J. Indian Inst. Sci., 66, Jan. 1986, pp. 29-32

Short Communication

Glycol dimercaptoacetate as a new masking agent: Determination of zinc in presence of cadmium

D.N. PUROHIT

Department of Chemistry, School of Basic Science and Humanities, M.L. Sukhadia University, Udaipur 313 001, India.

Received on February 13, 1984; Revised on April 16, 1984.

Abstract

Glycoldimercaptoacetate has been introduced as a new masking agent. Zinc has been determined complexometrically in the presence of a large excess of cadmium using GDMA as a masking agent.

Key words: Masking agent, glycoldimercaptoacetate, complexometry, zinc and cadmium.

1. Introduction

It is well known that selectivity of complexometric method can be increased appreciably by masking the accompanying elements. For this purpose a wide range of complexing agents can be used[1-6]. An attempt has been made to develop glycoldimercaptoacetate (GDMA) as a masking agent. Using GDMA as a masking agent a simple method for the determination of zinc in the presence of large excess of cadmium is reported here.

2. Experimental

EDTA solution (0.05M) was prepared by dissolving 37.22 g of reagent grade CHELATON-3 (Chemapol, Prague) in water and diluting it to two litres. It was standardized against lead nitrate using xylenol orange as the indicator.

Solutions of metal ions (0.05M) were prepared by dissolving known quantities of analytical reagent-grade metal nitrates in distilled water and standardized gravimetrically or by EDTA titrations. A 1:100 mixture of methylthymol blue or xylenol orange with potassium nitrate was used as indicator.

Glycoldimercaptoacetate (Evans Chemicals, U.S.A.) was used as such or as its concentrated solution in dioxane.

3. Results

A preliminary study of the reactions of glycoldimercaptoacetate with metal ions qualitatively in the presence of EDTA revealed the advantages it offers as a good masking agent (Table I). A perusal of Table I reveals that the colour of Cu-EDTA remains unchanged in the acid medium on addition of GDMA *i.e.* EDTA is presumably not replaced by GDMA.

Table I
Reactions of glycol dimercaptoacetate

Ion	Remarks
Cu	Light yellow precipitate, insoluble in acidic and alkali media, so also in acidic and alkaline EDTA media. If GDMA is added to Cu-EDTA in acidic solution the blue colour is not changed. However, if the solution is alkaline, EDTA is replaced quantitatively by GDMA and the blue solution becomes colourless.
Cd	White precipitate, soluble in acid, alkali and EDTA. Cd gives no response to methyl thymol blue in the presence of GDMA. In alkaline medium, EDTA is quantitatively replaced by GDMA from a Cd-EDTA complex.
Pb	Light yellow precipitate, soluble in acid and alkali. In the presence of GDMA, Pb gives no response to methylthymol blue indicator. In alkaline medium, EDTA is quantitatively replaced from Pb-EDTA complex by GDMA.
Zn	No precipitate or colouration. With methylthymol blue indicator in the presence of GDMA, zinc gives blue-violet colouration. Zinc can be titrated quantitatively in the presence of GDMA by EDTA.
Ni	Slight turbidity, gives intense brown red colour with urotropine. EDTA has no effect on this colour which disappears on the addition of ammonia.
Co	Slight turbidity, which turns into intense, pink colouration or precipitate on adding urotropine depending upon Co concentration. The precipitate is insoluble in acid, alkali and EDTA.
Fe^{3+}	Slight turbidity which turns into green colouration on the addition of urotropine. The colour remains unaffected on the addition of NH_3 and EDTA.
Bi	Slight turbidity and on standing a white precipitate is formed. In alkaline medium, the EDTA is replaced quantitatively by GDMA from Bi-EDTA complex.

However, in a strongly ammonical solution of Cu-EDTA, EDTA is quantitatively replaced by GDMA (the solution is colourless). The liberated EDTA was titrated with calcium chloride using methylthymol blue as the indicator. The colour changes at the end point from grey to blue.

A certain amount of Cu(II) was taken. To it a known amount of excess EDTA was added. The solution was made ammonical and the excess EDTA titrated against calcium using methyl thymol blue as indicator. At the end point colour changes from grey to blue. To it a few drops of GDMA were added and the blue colour turns grey *i.e.*, EDTA of Cu-EDTA complex is replaced by GDMA. The liberated EDTA was again titrated against calcium (the

end point is indicated by a colour change from grey to blue). The amount of calcium consumed is equal to the amount of EDTA liberated and consequently to the amount of Cu(II) taken.

Similar experiments were repeated with Cd(II), Pb(II) and Bi(III) and it was possible to determine each metal ion quantitatively in the manner described above. It was observed that GDMA neither directly masked nor replaced zinc from Zn-EDTA complex in both acidic and alkaline media. Further, it was found that Cd(II) was masked directly by GDMA both at pH ~ 6 (adjusted with urotropine) and in strongly ammonical medium. This observation has been used in the determination of zinc in the presence of cadmium.

3.1 Determination of zinc and cadmium in a mixture

A certain amount of zinc- and cadmium-containing solution was taken and a few drops of GDMA was added to it to mask cadmium. A white precipitate appears, which is dissolved in minimum quantity of nitric acid and powdered urotropine is added to bring the pH to ~ 6. An intense red to pink colour develops on adding xylenol orange depending upon the amount of zinc present. This solution is titrated against EDTA till the colour at the end point sharply changes to yellow. The amount of EDTA consumed corresponds to the amount of zinc present. A second titration was carried out without GDMA and the EDTA consumed gives the amount of both zinc and cadmium present. Thus the amount of cadmium present is obtained. Using this procedure zinc was determined in the presence of varying amounts of cadmium. Representative results are given in Table II.

The new masking agent glycoldimercaptoacetate (GDMA) therefore makes the determination of zinc in the presence of cadmium very simple. Zinc has been determined accurately in the presence of large amounts of cadmium.

4. Discussion

It is in general necessary to separate cadmium and zinc for their complexometric determination in a mixture, as these have almost identical stability ($\log K_{Cdy} = 16.46$, $\log K_{Zny} = 16.50$).

Table II
Determination of zinc and cadmium

Taken, mg		
Zn	Cd	Remarks
3.27	5.62	The amounts
3.27	11.24	of Zn and Cd
3.27	16.86	found are
3.27	22.48	exactly the
3.27	28.10	same as taken

For complexometric determination of zinc in the presence of cadmium, Kinnunen and Wennerstrand[7] eliminated cadmium by precipitation with thiourea, whereas Pribil[8] used diethyldithiocarbonate for the precipitation. In an another method Pribil and Vesely[9] reported the elimination of cadmium as $Cd(phen)_2I_2$ which has the advantage that no adsorption of zinc occurs. However, there is only one method[6] known wherein zinc and cadmium are determined complexometrically without prior separation of cadmium. In this method, β-mercaptopropionic acid (MPA) is employed to mask cadmium and zinc is titrated with triethylene tetramine hexa-acetic acid (TTHA) using xylenol orange as indicator. To this solution is then added a known excess of 1,2-diamino cyclohexane-N,N,N',N'-tetraacetic acid (DCTA) which forms Cd-DCTA complex by quantitatively replacing MPA from the Cd-MPA complex. The excess of DCTA is titrated with zinc nitrate. This method suffers from the disadvantage of the need to use two complexones (TTHA and DCTA) which are expensive as compared to EDTA. The proposed new masking agent, GDMA, is superior to the existing one since here only one inexpensive complexone *i.e.* EDTA is used. Further, the proposed method is very accurate, more simple and less time consuming as compared to the existing one.

References

1. FLASCHKA, H. AND HUDITZ, F. — *Z. Analyt. Chem.* 1952, **137**, 104.
2. FLASCHKA, H. AND AMIN, A.M. — *Mikrochim. Acta*, 1953, 414.
3. PRIBIL, R. — *Coll. Czech. Chem. Comm.*, 1954, **19**, 58,64,465.
4. PRIBIL, R. AND ROUBAL, Z. — *Coll. Czech. Chem. Comm.*, 1954, **19**, 1162.
5. PRIBIL, R. AND VESELY, V. — *Talanta*, 1961, **8**, 880.
6. PRIBIL, R. VESELY, V. — *Talanta*, 1965, **12**, 475.
7. KINNUNEN, J. AND WENNERSTRAND, B. — *Chemist Analyst*, 1954, **43**, 34.
8. PRIBIL, R. — *Chem. Listy*, 1953, **47**, 1173; *Coll. Czech. Chem. Comm.* 1953, **18**, 783.
9. PRIBIL, R. AND VESELY, V. — *Talanta*, 1964, **11**, 1613.