

The determination of magnesium with titan yellow; masking interferences with phosphates

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Summary

Used with Bradfield's method of determining Mg, phosphate was found to be very effective as an agent masking heavy-metal interferences.

1. Introduction

The use of ethylene glycol bis-(β -aminoethylether)-N,N,N',N'-tetraacetic acid (EGTA) as a masking agent for the interference of Ca in the determination of Mg with titan yellow has been proposed by BRADFIELD (1961, 1962). This procedure also prevents the formation of phosphate precipitates at high phosphate levels, thus making it possible to make use of the phosphate-complexing properties in preventing interference by the heavy metals.

The necessary introduction of a fairly high phosphate level called for some modifications in Bradfield's procedure. The concentrations of EGTA and triethanolamine had to be raised, and Mn had to be introduced into the complexing solution.

To minimize the number of additions, the polyviol-titan yellow reagent solution and the compensating solution were mixed in advance. This mixture had to be renewed every other day.

The standard curve is S-shaped because the solubility product of $Mg(OH)_2$ is not reached with the low Mg concentrations. To overcome this difficulty of the curve, some Mg has to be included in the compensating solution, taking into account the Mg contamination in the alkali.

2. Reagents

- a. *Compensating solution*: dissolve 10 g of ethylene glycol bis-(β -aminoethylether)-N,N,N',N'-tetraacetic acid (EGTA manufactured by Fluka AG; Bucks SG; Switzerland) in the minimum volume of KOH 6 N (about 11 ml) and neutralize to pH 7 (indicator paper) with HCl 1 N. Then add 20 ml of triethanolamine, 0.0813 g of $MnSO_4 \cdot 4 aq$ and 0.0894 g of $AlCl_3 \cdot 6 aq$ (both dissolved in advance in a small quantity of distilled water) and 10 ml of Mg-standard solution (100 ppm). Make up with distilled water to a total volume of 400 ml. This compensating solution may be stored for at least a month.

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- b. *Mg-standard solution (100 ppm)*: dissolve 1.013 g of $\text{MgSO}_4 \cdot 7 \text{ aq}$ in distilled water and make up to one litre.
- c. *Titan yellow reagent*: add to 10 ml of 0.1 % aqueous titan yellow (Merck) 5 ml of 1 % polyvinyl alcohol (BDH) in distilled water, then 25 ml of 1.75 % KH_2PO_4 in distilled water and 50 ml of glycerine, and make up to a 100 ml volume with distilled water. Use a fresh 0.1 % titan-yellow solution every day.
- d. *Reagent mixture*: mix titan-yellow reagent (no. 3) with an equal volume of compensating solution (No. 1).
- e. *KOH 6 N*: dissolve 336.6 g of NaOH and make up to one litre with distilled water.
- f. *NaOH 4 N*: dissolve 160 g of NaOH and make up to one litre with distilled water.
- g. *NaOH 3.5 N*: dissolve 140 g of NaOH and make up to one litre with distilled water.

In the Laboratory of Soils and Fertilizers, Mg determinations are usually carried out either on Morgan soil extracts (LUNT *et al.*, 1950; SCHUFFELEN *et al.*, 1961) or on plant material after wet digestion according to LINDNER and HARLEY (1942) and LINDNER (1944) or SCHAUMLÖFFEL (1960). In order to adjust the determination of Mg to these three different conditions it was found necessary to use different alkali additions for each. Thus the same, fairly complex, reagent mixture could be used for all three conditions, only the concentrations and the kind of alkali being changed in order to introduce the amount of Mg required to reach the solubility product of $\text{Mg}(\text{OH})_2$. When very acid digests (*e.g.* the Lindner-Harley digest) have to be neutralized, NaOH, being less contaminated with Mg, is preferred to KOH, thus preventing the introduction of an excessive amount of Mg.

3. Procedure for a Morgan soil extract

Extraction: 20 g of air-dry soil are mechanically shaken for 30 minutes with 50 ml of the extracting solution (100 g of sodium acetate + 30 ml of glacial acetic acid, diluted to 1 litre with distilled water). An extract can be decolourized, if necessary, with 0.1 g of Medicinal Norit for each 10 ml of the extract. Extracts of sandy soils are diluted with Morgan's solution in the ratio of 1 : 5 and extracts of clay soils in the ratio of 1 : 20.

Pipette 2 ml of the diluted extract into test tubes and add 2 ml of the reagent mixture and 1 ml of NaOH 3,5 N, shaking the tubes after each addition. Measure after one hour (keep the test tubes in the dark (VAN WESEMAEL, 1961) at 550 n.m. and compare the results with a standard series containing 0-2-4-6-8-10-12-16 and 20 γ of Mg in 2 ml of standard solution.

4. Procedure for a Lindner-Harley digest of plant material

(SCHUFFELEN *et al.*, 1961)

Digestion: weigh out 0.6 g of air-dry plant material in a 100 ml volumetric flask. Add 5 ml of sulphuric acid (*s.g.* 1.84) and (if possible) keep overnight to prevent excessive foaming. Use 4 ml of sulphuric acid for the blank.

Heat on a hot plate and swirl gently to prevent foaming. Should foam enter the neck

of the flask, add 1 or 2 drops of hydrogen peroxide (A.R. standard). After 10-minute intervals add 5 to 10 drops of hydrogen peroxide. Repeat this procedure until the resulting solution remains clear after 10 minutes at full heat (ca. 280 °C). Fill up to the mark with distilled water.

This solution has to be diluted 1 : 1 with distilled water to prevent crystallisation of K_2SO_4 after the final addition of KOH for the Mg-determination.

Pipette 2 ml of the 1 : 1 diluted extract into test tubes and add 2 ml of the reagent mixture and 1 ml of KOH 6 N, shaking the tubes after each addition. Measure after one hour (keep the test tubes in the dark (VAN WESEMAEL, 1961)), at 550 n.m. and compare the results with a standard series in diluted sulphuric acid (20 ml concentrated sulphuric acid per litre).

5. Procedure for a Schaumlöffel digest of plant material (SCHAUMLÖFFEL, 1960)

Digestion: weigh out 1 g of air-dry plant material in a 50 ml graduated flask. Next add 10 ml of an acid mixture ($HNO_3 : HClO_4 : H_2SO_4 = 10 : 1 : 0.25$) and (if possible) keep overnight to prevent excessive foaming. Heat moderately on a hot plate. It should take 40 minutes or more for the HNO_3 to distil off. Afterwards the heat is raised to full. Destruction is complete when only the sulphuric acid is left. Fill up to the mark with distilled water.

Pipette 2 ml of the digests into test tubes and add 2 ml of the reagent mixture and 1 ml of NaOH 4 N, shaking after each addition. Measure after one hour (keep the test tubes in the dark (WESEMAEL, 1961)) at 550 n.m. and compare the results with a standard series in diluted sulphuric acid (9 ml concentrated sulphuric acid per litre).

6. Interferences

No interferences were detected with 5000 γ Ca; 300 γ Ni; 300 γ Co; 300 γ Cu; 200 γ Al; 300 γ Mn; 300 γ Fe³; 150 γ Zn.

The Mg concentration was determined in a Morgan extract of a number of soils, using the described titan-yellow method and the atomic absorption method employed in this laboratory (TABLE).

TABLE

Soils	Mg ppm with	
	atomic absorption procedure	titan-yellow procedure
Reclaimed peaty soil	6.5	6.7
Reclaimed peaty subsoil	10	10.7
Sandy soil	11	11
Sandy soil	17	18.2
Sandy soil	34	37
Loamy brook soil	41	44
Medium heavy clay soil	42	41
Glasshouse soil	101	99
Peaty clay soil	112	120
Reclaimed peaty soil	115	111
Glasshouse soil	134	130
Clay soil	141	146
Glasshouse soil	225	233
Heavy clay soil	328	329

The agreement between the results is very satisfactory.

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