

Separation Of Magnesium From Manganese And Zinc

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Abstract :

Magnesium ions , with concentration as low as 10^{-4} M have been quantitatively separated from Mn(II) and Zn(II) ions by precipitations with some halogen substituted of diphenylthiocarbazone in a buffered solution of about 50% V/V aqueous – dioxan .

As a precipitant the di-p-iodophenylthiocarbazone in dioxan solution was employed . The use of this ligand is promising for both qualitative test and quantitative determination of traced of magnesium. Preliminary work with the di-p-fluoro, di-p-chloro, di-p-bromo, and di-m-trifluoromethylphenylthiocarbazone indicated the formation precipitates analogous to the magnesium di-p-iodo- compound .

: الخلاصة :

تم فصل ايونات المغنيسيوم ذات تركيز واطئ نحو 10^{-4} مولاري من ايونات المنغنيز والزنك بترسيبها بواسطة مشتقات الديثايزون الهالوجينية في محلول بفر مائي للدايوكسان تبلغ نسبة المزج الحجمية فيه نحو 50 بالمائة واستخدام كمرسب المركب داي ايودو فنيل ثايو كاربازون في محلول الدايوكسان. وقد تبين ان استخدام هذا المركب يعطي نتائج جيدة عند استخدامه في كلا التحليلين الوصفي والكمي لمقادير ضئيلة من المغنيسيوم. اما بالنسبة للمشتقات الاخرى كالداي بارافلورو ، كلورو ، برومو وميتافلورو مثيلفنيلثايوكاربازون فالدراسات الاولى تشير الى انها تعطي رواسب مماثلة لمركب الايودو .

Introduction

Many heterocyclic azo dyes have been investigated and used as photometric reagents in the determination of Metal ions (Anderson & Nickless, 1967, Feri, *et al.*, 1971, and Chand & Zhou , 1986) .

Several methods of precipitation of Mg(II) ions for the purpose of separation and quantitative determination are known.

As precipitants phosphate and oxine give respectively $Mg(NH_4)(PO_4).6H_2O$ and $Mg(C_9H_6ON)_2.2H_2O$ (Vogel , 1982) . In one of the procedures employed for the separation of Mg(II) from Mn(II) and Zn(II) ions (Vogel, 1982, 1966) with Na_2EDTA , fairly stable complexes are formed. Addition of sufficient amount of sodium fluoride solution causes a displacement of magnesium while Mn(II)EDTA and Zn(II)EDTA complexes are not affected . In the filtrate , Separation of Zn(II) from Mn(II) ions can be accomplished by the use of potassium cyanide to form the stable Zinc cyano – complex $[Zn(CN)_4]^{-2}$.

In another the Zinc ion is precipitated as the Zinc sulfide from a solution containing sulfuric acid and ammonium sulfate at pH of 2-3 (Erdey, 1965).

The spectrophotometric methods determination of manganese and Zinc with organic reagents like hydrazones , oxines and Heterocyclic azo ligands use as photometric reagents (Hussain & Jassium 1989 , Murthy , *et al.* , 1989) .

Oxadiazole and triazole derivatives have been determined of Mn(II) and Zn(II) spectrophotometrically (Ayad , 1998) .

In this work Mg(II) ions with concentration as low as 10^{-4} M in solutions containing Mn(II) and Zn (II) ions were precipitated and separated using some halogenated derivatives of dithizone . Under the condition of precipitation , both

manganes and Zinc ions form soluble and stable complexes while magnesium ions form brown precipitate .

Experimental

Materials

Dithizone, halogen substituted derivatives of diphenylthiocarbazone, was obtained from the Fisher Scientific Company .

These dithizones were purified by precipitation with absolute ethanol from their solution in freshly distilled chloroform that was treated with $\text{NH}_2\text{OH}.\text{HCl}$ (Erdey, 1963). The melting points of the compounds and the absorption spectra , in the visible range , were compared with those previously reported (Table 1) .

Table 1
Melting Point For Dithizones And the Absorptivity Data In Chloroform Solution at 25°C

Diphenylthiocarbazone	m.p.°c	λ_1 max nm	λ_2 max nm
Di-p-fluorophenyl ($\text{C}_{13}\text{H}_{10}\text{F}_2\text{N}_4\text{S}$)	144-150 (a)146-148	606 606	477 477
Di-p-chlorophenyl ($\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{N}_4\text{S}$)	172-173 (b)173-174	622 (a)621	458 458
Di-p-bromophenyl ($\text{C}_{13}\text{H}_{10}\text{Br}_2\text{N}_4\text{S}$)	150-151 (b)151-152	626 (a)625	458 458
Di-p-Iodophenyl ($\text{C}_{13}\text{H}_{10}\text{I}_2\text{N}_4\text{S}$)	159-160 (a)160-161	635 635	466 464
Di-m-trifluoromethyphenyl ($\text{C}_{15}\text{H}_{10}\text{F}_6\text{N}_4\text{S}$)	130-131 (a)128-129	610 610	443 445

(a) reported values (Oh & freiser , 1967) .

(b) Reported values (Pupko & Pelkis , 1965) .

All the chemical were of B.D.H and Fluka grade . buffer solutions used were prepared from HCOOH , $\text{HC}_2\text{H}_3\text{O}_2$, $\text{NaC}_2\text{H}_3\text{O}_2$, NaH_2Po_4 and NaOH . 1,4-dioxan was purified by refluxing with metallic sodium and then treated with hydroxylamine hydrochloride (Freiser, 1965). Saturated solutions of dithizones in 1,4-dioxan were freshly prepared and treated with a few crystals of $\text{NH}_2\text{OH}.\text{HCl}$ also .

Apparatus :

A Cary 14 Spectrophotometer was employed for obtaining the absorptivity data, and Bachman Research pH meter equipped with a glass – Calomel electrode pair was used for pH adjustment .

Precipitation of magnesium (II) ions as MgD_2X_2 and $\text{MgD}_2(\text{CF}_3)_2$.

Several series of buffered authentic solutions with pH ranging from about 3 to 8 were prepared for each of $\text{Mg}(\text{II})$, $\text{Mn}(\text{II})$ and $\text{Zn}(\text{II})$ ions . Within each series the metal ion concentration was between $1 \times 10^{-2} - 1 \times 10^{-4} \text{ M}$. To (5mL) of the buffered metallic ion solution an equal volume of dioxin to prevent the partial precipitation of the reagent itself , was added followed by dropwise addition , with stirring , of the reagent solution . Among the metal ions studied $\text{Mg}(\text{II})$ ion was found to be the only one that gave precipitates with all five halogenated dithizones . The formation of the

precipitates began at a pH of about 6.0 and at 4.5 in the case of di-m-CF₃- reagent . But the parent reagent diphenylthiocarbazone , Showed no sign of precipitation .

Manganese and Zinc ions under the same conditions gave soluble complexes .

The former colored the solution with dull Yellowish orange and the latter with light red .

After digestion at about 75°C for half an hour then cooling , the precipitate was filtered , washed with several portions of dioxan the distilled water and dried in the oven at 110°C .

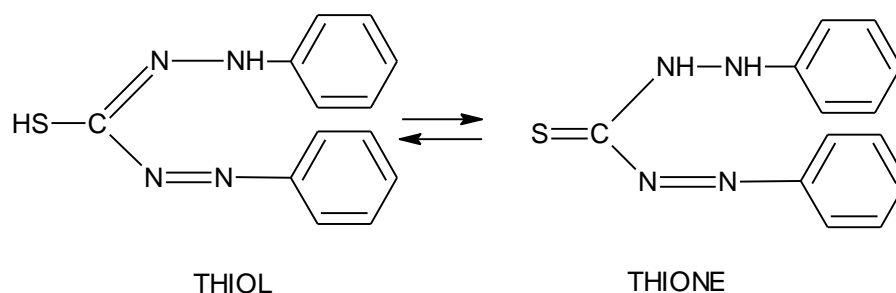
Ignition of the precipitate then dissolving in dilute hydrochloric acid reveals the presence of magnesium ions when qualitative test was performed using 8-hydroxyl quinoline . The separation of Mg(II) ions from solution containing Mn(II) and Zn(II) ions using the di-p-iodo-compound was carried out in solutions containing as low as 1-2 mg of magnesium ions per 25 mL of the aqueous solution .The pH of the solution was adjusted to about 7-8 using phosphate buffer then equal volume of dioxin was added . After heating the mixture to about 65°C , saturated solution of di-p-iodophenylthiocarbazone was slowly added with stirring . The turbid solution was then digested over a steam-bath for half an hour and filtered . The filtrate was tested for complete precipitation . After washing , drying at 110°C , cooling and then weighing , the constant weight obtained corresponds closely to the formula MgC₁₃H₈I₂N₄S .

Discussion

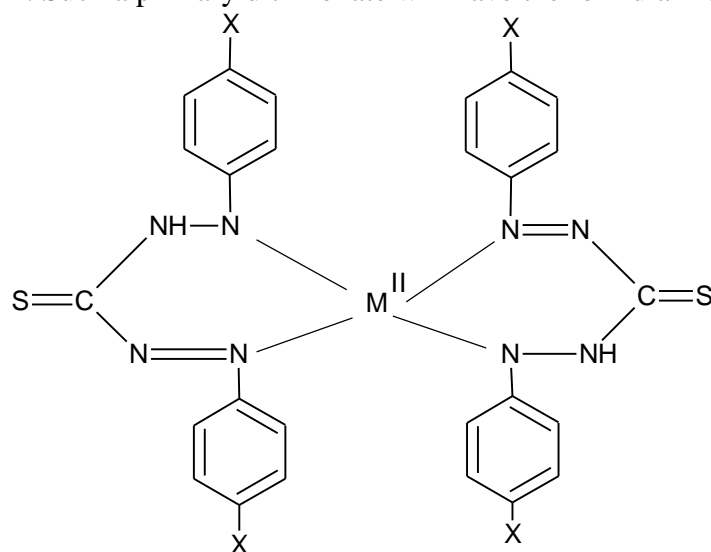
Diphenylthiocarbazone H₂D_z and its halogen derivatives H₂D_zX₂ (X= F, Cl, Br and I) , as well as the H₂D_z(CF₃)₂ compound are violet black solids which are sparingly soluble in water but dissolve in most organic solvents and to a lesser degree in non-polar hydrocarbons . Their solutions in 1,4 dioxan are blush-green and rather unstable . The stabilities toward oxidation were found to decrease in the order F>Cl>Br>I>CF₃ and in the opposite sequence with respect to their pka values (Abid & Freiser, 1970) . While the pka of the di-p-F-phenyl-is 4.99 , that the di-m-CF₃- is 2.57. However , their solution stabilities can be increased by treating both the solvent and the reagent solution with reducing agent such as NH₂OH.HCl .

This will regenerate the dithizones if they have been oxidize as far as to diphenylthiocarbazone .

The choice for the di-p-I- reagent in carrying out the separation is based upon the fact that its dioxan solution is rather stable and that it has the highest molecular weight (507.8) , and so a small weight of Mg(II) ions will form relatively large amount of precipitate . Dithizone and its halogenated derivatives may exist in an organic solvent in both the thiol and thione forms :



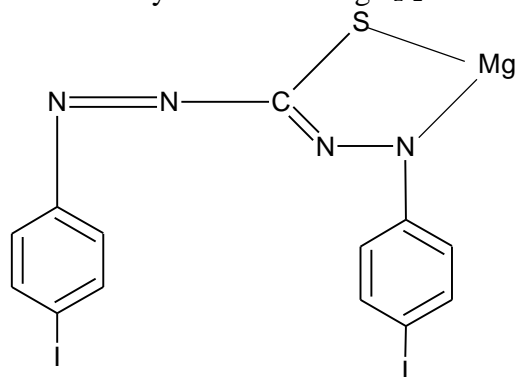
They also form two types of compounds . The first type include primary dithizonate , bidentate chelates , formed with the ligand in its keto or thione form by replacement of one hydrogen in the amino group and coordination to the double – bonded nitrogen . Such a primary dithizonate will have the formula $M(II)(HD_zX_2)_2$



Mono and divalent metals primary dithizonates are well known and many of them have been isolated in solid crystalline form (Marcus –Kertes , 1968) .

They are stable in acid and neutral media . The second types is formed with the ligand in its enol or thiol form by the additional replacement of the hydrogen of the sulphohydryl group . Some metal ions form both the primary and the secondary dithizonates . The primary complexes are preferentially formed in acidic solution and the secondary in alkaline medium (Sandell , 1969) .

Dealing with magnesium (II) ion the experimental results indicated that in slightly basic solution the secondary dithizonate MgD_zI_2 is formed .



(MgD_zI_2)

The formation of the precipitate is to be according to the following reaction .
 $Mg(II) + C_{13}H_{10}N_4I_2S \rightarrow MgC_{13}H_8N_4I_2S + 2H^+$

The precipitation of $Mg(II)$ ions by the electron withdrawing substituted dithizone , and not by the dithizone itself is perhaps due to the change of charge density which in turn increased the acidity of the reagent as was reflected in corresponding decrease in the pka values (Hussain & Jassium , 1989) these ligands , and for the reaction to take place in basic media one can predict the displacement of both hydrogens similar reactions under almost the same condition using the other

halogen derivatives were carried out for qualitative purpose and it is expected that they form with Mg(II) ions secondary dithizonate too . It should be mentioned that the above method of estimating magnesium – requires a great care and in general it is somewhat troublesome . But such a procedure is advantageous in the presence of Mn(II) and Zn(II) ions , whenever there is a need for trace determination . As so the identification of Mg(II) ion the test by the formation of $MgDzI_2$ exceeds in its sensivity that of 8-hydroxy quinoline .

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