

## Use of Dowex-50 to Separate Interfering Ions in the Determination of Magnesium in Soil Extracts by Titan Yellow

S. K. TOBIA and N. E. MILAD

Faculty of Science, Ein-Shams University, Abbassia, Cairo, Egypt

A simple and rapid separation of magnesium from interfering ions has been attained by using a single column of the cation exchanger, Dowex-50, in the potassium form. The anions, iron, aluminum, and most of the manganese are first separated by treating the solution with 5% ammonium citrate at pH 7 and passing it through the column. Magnesium is then separated from calcium by chromatographic elution with 0.025M citrate solution at pH 7.5. A modified method for the direct determination of magnesium by Titan yellow in the eluates is described.

THE PRINCIPAL IONS usually found in soil extracts and which may interfere with the determination of magnesium by Titan yellow are:  $\text{Ca}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Al}^{+++}$ ,  $(\text{NH}_4)^+$ ,  $\text{Cl}^-$ ,  $(\text{SO}_4)^{--}$ , and  $(\text{PO}_4)^{---}$ . Methods of dealing with these ions involve addition of compensating solutions (4, 7, 8), addition of complex formers (7, 5), or separation by precipitation (6). In all these methods, the limit of the useful range is about 5 p.p.m., above which the curve approaches horizontally with the concentration axis. By adjusting the concentrations of Titan yellow, sodium hydroxide, gelatin, and hydroxylamine hydrochloride, as well as the temperature and time of matching, the authors were able to increase the range up to 10 p.p.m. of magnesium.

The procedure adopted was based on the following final concentrations: gelatin 0.02%, sodium hydroxide 0.06N, Titan yellow 0.006%, and hydroxylamine hydrochloride 0.1%. The lake was formed at 20° C. and the extinction was measured 5 minutes after mixing. Under these conditions, the effect of  $\text{Ca}^{++}$ ,  $\text{Al}^{+++}$ , and  $(\text{PO}_4)^{---}$  did not become constant at any concentration and their interference could not be eliminated by the addition of compensating solutions.

In case of manganese, the upper limit permissible without interference was found to be 0.5 p.p.m. of the final solution. Moreover, complexing substances such as tartrate, hydrazine sulfate, or mannitol did not prevent the interference of manganese, iron, or aluminum, respectively. The latter metals were removed by precipitation as hydroxides, and calcium as oxalate. The procedure was tedious and time-consuming, but the experimental error did not exceed  $\pm 3\%$ . Separation of the interfering ions through the application of synthetic cation exchange

resins was believed to be more convenient and a possible solution to the problem.

In general, the separation of inorganic cations by ion exchange resins, involves the adsorption of these cations on the top portion of a resin bed and elution by a suitable complexing agent. The degree of separation for a given experimental arrangement depends on variables such as size of the resin particles, dimensions of the column, concentration and pH of the eluting agent, temperature, and flow rate. For example, Tompkins, Khym, and Cohn (11) separated strontium from barium by using an Amberlite IR-1 column, 1 sq. cm.  $\times$  100 cm., and eluting with 5% ammonium citrate at pH 5. Separation of milligram amounts of strontium, barium, and radium by a column of Dowex-50, 1 sq. cm.  $\times$  15 cm., and elution with 0.5M citrate solution at pH 7.5 to 8 have been reported by Tompkins (10). The present work has been undertaken to investigate the possibility of using Dowex-50 for the complete recovery of magnesium from soil extracts in the highest possible state of purity and in a reasonable operating time.

### Materials and Apparatus

**Resin.** Cross-linked Dowex-50 cation exchange resin of 100- to 200-mesh size was used. The resin was washed in turn with distilled water, 6N hydrochloric acid, and distilled water again until free from chloride. Finally, the resin was converted to the potassium form with 1M potassium chloride and stored in distilled water until loaded on the column.

**Eluting Solutions.** These were prepared from analytical reagent grade ammonium citrate and the pH adjusted with 1 to 2 ammonium hydroxide and measured on a pH meter.

**Column.** A borosilicate glass tube 0.3 sq. cm.  $\times$  50 cm. was used. Its lower end was drawn out into a narrow tube about 2 mm. in diameter, and a pad of glass wool was inserted to support the resin bed. The reservoir containing the effluent solution consisted of a cylindrical funnel 3 cm. wide and 20 cm. long, with a narrow stem to fit into the tube by a thin rubber collar. With a 10-cm. resin bed, the "gravity feed" of the eluting solution gave a flow rate of approximately 3.5 ml. per sq. cm. per minute.

The solution containing the different ions was a synthetic mixture to simulate a soil solution. The concentrations of the different ions, in parts per million, were as follows:

Ca	500	N(NH <sub>4</sub> )	5	Fe	3
Mg	50	N(NO <sub>3</sub> )	50	PO <sub>4</sub>	3
Na	90	Mn	10	SO <sub>4</sub>	300
K	50	Al	5	Cl	900

**Procedure.** Two milliliters of the test solution were treated with 1 ml. of 5% ammonium citrate solution at pH 7 and then passed through the resin bed. The effluent solution containing the anions together with iron, aluminum, and manganese, as complex citrate anions, was discarded. The resin was then washed with two 5-ml. portions of distilled water to remove any remaining anions. Magnesium and calcium were separated by complex elution using 0.025M ammonium citrate solution at pH 7.5. The elution was carried out at a rate of 3.5 ml. per sq. cm. per minute and samples of the eluent were collected. The resin was reconditioned between runs by passing suitable quantities of 1M potassium chloride solution through the column.

For the determination of magnesium by Titan yellow, in the presence of citrate, the following procedure was satisfactory:

An aliquot of the eluate was pipetted into a 50-ml. graduated flask and diluted with water to about 30 ml. Six milliliters of 1% gelatin solution were added followed by 1 ml. of 5% hydroxylamine hydrochloride, 6 ml. of 10% sodium citrate, and 3 ml. of 0.1% Titan yellow solution. The color was developed at 30° C. by the addition of 1 ml. of 3*N* sodium hydroxide and the extinction was measured 20 minutes after mixing by a Unicam colorimeter using the 1-cm. cell and the green filter.

### Results and Discussion

Ammonium citrate was first added to the test solution in order to convert iron, aluminum, and manganese into complex citrate-anions. On passing the solution through the resin bed and washing the latter with water, the effluent was free from magnesium, but manganese, iron, aluminum, and calcium were present. Quantitative analysis of the effluent solution showed that, of the total original amounts of cations, 3% of calcium, 70% of manganese, and almost all iron and aluminum were eluted. Under the experimental conditions, the iron and aluminum citrate complexes were sufficiently stable to resist decomposition by the exchanger. On the other hand, 30% of manganese and 97% of the calcium were retained by the resin.

In trying to find the optimum operating conditions for the separation of magnesium and calcium by complex

elution, ammonium citrate was used as an eluting solution. The alkaline earths are known to form complexes with (Cit)<sup>---</sup> and (HCit)<sup>--</sup> ions; those formed with (Cit)<sup>---</sup> are more stable than those formed with (HCit)<sup>--</sup> (9). Magnesium may also form such complexes as it resembles the alkaline earths. A citrate solution at pH 7 was first used as the per cent of the (Cit)<sup>---</sup> ion at this pH was found to be 93.7 (2). Using the resin in the hydrogen form, partial separation of magnesium from calcium started to take place at a concentration of 0.025*M*. Above this concentration, cationic displacement was dominant over complex elution. The effect of varying the pH of the citrate solution at the above concentration was then studied. A gradual increase in pH from 7 to 7.5 had the effect of increasing the rate of elution of magnesium but did not improve the separation. Above pH 7.5, the rate of elution of magnesium started to decrease and at pH 8 no magnesium was eluted showing that the pH has approached its precipitation value and the tendency toward hydroxide formation has offset the extent of complex ion formation.

The incomplete separation of magnesium from calcium was thought to be due to changes in the pH of the citrate solution during elution, and that separation might be improved by using resins saturated with cations other than

hydrogen. Resins in the ammonium, sodium, and potassium forms were used. With the ammonium resin, the eluates containing the magnesium were contaminated with some calcium. The contaminated calcium increased with increasing amounts of calcium present in the original solution. With sodium and potassium resins, complete separation took place. One hundred per cent of magnesium, free from calcium, was recovered and only 93% of calcium was then eluted. The separation gap was wider with the potassium than with the sodium resin.

The poor separation of calcium and magnesium with the ammonium saturated resin could be attributed to a greater decrease in pH of the ammonium citrate buffer upon leaching through this resin compared with the potassium or sodium resins.

The difference in the behavior of the resins saturated with different cations may also be explained as being due to the differences in the affinities of the cations to the resin. Boyd, Schubert, and Adamson (3) showed that the exchanging powers of the cations depend on the radius of the hydrated ion in solution. As this radius decreases, the adsorption by the exchanger increases. Accordingly, the sequence of adsorption will be  $K^+ > NH_4^+ > Na^+$ .

When the ammonium resin is employed, the concentration of the  $NH_4^+$  ions (0.025*M*) in the eluting solution

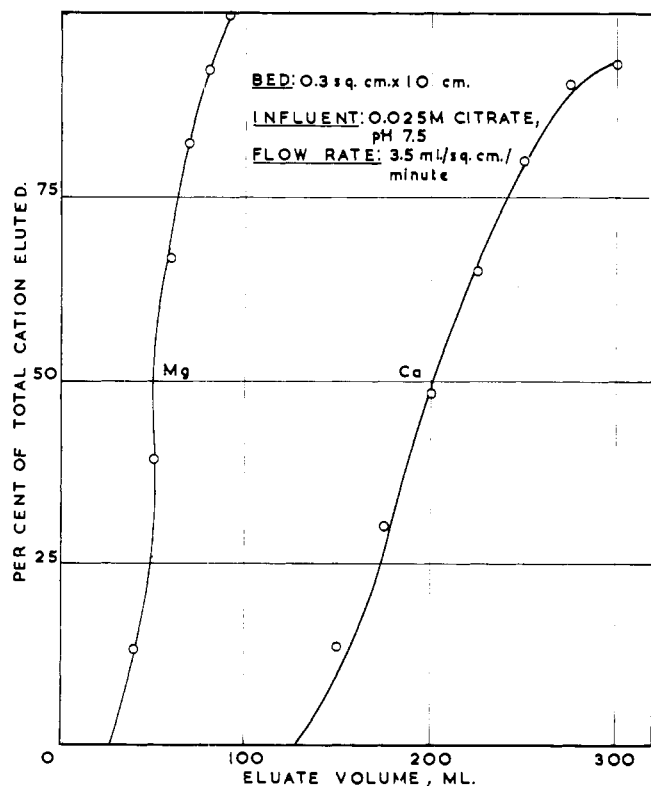


Figure 1. Separation of magnesium from calcium by Dowex-50

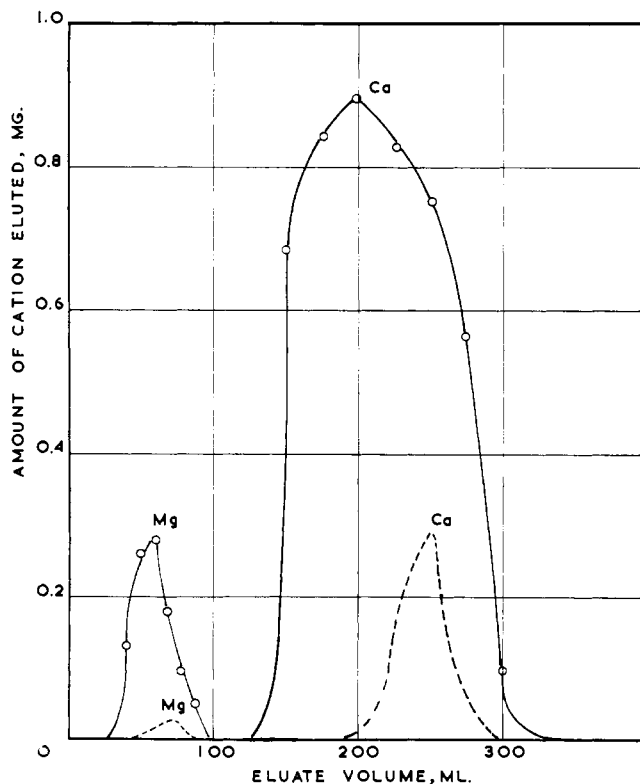


Figure 2. Elution curves for solutions containing different amounts of magnesium and calcium

Solutions contain:  
 - - - - - 0.05 mg. of Mg and 0.5 mg. of Ca  
 ——— 1.00 mg. of Mg and 5.0 mg. of Ca

will probably be high enough to displace all the magnesium, together with some calcium at the same time, thus leading to a poor separation. When the potassium resin is used, ionic exchange will take place between the  $K^+$  ions on the resin and the  $NH_4^+$  ions in the ammonium citrate buffer. The eluting solution will, therefore, contain both  $NH_4^+$  and  $K^+$  ions of total concentration of 0.025M. As  $K^+$  ions have a higher affinity for the exchanger than the  $NH_4^+$  ions, the former will be preferentially adsorbed and will be responsible for the displacement of  $Mg^{++}$  and  $Ca^{++}$  ions on the resin. The concentration of these  $K^+$  ions being less than 0.025M will be just enough to allow for separation by complex elution. Similarly, in the case of the sodium resin,  $NH_4^+$  ions of a concentration less than 0.025M will be responsible for the separation of magnesium from calcium.

To explain why the separation gap is wider with the potassium than with the sodium resin, the concentration of the  $K^+$  ions in the eluting solution passing through the potassium resin must be assumed to be less than that of the  $NH_4^+$  ions present in the eluting solution passing through the sodium resin.

From the above, the effectiveness of separation seems to depend mainly on the concentration of the displacing ion. The smaller the concentration, the better will be the separation. This may explain why the separation gap is wider with the potassium than with the sodium resin.

The manganese remaining on the column was completely eluted with the magnesium but its concentration in the eluates was too small to interfere with the magnesium determination.

To determine the per cent of total cation eluted as a function of eluate volume, a solution containing 1 mg. of magnesium and 5 mg. of calcium was used. Magnesium was determined in the eluates by Titan yellow, as described before, while calcium was determined by the Unicam flame photometer. Results are shown in Figure 1.

In order to determine the effect of variations in the relative concentrations of magnesium and calcium on the efficiency of separation, a series of runs was made using solutions containing known amounts of magnesium ranging from 0.1 to 1 mg. and calcium from 0.5 to 5 mg. The magnesium-calcium ratio was also varied between the limits 1/50 to 2. In all cases, magnesium was eluted completely in about a 100-ml. volume, beginning approximately at 30 ml., and complete separation from calcium took place. However, the separation gap became gradually smaller with increasing amounts of calcium. For example, the gap with 0.5 mg. of calcium was about four times wider than that with 5 mg. of calcium as shown in Figure 2.

When the method was applied to soil extracts, it was necessary to bring the pH of the solution just above 7 by dilute potassium hydroxide solution before the addition of the ammonium citrate. On passing the solution through

the resin, it was observed that the colloidal organic matter in the soil extracts was not retained by the resin to any appreciable extent and passed almost completely in the effluent. The eluates containing the magnesium were clear and practically free from organic matter, thus allowing for the direct determination of magnesium by Titan yellow.

By assembling a number of columns, magnesium was determined in the acid extracts of some soils in a relatively short time and with a high degree of accuracy. The accuracy of determination was tested by the addition of calculated amounts of magnesium to the soil extracts and determination of the recovered magnesium. Results are shown in Table I. The recovery of the added magnesium was almost complete and the maximum error did not exceed 0.5%.

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Table I. Magnesium in Soil Extracts

(P.p.m. of solution)<sup>a</sup>

Soil No.	Magnesium	Add 100 P.P.M. Mg		Error, %
		Calcd.	Obs.	
1	162	262	263	+0.38
2	87	187	187	0
3	112	212	213	+0.47
4	142	242	242	0
5	300	400	402	+0.5

<sup>a</sup> Extraction was carried out by a sodium acetate-acetic acid buffer at pH 4.5.

## PESTICIDE TOXICITY

### Biological Activity of Several O,O-Dialkyl Alpha-Acyloxyethyl Phosphonates

INCREASING EMPHASIS is being placed on the development of insecticides of low mammalian toxicity. This selectivity requirement has been met with the organophosphate insecticides malathion,

<sup>1</sup> Present address, Department of Entomology, Alabama Polytechnic Institute, Auburn, Ala.

S - [1,2 - bis(ethoxycarbonyl)ethyl]O,O-dimethyl phosphorodithioate (18); Chlorthion, O-(3-chloro-4-nitrophenyl)-O,O-dimethyl phosphorothioate (13, 23); Trolene, O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate (17); and Dipterex, O,O-dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate (12).

B. W. ARTHUR<sup>1</sup> and J. E. CASIDA

Department of Entomology, University of Wisconsin, Madison, Wis.

Dipterex with its phosphonate bond differs in structure from most other phosphorus insecticides with phosphate, phosphorothiolate, and phosphorothioate groupings.

The low mammalian toxicity of Dipterex may be attributed to several factors: The lability of the cholines-