 40°C, the absorbance is at a maximum and constant between 27 and 34°C. All determination was done at room temperature (27 ± 1°C). Fig ii. shows the effect of temperature on absorbance of Fe(II), Fe(III), Mn(II) and Cr(III) H_2BMPDE/ chloroform extract.

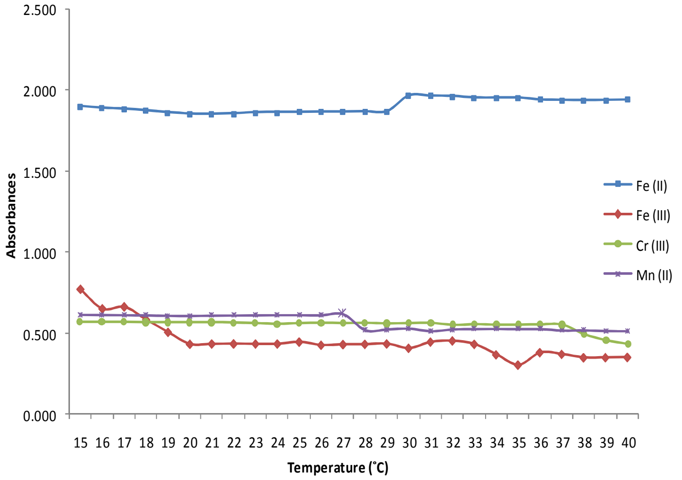


Fig.ii: Effect of temperature on absorbance of 0.2mg/mL Fe(II), Fe(III), Mn(II) and Cr(III) extracted from 10^{-4} H_2SO_4 using equal volume (5mL) of aqueous phase and 1.86mg/mL H_2BMPDE/$CHCl_3$ solution. Contact time 5min for Fe(II)and 10min for Mn(II), Cr(III) and Fe(III)

3.3 Phase volume Ratio

Variation in volume of the aqueous phase from 5 to 20 mL had little or no effect on the extraction efficiency. A working volume of 5mL is recommended for ease of manipulation. Fig iii Shows the effect of volume variation on the absorbance of Fe(II), Fe (III), Mn(II), and Cr(III) H_2BMPDE/ Chloroform extract.

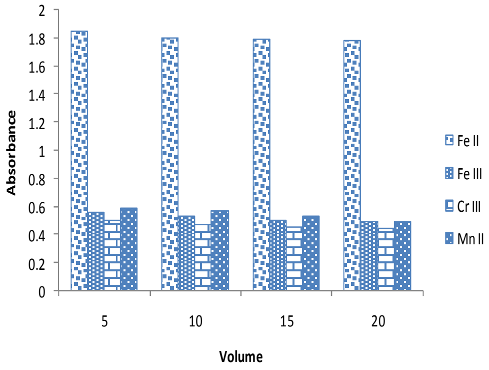


Fig. iii: Effect of volume of chloroform on the absorbance of 0.02mg/mL Fe(II), Fe(III), Mn(II), and Cr(III) extracted from 10^{-4} HCl and 1.86mg/mL H_2BMPDE/$CHCl_3$ solution

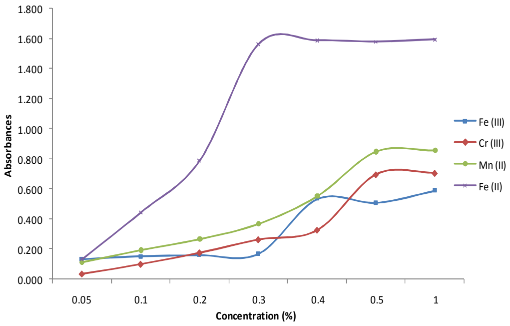


Fig. iv: Effect of concentration of ligand on the absorbance of Fe(II), Fe(III), Mn(II), and Cr(III) extracted from 10^{-4} HCl and 5mL $CHCl_3$ solution

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3.4 Effect of concentration of H_2BMPDE

The efficiency of analyte extraction was dependent on H_2BMPDE concentration as shown in fig iv. As it is demonstrated, the extraction efficiency increases with an increase in ligand concentration and leveled off at concentration greater than 2.2×10^{-4} mol/L (0.3%). A concentration of 4.73×10^{-4} mol/L (0.5%) H_2BMPDE solution was used in the experiment. This is so because the concentration of chelating agent greatly affects extraction efficiency in solvent extraction since excess chelate can form a stable and stoichiometric metal chelate. Therefore, if the amount of chelate is not enough to form complex with metal ion, error should occur[18].

3.5 Extraction from acid solutions

The extraction of Fe(II), Fe(III), Mn(II) and Cr(III) from acid media with 0.5% H_2BMPDE and an equal volume of chloroform is shown in fig v-viii respectively".

Iron(II) is quantitatively extracted from all four acids when these are present in the concentration range of 0.001-0.0001M. At higher acidity a sharp decrease in extraction is observed at 0.01M for all acid HCl, H_2SO_4, HNO_3 and $HClO_4$ as a result of the protonation of the ligand, H_2BMPDE, according to the equations

$$H_2BMPDE + H^+ \rightleftharpoons H_3BMPDE^+ ;\log K_1 = 4.57 \qquad 1$$

$$H_3BMPDE + H^+ \rightleftharpoons H_4BMPDE^+ ;\log K_2 = 3.82 \qquad 2$$

At 0.01M HNO_3 concentration, an unextractable pinkish complex is formed but was not investigated. The extraction of iron(III) from various acid solution follow a trend related to that of iron(II) for sulphuric acid, hydrochloric acid, perchloric acid and nitric acid. The extraction of Fe(II) shown in figs v and vi shows a general decrease with increasing acidity of the aqueous phase according to the equation. Similarly, the extraction of Fe(III) shows a decrease with increasing acidity however, at concentration of 2M for HNO_3 and $HClO_4$ an observed rise in extraction was seen possibly because of extraction of a deprotonated complex specie though not investigated.

$$M^{n+} + mH_3BMPDE^+ + nX^- \overset{kex}{\rightleftharpoons} M(H_2BMPDE)_M^{n+}\, nX^- + mH^+ \qquad 3$$

Extraction constant is

$$kex = \frac{[M\,(H_2BMPDE)_M^{n+}\cdot nX^-][H^+]^M}{[M^{n+}][H_3BMPDE^+]^M[X^-]^n} \qquad 4$$

Where $X = Cl^-,\ ClO_4^-,\ NO_3^-,\ \text{or}\ HSO_4^-,$

Hence,

$$\log D = M\log[H_2BMPDE] + n\log[X^-] + M\log K_1 + \log kex \qquad 5$$

Plots of log D vs log [H_2BMPDE] at pH 4 – 8 at constant ionic strength of 0.0001M, maintained by chloride, perchlorate, sulphate or nitrate ion are linear with slopes of 2 and 1 for Fe(II) and Fe(III) respectively. Similar plots of log D vs log [X^-] at 0.0001M H_2BMPDE concentration and pH 4 – 6 are also linear with slopes of 2 and 1 for Fe(II) and Fe(III) respectively.

These results suggest formation of ion – association complexes of the type $[Fe^{II}\,(H_2BMPDE)_2^{2+}]2X$ and $[Fe^{III}\,(H_2BMPDE)\,(OH)_2^{+}]X$ as the predominant species at low acidity

whereas at high acidity concentration, the equilibrium shifts to the left preventing complex formation. The log K_{ex} values obtained from these plots are 1.5 and 1 for Fe(II) and Fe(III) respectively. The extraction of Mn(II) and Cr(III) from acid media is low but increases with increasing pH according to the equations 3,4 and 5.Plot of log Dvs log [H_2BMPDE] at constant ionic strength 0.0001M are linear with a slopes of 2 and 1 in the pH range 5 – 8 for manganese and chromium respectively. This suggest the extraction of

$[Mn^{II}(H_2BMPDE)_2^{2+}]2X^-$ and $[Cr^{III}(H_2BMPDE)(OH)_2^+]X^-$complexes at pH below 8. The log Kex values obtained on the basis of equation 7 is -0.3 and 0.4 for manganese and chromium respectively. Lloret *et al* (1989) has determined that Fe(III) H_2BMPDE complex is mononuclear while(Nwabue and Okafor,1982) noted that Fe(II) and Fe(III) complexes of a H_2BMPDE – type ligand is dinuclear and mononuclear respectively. Lloret *et al* [21] and Tantaru *et al* [22] reported mononuclear Cr(III)H_2BMPDE complex and dinuclear complex of manganese - H_2BMPDE type ligand respectively in aqueous solution.

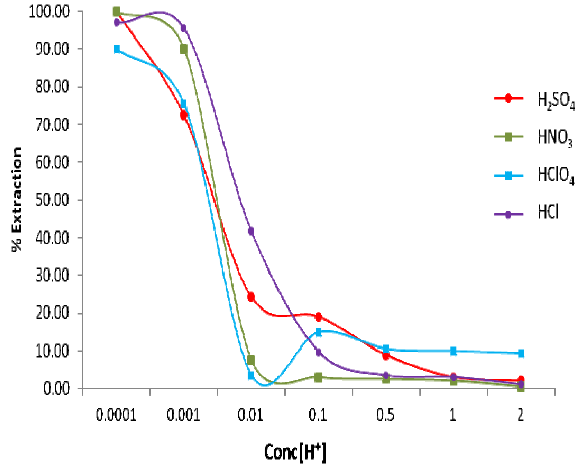

Fig. v: Extraction of Fe(II) as a function of acid concentration H_2SO_4, HNO_3, $HClO_4$, HCl. Equal volumes (5mL) of aqueous phase and 1.86 mg/mL H_2BMPDE/$CHCl_3$ solution

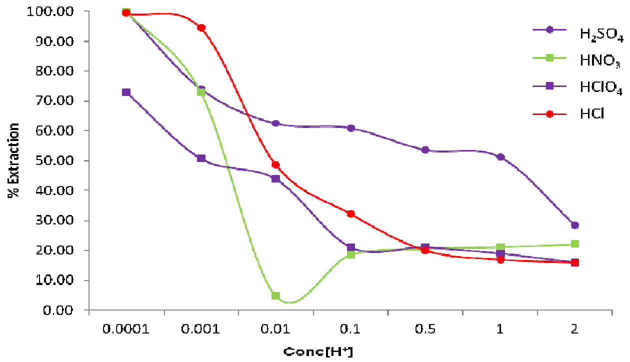

Fig. vi: Extraction of Fe(III) as the function of acid concentration H_2SO_4,HNO_3, $HClO_4$, HCl. Equal volume (5mL) of aqueous phase and 1.86mg/Ml H_2BMPDE/$CHCl_3$ solution

3.6 Effect of Salting Out Agents

The effect of chloride, nitrate, sulphate and perchlorate ion on the extraction of Fe(II), Fe(III), Mn(II) and Cr(III) using 1.86mg/mL H_2BMPDE solution in chloroform in a constant acidity is shown in fig ix. As shown in fig ix, the salting out effects is pronounced more in the perchlorate, nitrate and sulphate system than in the chloride system that has almost negligible effect in the extraction of Fe(II). In the case of Fe(III) at constant acidity strength of 0.001M,the extraction is quantitative. Therefore, for both iron species, the extraction is consistent with the equilibrium suggested in equation (3). Similar profile of extraction is seen in Mn(II) and Cr(III) system where the salting out effect enhanced the extraction of Mn(II) and Cr(III). Similar observation has been shown [18,20] using bis(salicylidene)phenylenediamine(Salphen) and bis(acetylacetone)ethylenediamine (Acacen)respectively.

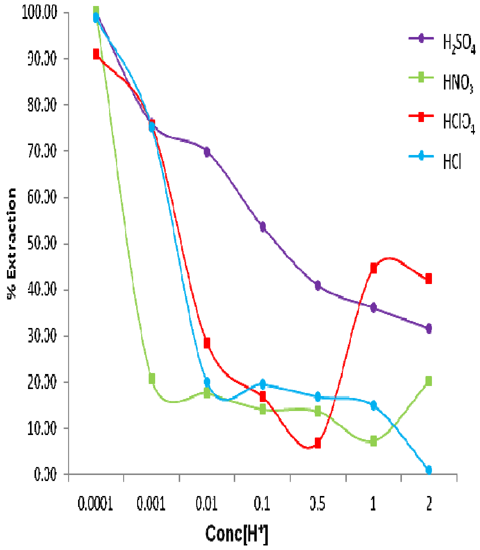

Fig.vii: Extraction of chromium (III) as a function of acid concentration H_2SO_4,HNO_3, HClO4, HCl. Equal volume (5mL) of aqueous phase and 1.86mg/mL H_2BMPDE/$CHCl_3$ solution

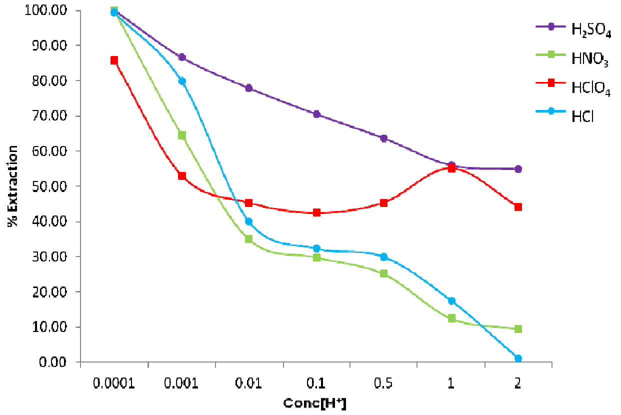

Fig. viii: Extraction of Mn(II) as a function of acid concentration H_2SO_4,HNO_3, HClO4, HCl. Equal volumes (5mL) of aqueous phase and 1.86mg/mL H_2BMPDE/$CHCl_3$ solution

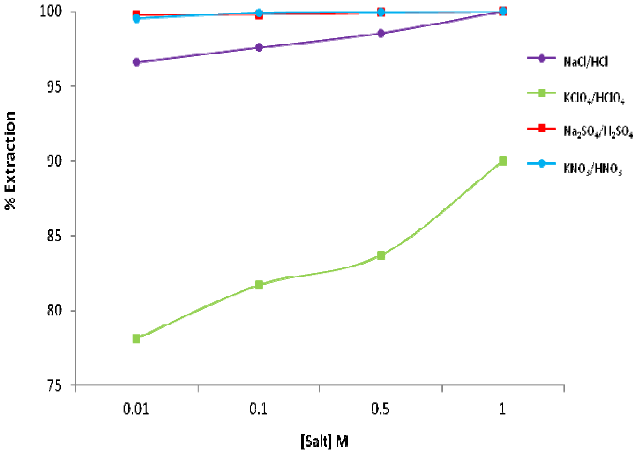

Fig. ix: Effect of Salting out Agents on the extraction of 0.02mg/mL Fe(II) from 10^{-2}M HCl, H_2SO_4, HNO_3 and $HClO_4$ with an equal volume (5mL) of aqueous phase and 1.86mg/mL H_2BMPDE/$CHCl_3$ solution

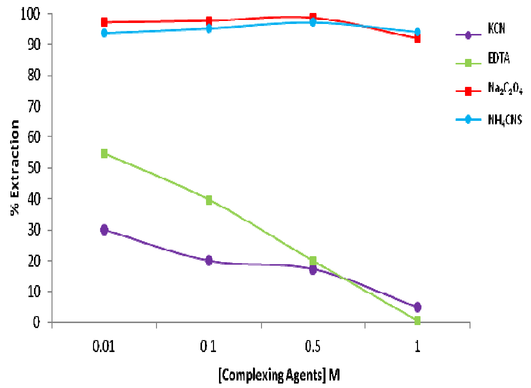

Fig. x: Effect of Masking Agent on the Extraction of 0.02mg/mL Fe(II) from 10^{-4}M HCl, H_2SO_4, HNO_3 and $HClO_4$ with an equal volume (5mL) of aqueous phase and 1.86mg/mL H_2BMPDE/$CHCl_3$ solution at 27±1°C.

3.7 Effects of Masking Agents

The extraction of Fe(II) from 0.0001M hydrochloric acid is influenced by the presence of various masking agents as shown in fig x. Thiocyanate and oxalate ions have negligible effect on the extraction. Complete masking of Fe(II) is achieved at cyanide or EDTA concentration of 0.1 – 1M concentration. The extraction of Fe(III), Mn(II) and Cr(III)from 0.0001M hydrochloric acid in the presence of cyanide, thiocyanate, EDTA and oxalate shows negligible effect in their masking action as observed in all the three metals. The stripping of Fe(II), Fe (III), Mn(II) and Cr(III)with various acid solutions from chloroform extract was studied. Two back extraction of Fe(II) and Fe(III) with 2M hydrochloric acid (equilibration for 2min) gave quantitative recovery, but equilibration for 3min was needed for the complete recovery of Mn(II) with 2M hydrochloric acid and 3M hydrochloric acid for Cr (III).

3.8 Spectral studies

The absorption spectra of H_2BMPDE and chloroform extract of Fe(II), Fe(III), Mn(II) and Cr(III) complexes, measured against a reagent blank, are shown in fig xi. The spectra of the reddish brown iron(II) complexes have maxima at 445nm while the light green iron (III)have maxima at 390nm. The light yellow manganese (II) complex and light pink chromium (III) complex have similar spectra with maxima at 405 and 415nm respectively.

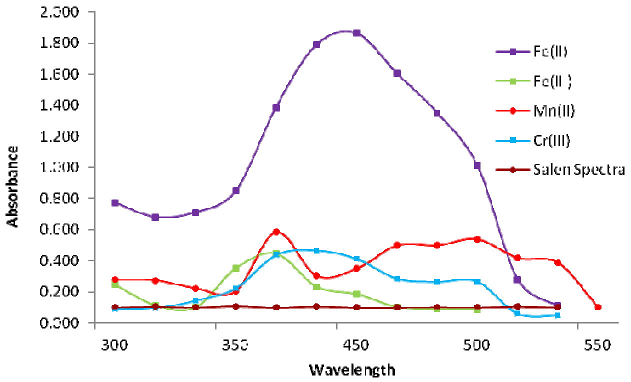

Fig. xi: Absorption spectra of 0.5% H_2BMPDE/$CHCl_3$ and its chloroform extract of its Fe(II), Fe(III), Mn(II), and Cr(III) complex ion solution

3.9 Choice of solvent

Chloroform, carbon tetrachloride, benzene and toluene were tried as solvents. H_2BMPDE is readily soluble in chloroform and sparingly soluble in others. Chloroform shows a better separation and highest absorbance for all the complexes and is therefore used for all the determinations.

3.10 Analytical Performance

Table i summarizes the calibration and other data. The performances characteristics of the method were obtained by processing standard solution of the metals. The calibration curve was constructed by processing 5mL of standard solution (in quadriplicate) under optimum condition of spectrophotometric determination. The graph of absorbance versus Fe(II), Fe(III), Mn (II) and Cr(III) concentration were linear over the range of 5-20µgL^{-I}

Table i: Spectra data for the complexes with *H_2BMPDE*

Parameter	Fe(II)	Fe(III)	Mn(II)	Cr(III)
$A_{max,}$nm	445	390	405	415
E, 10^4 LMol^{-1}cm^{-1}				
(HNO_3)	4.23	3.46	1.78	1.50
Linear range µg/mL	5-20	5-20	5-20	5-20
Correlation coefficient	0.9994	0.9980	0.9892	0.9873
Limit of detection µg/mL	0.001	0.001	0.002	0.002
Sandel sensitivity µg/mL	0.01	0.01	0.01	0.01

3.11 APPLICATION OF THE METHOD

The efficiency of the method in extraction of iron (II), iron (III), manganese (II) and chromium (III) in the presence of various cations was examined . Iron(II) is quantitatively co-extracted with iron(III) under the conditions used but iron(II) can be masked with 0.1M KCN prior to the determination of the later. Chromium is quantitatively co-extracted with each other under the conditions used for manganese. However, manganese is not extracted above 2MHCI concentration whereas chromium is about 30% extracted. A triple extraction of chromium at this acid concentration gave practically complete separation from manganese. These separation methods were tested with mixtures of iron and manganese or chromium, and of manganese and chromium. Recovery was quantitative and the results were reproducible.

3.12 Effect of Diverse ions

The effect of some ions in the determination of iron(II), iron(III), manganese(II) and chromium(III) in the spectrophotometric method recommended was examined. 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), manganese (II) and chromium(III) do not interfere significantly. The result is presented in table ii.

Table ii: Separation factors of various metal ions with respect to (II), iron (III), manganese (II) and chromium (III) extracted from 0.0001M HCI with 1.86 mg/mL *$H_2BMPDE/CHCI_3$*

COEXISTING ion	CONCENTRATION	Dfe (II)/Dmetal	DFe (III)/Dmetal	DMn (II)/Dmetal	DCr (III)/Dmetal
Na^+	$2.17*10^{-5}$	0.99	0.985	0.998	0.290
Pb^{2+}	$2.41*10^{-6}$	0.965	0.947	0.886	0.180
Cu^{2+}	$4.24x10^{-5}$	2.08	1.03	2.08	2.09
Ni^{2+}	$4.24x10^{-5}$	1	0.49	1.2	1.0
Cr^{3+}	$48x10^{-5}$	0.99	0.49	1	-
Mn^{2+}	$4.55x10^{-5}$	1.0	0.49	-	1.0
Mg^{2+}	$2.08*10^{-5}$	0.98	0.998	0.396	0.193
AI^{3+}	$9.25*10^{-6}$	0985	0.143	0.396	0.20
Fe^{2+}	$4.46x10^{-5}$	-	2.01	1.0	1
Fe^{3+}	$4.47 x 10^{-5}$	2.0	-	2.01	2.2
K^+	$1.28*10^{-5}$	0.98	0.98	0.297	0.288
Zn^{2+}	$7.69*10^{-6}$	1.87	0.140	0.186	0.088
Co^{2+}	$1.05 x 10^{-5}$	12.2	10.94	12.4	12.11
CH_3C00^-	$8.47*10^{-6}$	0.17	0.192	0.990	0.995
$N0_3^-$	$8.47*10^{-6}$	0.185	0.994	0.933	1.95
CI^-	$1.41*10^{-5}$	0.980	0.490	0.920	0.966
$S0_4^{2-}$	$5.20*10^{-6}$	0.129	0.494	0.912	0.956

3.13 Stoichiometry/ Composition of the Complex

Job's method and the mole-ratio method indicate a mole ratio of 1:2 and 1:1 for iron(II) and iron(III) complexes respectively. For the Mn(II) and Cr(III) complexes, a 1:2 and 1:1 mole ratio is observed. This supports the $Fe^{II}(H_2BMPDE)_2.2X$, $Fe^{III}(H_2BMPDE)(OH)_2.X^-$, $Cr^{III}(H_2BMPDE)$, $Mn^{II}(H_2BMPDE)_2$ stoichiometries postulated from the log-log plots of distribution ratio vs ligand concentration at constant ionic strength respectively. The structure suggested for the iron complex is octahedral. It is possible that the complex is a mixed ligand compound in which the two X^- ion would occupy the trans-positions on the octahedron. The structure of the Fe(III) complex could be an ion association ligand complex analogous to that of Cr(III), $[Cr^{III}\ (H_2BMPDE)\ (OH)_2^{+}]X^-$ or a mixed ligand complex. Mn(II) complex is possibly octahedral just like the Fe(II) complex $[Mn^{II}\ (H_2BMPDE)_2^{2+}]2X^-$ .Similar structures have been reported[13] for some H_2BMPDE complex where they co-ordinate tetravalently with the same metal ion on the same plane.

3.14 Applications/ Analysis of Real Samples

An optimized procedure was applied to the determination of trace Fe(II), Fe(III), Mn(II) and Cr(III) from tap water and well water. Unknown water sample was analyzed using the same method described for Fe(II), Fe(III), Mn(II) and Cr(III) determination and finally, a recovery test was performed to evaluate the reliability of the proposed method. 1mg/L of Fe(II), Fe(III), Mn(II) and Cr(III) was added to each sample and the spiked samples were analyzed by the given procedure. The extraction was probably above 100% in some water samples because these samples contain an overload of the ions being extracted or a redox process has taken place or may be a presence of chelating specie in the water sample. Reproducible results of less than 0.5% RSD and recoveries of 98-103% were obtained for the analysis of trace Fe, Mn(II) and Cr (III). The results are shown in table iii. The regression and ANOVA results shows that at 95% confidence level ($p<0.05$) the results as compared to other methods are statistically significant.

Table iii: Analysis of natural sample (tap water and well water) for Fe(II), Fe(III), Mn(II) and Cr(III) by the recommended procedure

Elements	Samples	Amount Added (mg)	Amount found (mg)	% Recovery
Fe (II)	Tap water	0	0.20	
		1	1.21 *0.01	101
	Well water	0	0.24	
		1	1.26 *0.4	102
Fe (III)	Tap water	0	0.20	
		1	1.22 *0.02	102
	Well water	0	0.25	
		1	1.28 *0.2	103
Mn (II)	Tap water	0	0.00	
		1	0.99 *0.00	99
	Well water	0	0.06	
		1	1.04 *0.1	98
Cr (III)	Tap water	0	0.00	
		1	1.01 *0.001	98
	Well water	0	0.01	
		1	1.00 *0.4	99

**Relative standard deviation for the mean value of 5 measurements*

CONCLUSION

In this study, H_2BMPDE was used as a chelating agent for the extractive spectrophotometric determination of Fe(II), Fe(III), Mn(II) and Cr(III) in various acid solutions of different concentrations. The effectiveness of this method has been used in the determination of metals in tap and well water. The result shows that the proposed method is simple, rapid, safe, flexible, reliable, cheap and of high extraction efficiency for the determination of these metals.

Acknowledgements

The authors are grateful to colleagues at the department of Industrial chemistry Ebonyi State University, Abakaliki and to Prof. P Ukoha of the department of pure and industrial chemistry, university of Nigeria Nsukka for their advice and encouragement.

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