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The Interaction between Oxalic Acid and Divalent Ions—Mg^{2+}, Zn^{2+} and Ca^{2+}—in Aqueous Medium

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ABSTRACT

The reactions of oxalic acid with Mg^{2+}, Ca^{2+} *and* Zn^{2+} *in aqueous medium were investigated. When 0·01*M *oxalic acid solutions spiked with various levels of* Zn^{2+} *were titrated against standard* $KMnO_4$ *solutions, a linear relationship was obtained between the amount of precipitated oxalate and the metal ion concentrations. A similar observation was made for* Ca^{2+}*, but higher proportions of the oxalate were precipitated at equivalent metal ion concentrations. The relationships were also confirmed by titrating standard metal ion solutions, spiked with various levels of oxalic acid, against standard EDTA solutions. When* Mg^{2+} *was present in solution with* Zn^{2+} *or* Ca^{2+} *or with the mixture, it inhibited the precipitation of the oxalates. The inhibitory action was most noticeable when the metal ions were present in solution in a 1:1:1 molar ratio. In all cases, the higher the proportion of* Mg^{2+}*, the less the precipitation of the oxalates of the other two metals.*

INTRODUCTION

Both calcium and magnesium, among other minerals, have been described as nutritionally essential to man (Harper *et al.*, 1977). In the same way, the nutritional importance of zinc has been well reviewed (Halsted *et al.*, 1974). These three minerals have been shown to be commonly found in foodstuffs, but their availability after the ingestion of the foods, has been found to be dependent on their solubilities at the points of contact with the absorbing membranes (Adolph & Liang, 1942). Investigation carried out by a number of workers (Tisdalf & Drake, 1938; Kohman, 1939; Spiers, 1939) showed

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that noticeable proportions of the metals were nutritionally unavailable. This was attributed to the formation of insoluble salts, which could be oxalates (Pierce & Appleman, 1943; Lovelace *et al.*, 1950) or phytates (Kohman, 1945), or both. This fact is, however, of great concern to nutritionists because it has also been found that foods rich in oxalate, such as rhubarb, will protect teeth against acid erosion from cola beverages and lemon juice (Pierce & Appleman, 1943). It is therefore necessary to properly investigate the reactions between these metals and the acid, as has been done for phytic acid (Cream & Haisman, 1963). In the present work, the reactions between the metals and oxalic acid in aqueous medium are examined.

MATERIALS AND METHODS

The experiment was carried out in two parts. In the first part, standard solutions of oxalic acid, containing various levels of each of the metal ions or of the mixture, were prepared. Each solution was well shaken and left to stand for about 30 min before filtering through a Whatman No. 1 paper. Portions of the filtrate (25 cm^3) were pipetted into a 250 cm^3 conical flask and 20 cm^3 of MH_2SO_4 added. The flask and content were heated to about 70°C and the excess oxalic acid titrated with a standard potassium permanganate solution.

In the second part, standard solutions of each metal ion or mixtures of the metal ions, containing various levels of oxalic acid, were prepared. These were shaken well and left to stand for about 30 min before filtration; 25 cm^3 of the filtrate were pipetted into a 250 cm^3 conical flask and 20 cm^3 of ammonia buffer (pH 10) added. The excess metal ion/ions was then titrated against standard EDTA solution using solochrome black T as indicator.

RESULTS AND DISCUSSIONS

Reactions between oxalic acid and the metal ions

Oxalic acid solutions (0·01M) were spiked with various concentrations of each of the metal ions and then titrated against 0·004M potassium permanganate; the results obtained are shown in Fig. 1(a).

A linear relationship was obtained between the amount of soluble oxalate removed and the amount of Ca^{2+} or Zn^{2+} added. Above 0·002M metal ion, however, the proportions of soluble oxalate removed became increasingly greater for Ca^{2+} than for Zn^{2+}, at equal metal ion concentrations. At

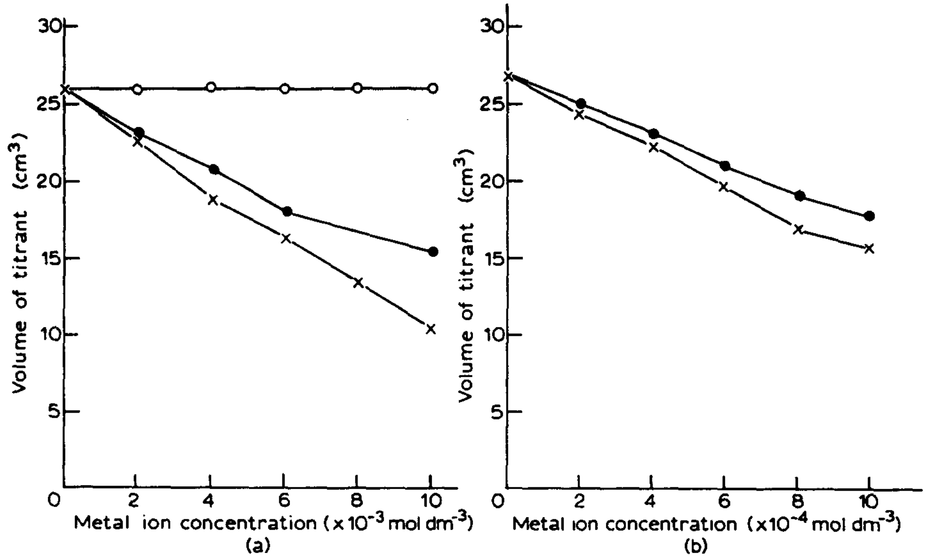

Fig. 1. Titre values obtained for the titrations between standard potassium permanganate solution and oxalic acid solutions spiked with varying concentrations of metal ions. (a) 4×10^{-3}M $KMnO_4$ versus 0·01M $(COOH)_2$. (b) 4×10^{-4}M $KMnO_4$ versus 0·001M $(COOH)_2$. ×, Ca^{2+}; ●, Zn^{2+}; ○, Mg^{2+}.

0·006M level, 36·9 and 30·8% of the total soluble oxalate had been removed by Ca^{2+} and Zn^{2+}, respectively. These proportions increased to 60·4 and 41·2%, respectively, at the 0·01M level. When these were repeated with more dilute solutions, a linear relationship still existed but, as shown in Fig. 1(b), the curves had smaller slopes. This meant that, at equivalent levels, smaller portions of the soluble oxalate were removed from solution. If these results are compared with those in Table 1, it can be seen that the variations could not have been due to lack of precision in the determinations. As shown in Table 1, a set of five readings had a standard deviation of 0·17 and the mean titre was not significantly different from the expected 25 cm^3.

It is also worth noting that, for the 0·001M oxalate solution, only 24·8 and 22·2% were removed at 0·006M levels of Ca^{2+} and Zn^{2+}, respectively. This fact tends to show that the proportion of soluble oxalate converted into insoluble oxalates by the metal ions depended on the ionic strength of the solution. This result is similar to what was observed for the reaction between phytic acid and calcium in aqueous medium (Cream & Haisman, 1963).

It was, however, found that addition of Mg^{2+} ions did not decrease the soluble oxalate even when present in solution in the mole ratio, [oxalate]:[Mg^{2+}], of 1:10. This is not surprising as it has previously been shown that magnesium oxalate easily forms a supersaturated solution (Pierce & Appleman, 1943) and this might be responsible for the non-reduction of the soluble oxalate on addition of Mg^{2+} ions.

TABLE 1
Titres obtained for the Titration between Various Oxalic Acid Solutions and Potassium Permanganate Solutions

Concentration of oxalic acid	*Concentration of permanganate*	$\frac{[KMnO_4]}{[H_2C_2O_4]}$	*Volume of* $KMnO_4$ *used* (cm^3)
0·10M	0·040M	2/5	25·20
0·08M	0·032M	2/5	25·00
0·06M	0·024M	2/5	25·10
0·04M	0·016M	2/5	25·00
0·02M	0·008M	2/5	25·40
		Mean	25·14
		Standard Deviation	0·17

Volume of oxalic acid solution used in each case = 25 cm^3.

These observations were also confirmed when metal ion concentrations were kept constant and the amounts of oxalic acid added varied. From the results shown in Fig. 2, no change was observed in the level of Mg^{2+} ions in solution even at the 0·010M oxalic acid level. For both Zn^{2+} and Ca^{2+}, however, there were gradual reductions in the metal ion concentrations as the oxalic acid level was being increased. At the 0·01M oxalic acid level, 81·2

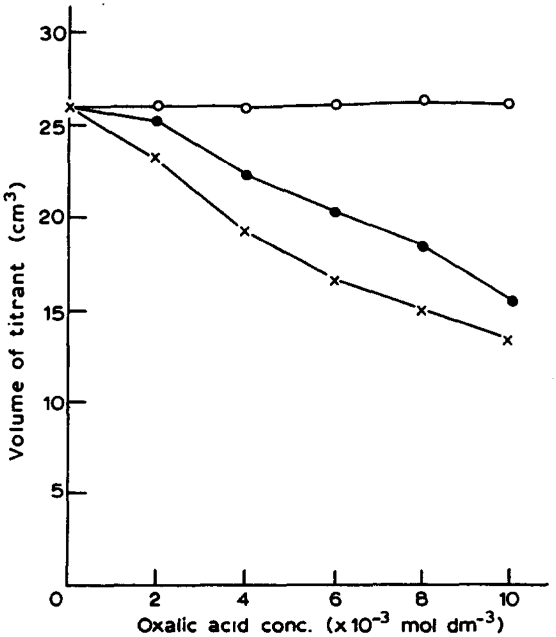

Fig. 2. Titre values for titrations between 0·01M EDTA and 0·01M metal ion solutions spiked with varying concentrations of oxalic acid. ×, Ca^{2+}; ●, Zn^{2+}; ○, Mg^{2+}.

and 68·3% of the original Ca^{2+} ion and Zn^{2+} ion in solution had been respectively precipitated. However, when solutions of lower concentrations were used, lower proportions of the metal ions were precipitated.

Interaction between oxalic acid and the mixtures of metal ions in solution

Mg^{2+}/Ca^{2+} mixture

Despite the fact that, of the three metal ions, Ca^{2+} ions gave the largest precipitate with oxalic acid, when present in the same solution with Mg^{2+}, the proportion precipitated varied with ratios of the molar concentrations of both metal ions in solution (Fig. 3). At the 0·01M oxalic acid level, i.e. 1:1:1 ([oxalate]:[Mg^{2+}]:[Ca^{2+}]) mole ratio, only 25·9% of the total initial metal

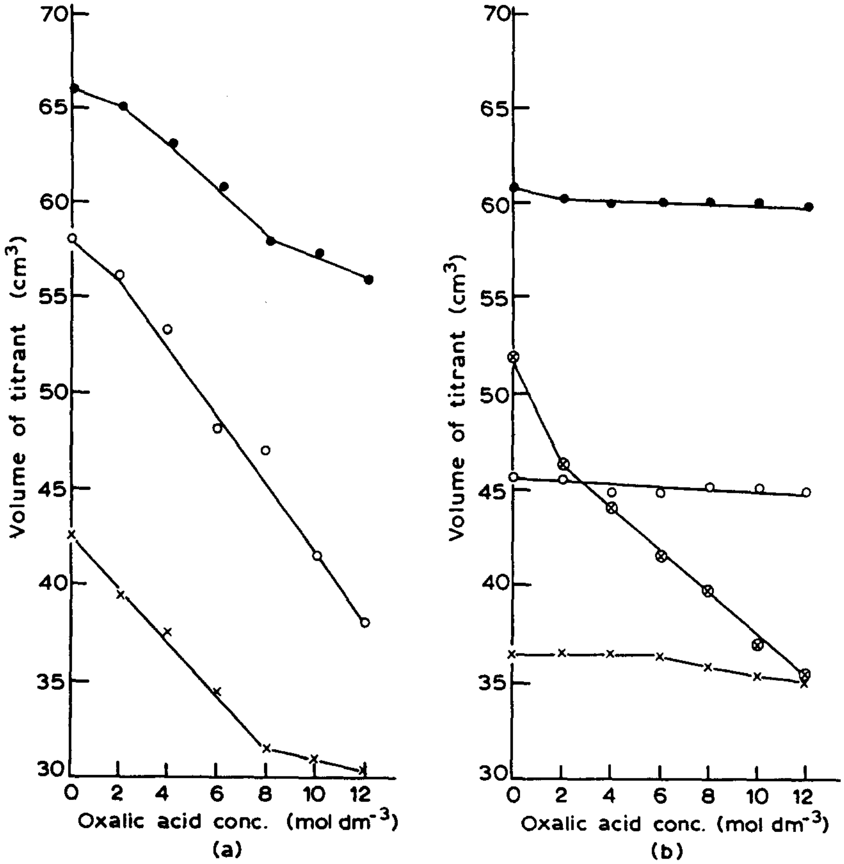

Fig. 3. Titres obtained for the titrations between 0·01M EDTA solution and solutions of mixtures of metal ions, spiked with various concentrations of oxalic acid. (a) ×, 0·01M in Mg^{2+}/0·01M in Ca^{2+}; ○, 0·01M in Mg^{2+}/0·02M in Ca^{2+}; ●, 0·02M in Mg^{2+}/0·01M in Ca^{2+}. (b) ×, 0·01M in Zn^{2+}/0·01M in Mg^{2+}; ○, 0·02M in Zn^{2+}/0·01M in Mg^{2+}; ●, 0·01M in Zn^{2+}/0·02M in Mg^{2+}; ⊗, 0·01M in Zn^{2+}/0·01M in Ca^{2+}.

ion concentration had been precipitated. This was rather low when compared with the expected value (40·6%) because, at the same level of oxalic acid, 81·2% was precipitated when only Ca^{2+} ions were present in solution. When the metal ions were present in the molar ratio 2:1 ($[Mg^{2+}]$:$[Ca^{2+}]$), the proportion precipitated (13·1%) at the 0·01M oxalic acid level was also quite low compared with the expected value of about 27%. At 1:2 ($[Mg^{2+}]$:$[Ca^{2+}]$) molar ratio, however, the proportion precipitated (28·5%) was comparable with the expected. Because Ca^{2+} was in excess, it seemed to have overshadowed the inhibiting effect of magnesium.

Mg^{2+}/Zn^{2+} *mixture*

As shown in Fig. 3, the presence of Mg^{2+} with Zn^{2+} in solution, seems to have repressed the precipitation of the metal ions by oxalid acid. At the 0·01M oxalic acid level, and with the metal ions present in the mole ratios 1:1, 1:2 and 2:1 ($[Mg^{2+}]$:$[Zn^{2+}]$), the proportion precipitated (0·03, 0·03 and 0·01%, respectively) were very low when compared with those expected (34·1, 22·7 and 22·7%, respectively). With these results, it could be said that the inhibitory action of Mg^{2+} was more pronounced with the precipitation of zinc oxalate than with that of calcium oxalate.

Zn^{2+}/Ca^{2+} *mixture*

With Zn^{2+} and Ca^{2+} in the same solution, there was a gradual increase in the proportion of metal ions removed from solution, as the oxalic acid content of the solution was gradually increased. It was noticeable, however, that at the 0·01M oxalic acid level (Fig. 3) only 28·0% of the metal ions had been precipitated as opposed to about 37·8% as expected. This might be due to the presence of Zn^{2+} in solution as it appeared to form precipitates with oxalic acid less readily than Ca^{2+}.

$Mg^{2+}/Zn^{2+}/Ca^{2+}$ *mixture*

When 0·01M oxalic acid solutions, spiked with different levels of the mixtures of Mg^{2+}, Zn^{2+} and Ca^{2+}, were titrated against standard potassium permanganate solutions, the results shown in Fig. 4 were obtained. When the metal ions were present at the 1:1:1 mole ratio, the decrease in soluble oxalate, as the concentrations of the metal ions were gradually increased, was very gradual. At the 0·01M level, only 19·2% decrease in the soluble oxalate had been achieved. This is surprising in that both Zn^{2+} and Ca^{2+} showed rather large decreases in the soluble oxalate between the 0 and 0·01M levels. Within the same concentration range, however, no noticeable changes were obtained for Mg^{2+} alone. This probably means that Mg^{2+} ions must be interfering with the interaction of both Zn^{2+} and Ca^{2+} with the oxalate ion. When the experiment was repeated by doubling the proportion of each

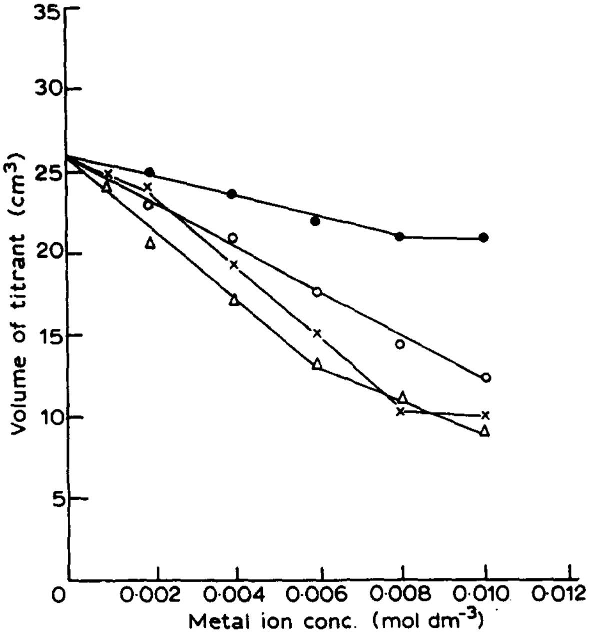

Fig. 4. Titres obtained for 0·004M $KMnO_4$ solution titrated against 0·01M oxalic acid spiked with mixtures of Mg, Zn and Ca ions in varying molar ratios. Mole ratio $[Mg^{2+}]$:$[Zn^{2+}]$:$[Ca^{2+}]$: ●, 1:1:1; ×, 1:2:1; ○, 2:1:1; △, 1:1:2.

metal ion, in turn, the results (Fig. 4) showed that the loss in the soluble oxalate increased steadily as the metal ion concentrations increased from the 0·001 to 0·01M. These decreases were more pronounced than those obtained with oxalic acid solutions containing single metal ions. It is worth noting that when the metal ions were present in solution in a 2:1:1 ($[Mg^{2+}]$:$[Zn^{2+}]$:$[Ca^{2+}]$) mole ratio, a gradual decrease in soluble oxalate was still observed despite the fact that Mg^{2+} alone had no apparent effect on the soluble oxalate. The decreases were, however, still less pronounced than those observed when either Zn^{2+} or Ca^{2+} was doubled in the mixture.

When the experiment was repeated by spiking solutions of metal ion mixtures with different levels of oxalic acid, the results in Fig. 5 were obtained. When the metal ions, Mg^{2+}, Zn^{2+} and Ca^{2+} were present in the same solution in a 1:1:1 molar ratio not much precipitation was achieved as the oxalic acid level in the solution was increased from 0·0 to 0·01M. At the 0·01M oxalic acid concentration, only 6·9% of the total metal ion concentration was precipitated. When compared with the 27·9% precipitation at the same oxalate level, with only Zn^{2+} and Ca^{2+} present at the 1:1 molar ratio, this could be considered a great reduction in the interaction of the metal ions with the oxalate. Also at a molar ratio of 2:1:1 ($[Mg^{2+}]$:$[Zn^{2+}]$:$[Ca^{2+}]$), there was little or no improvement in the

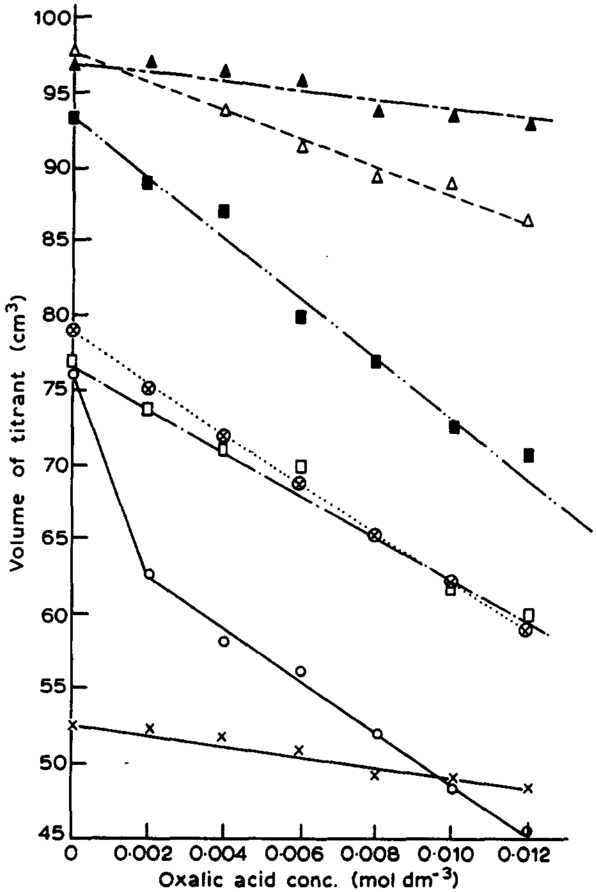

Fig. 5. Titres obtained for 0·01M EDTA titrated against solution of mixtures of Mg^{2+} with Zn^{2+} and Ca^{2+} and also Na^{2+} with Zn^{2+} and Ca^{2+}, spiked with various concentrations of oxalic acid. Mole ratio $[Mg^{2+}]$:$[Zn^{2+}]$:$[Ca^{2+}]$: ×, 1:1:1; △, 2:1:1; □, 1:2:1; ⊗, 1:1:2; ■, 1:2:2; ▲, 2:2:1. Mole ratio $[Na^{2+}]$:$[Zn^{2+}]$:$[Ca^{2+}]$: ○, 1:1:1.

proportion of the metal ions precipitated (8·0%) at this same oxalate level. At 1:2:1 and 1:1:2 molar ratios, however, 16·1 and 21·0% were respectively precipitated at the 0·01M oxalate level. When the proportions of Zn^{2+} and Ca^{2+} in solution doubled that of Mg^{2+} (i.e. 1:2:2), as much as 22·0% of the total metal ion concentration was precipitated at the 0·01M oxalic acid level. On the other hand, when the proportion of Mg^{2+} and Zn^{2+} doubled that of Ca^{2+}, only 3·0% was precipitated at that same oxalic acid level. From these observations, the presence of Mg^{2+} ions in solution had an effect on the precipitation of the oxalates of both Zn^{2+} and Ca^{2+}. This observation was further checked by replacing the Mg^{2+} in solution with Na^{+} ions. At the 0·01M oxalic acid level, 36·2% precipitation was achieved. This showed that the inhibitory action was peculiar to Mg^{2+} ions. This finding corroborated earlier observations by Bothor *et al.* (1982), Lanteva *et al.* (1976) and

Nancollas *et al.* (1978), that Mg^{2+} had an inhibitory action on formation of some precipitates.

CONCLUSIONS

The presence of Mg^{2+} in solution inhibited the precipitation of calcium and zinc oxalates. This effect was more pronounced with zinc than with calcium. This inhibitory property was very noticeable when the metal ions were present in the same solutions at about equimolar proportions. In all cases, the higher the proportion of Mg^{2+} in solution, the less was the precipitation of the oxalates of the other two metals.

The fact that Mg has such an effect on the precipitation of both calcium and zinc oxalates is significant for the nutritionist because the availability of Ca and Zn in leafy vegetables high in oxalate content and which normally have high Mg levels (Pierce & Appleman, 1943), could actually be higher than anticipated.

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