Note

Radiometric Determination of Manganese by Metal Exchange of Zn(II)-EDTA in the Presence of PAN†

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A radiometric method for the determination of manganese, based on the exchange reaction between ^{65}Zn -EDTA and Mn in the presence of PAN has been developed. The Zn-PAN complex formed due to exchange, was proportional to Mn content. When the complex was extracted into chloroform from ammonia-ammonium chloride buffers, at pH 8.5, 4–50 μg Mn could be determined. Effect of diverse ions on the exchange has also been studied.

Key Words: manganese, radiometric analysis, metal exchange, zinc ethylenediaminetetracetate, 1-(2-pyridylazo)2-naphthol

1. Introduction

The present investigation is based on the exchange reaction of the type involving metals, a chelon such as EDTA and an additional ligand.

Where M and N are metal ions, Y the anion of the chelon and L an additional ligand.

Such reactions have been utilised for the calorimetric and extraction photometric determinations employing chelon such as EDTA, EGTA and PAN, (1-(2-pyridylazo)2-naphthol) as a chromogenic agent. The advantage being that metals which do not either react with PAN or form coloured complexes could also be determined.

Nakagawa and Tanaka^{3,4} have treated mathematically the exchange equilibrium of the type represented in Eq. (1) and extended the considerations to the establishment of conditions favourable to the indirect determination of the

metal M via solvent extraction of the species NL_n , N being added initially as its complex with a chelon, Y, L is here the chromogenic agent and extractant. Few calorimetric determinations have been reported for aluminium⁵ and calcium⁶. Radiometric method for the following exchange and subsequent determination is expected to make the procedure simpler and better sensitivity should be possible. However, no attempt has been reported which employed labelled N^*Y .

The present work is designed to develop a method for the determination of manganese using the exchange reaction.

The $\text{Zn}^*(\text{II})\text{-PAN}$ formed in the reaction can be extracted into chloroform. The activity of the extract should be proportional to the amount of manganese present.

2. Solutions and Reagents

(1) $\text{Zn}^*(\text{II})\text{-EDTA}$: 3.06×10^{-4} M solution of labelled zinc sulphate was adjusted to pH 8.5 and stoichiometric amount of EDTA was added.

(2) Manganese stock solution (1 mg/ml) was

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prepared by dissolving a suitable amount of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (BDH Analar), in double distilled water.

(3) 7.6×10^{-3} M solution of PAN (Renal) was prepared in methanol.

(4) $\text{NH}_4\text{Cl} - \text{NH}_4\text{OH}$ buffers were prepared in the pH range 8–10, using 1 M solutions.

(5) ^{65}Zn tracer solution was obtained from the Isotopes group, B.A.R.C., Bombay, India with a specific activity 18.5 GBq/g (0.5 Ci/g) Zn.

3. Development of the Method

3.1 Selection of pH

The 2.5 ml of $\text{Zn}^*\text{-EDTA}$ solution was taken in a series of tubes. One ml of PAN and 100 μg of Mn(II) were added. The pH was adjusted in the range 8–10 and the $\text{Zn}^*\text{-PAN}$ formed in each case was extracted into 2 ml of chloroform by equilibrating the phases for 2 minutes. The activity of 1 ml of the extract was measured using a scintillation counter with a well type NaI(Tl) detector.

3.2 Calibration

A set of $\text{Zn}^*\text{-EDTA}$ solutions were treated with 1 ml PAN and increasing amount of Mn(II) in the range 4–40 μg and then extracted as earlier. The activities of the extracts were corrected for blank value were plotted against the amount of manganese added to obtain calibration (Fig. 1).

4. Results and Discussion

The progress of the reaction (2) forward is

Fig. 1 Calibration plot.

Table 1 Determination of manganese

Amount of Mn taken (μg)	Amount of Mn found (μg)	Error (%)
5.12	5.14	+1.00
10.28	10.36	+0.80
15.08	15.00	-0.50
25.10	25.01	-0.40
50.25	49.50	-1.49

due to the high stability of Zn(II)-PAN complex. Similarly, the metal ion with higher stability constant with EDTA, compared to zinc is expected to shift the equilibrium far to the right and hence, can be more easily determined. It is only with these considerations the formation of Mn(II)-EDTA from Zn(II)-EDTA in the exchange equilibrium can be explained. Further, the concentration of PAN is another factor which sets the working pH limits for the determination. The selectivity of the determination will be dependent on the relative stability of the metal chelon complex, the complex of the metal with the auxillary chelating agent and those of the metal to be determined.

Zn-EDTA was found to be stable in both acidic and alkaline media⁹. However, it was stable in presence of PAN over the pH range 8 to 9 in ammonia-ammonium chloride buffers. At higher pH values the blank values were higher. Further, Mn(II) could replace zinc quantitatively in the above pH range and Zn-PAN formed could be conveniently extracted into chloroform under the same conditions.

A linear calibration (Fig. 1) was achieved in the range of 4–50 μg of Mn(II) . Few representative determinations were made in the above range (Table 1) and the precision of the method was better than 1%.

5. Interferences

Interference studies were made using 40 μg of Mn(II) which has sufficient for $\sim 50\%$ of zinc release, and 80 μg of each of the individual interfering ion.

Ag(I) , Ba(II) , Ca(II) did not interfere with the determinations as expected from the lower stability constants of their EDTA complexes,

as compared to Co(II), Cd(II), Co(II), Pb(II) interfered in the determination because of their higher stability constants of their EDTA complexes, as compared to Mn(II).

However, Cu(II), Hg(II) did not interfere, probably because of the higher stability of their PAN complexes.

In the presence of Mg(II), Bi(III), Ti(III) and Sb(III) zinc could not be displaced, due to which the determination was not possible. The phenomenon is beyond explanation in terms of the stability considerations as before.

Most of the common anions did not interfere. Phosphate, tartrate, oxalate and thiosulphate did not interfere hence can be used as masking

agents. However citrate interfered.

References

- 1) Nakagawa, G. and Tanaka, M.: *Talanta*, **9**, 917 (1962)
- 2) Nakagawa, G., Namiki, I. and Tanaka, M.: *ibid.*, **13**, 1135 (1966)
- 3) Vishnu and Srivastava, V.K.: *Current Sci.*, **31**, 330 (1962)
- 4) Inczedy, J., Nemeshegyi, G. and Erdey, L.: *Acta Chim. Hung.*, **43**, 1 (1965)
- 5) Vogel, A.I.: "A Text Book of Quantitative Inorganic Analysis" 3rd Ed., p. 418, Longmans Green and Co. Ltd., London (1969)