

Determination of micro quantities of magnesium

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Summary

Based on the work of UMLAND and HOFFMANN a method has been developed for the specific determination of micro amounts of Mg with 8-hydroxyquinoline.

1. Introduction

In the course of our work on cation exchange equilibria in soil suspensions a Mg-determination in the gamma range is needed. Because of these low quantities a concentration of the Mg present is necessary which can be executed by liquid-liquid extraction. In this case a possibility exists for the simultaneous separation of interfering elements. UMLAND and HOFFMANN (1957) propose chloroform extraction of the 8-hydroxyquinoline complex of Mg from a 2 % n-butylamine milieu at pH 11,2—11,3. Of the interferences observed by the authors only Cu, Ni, Zn, Fe, Mn, Al and Co are of interest for the Mg-determination in soil and plant material. Cu, Ni, Zn and Fe²⁺ can be complexed by KCN. For the masking of Fe³⁺ a reducing agent is supplementarily needed. The other interfering elements should be removed by a liquid-liquid separation at pH 9 and 11 respectively with 8-hydroxyquinoline but without n-butylamine.

If this procedure is followed difficulties may arise. To prevent precipitations at the rather high pH needed for the extractions potassium sodium tartrate has to be added. According to GENTRY and SHERRINGTON (1950), however, the presence of tartrate prevents a quantitative extraction of Al at pH 9. Furthermore the same authors (1946) point to a co-extraction of part of the Mg. These findings could both be reproduced in this laboratory. Therefore it does not seem advisable to adopt this procedure for the removal of the interfering cations.

Masking of the interferences was tried also. Use of KCN in connection with a reducing agent as advised by UMLAND and HOFFMANN masks the effects of Zn, Cu, Ni, Co and Fe (50 gamma of each). But Al and Mn still interfere. The effect of Al is suppressed by the addition of triethanolamine. Furthermore Mn is masked by formaldoxime but this calls for a rather rigid pH-control which complicates the method. Addition of all the complexing agents needed raises the extinction of the blanc considerably (probably owing to Mg-contamination of the reagents). Therefore this method was abolished.

A preliminary extraction of the interfering elements with sodiumdiethyldithiocarbamate at pH 7,6 finally brought the solution. According to BODE (1954 a, b) all the interfering ions except Al can be extracted. Combined with the masking of Al with triethanolamine the method can be made specific in the presence of the mentioned elements.

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2. Extraction and masking of interfering ions

BODE (1954 a) extracts with 25 ml of tetra and 5 ml of 0,1 % sodiumdiethyldithiocarbamate in the presence of 20 mg of ammoniumchloride. In order to get a complete removal of 250 gamma quantities of the interfering cations the concentration of the reagent has to be raised to 2 % and furthermore the electrolyte content of the solution has to be increased by adding a salt.

If 5 ml of 1 n ammoniumchloride is used for this purpose, the results show a co-extraction of the Mg which is prevented by employing 5 ml of 1 n sodium nitrate instead (1 ml of 1 n ammoniumchloride proves to be satisfactory also). Because of the above mentioned difficulties a sodiumchloride boric acid buffer of pH 7,6 is used.

The only interfering ion left with this procedure is Al which can be masked by triethanolamine. The amount advised by UMLAND and HOFFMANN did not prove to be sufficient. It is necessary to use 2,5 ml of triethanolamine to complex 250 gamma of Al completely.

With this method interferences of 250 gamma of Mn, Fe, Cu, Zn, Co, Ni or Al are found to be within experimental error, if 7,5 gamma of Mg is determined.

3. Sensitivity and reproducibility of the method

To increase the sensitivity of the method the final extraction of the Mg-oxine complex is performed with 10 ml of chloroform. This intensifies the colour of the Mg-complex but at the same time it means a loss of reproducibility.

Under these conditions the mean extinction value proves to be $0,189 \pm 0,005$ which corresponds with a variation coefficient of 2,75 % (7,5 gamma of Mg; nine replications; Beckman B spectrophotometer; 10 mm light path; 380 nm). This is considered sufficient for the purpose.

One difficulty however still exists. If measured against chloroform as a reference the blanc (no Mg) and the standard (in this case 7,5 gamma of Mg) are not reproducible. The difference between the two values is, however, constant and shows the characteristics cited above. For practical purposes this means that with every series a blanc as well as a standard have to be included and shaken simultaneously with a mechanical shaker.

This phenomenon has nothing to do with shaking time, nor does diffuse daylight influence the measurements. The time of standing before the measurements neither has any effect on blanc or standard. This problem is not yet solved.

4. Reagents

1. Tartrate solution: dissolve 26,2 g of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4 \text{H}_2\text{O}$ and 212,5 g of NaNO_3 and make up to 500 ml with distilled water.
8. Boric acid buffer; solution A: dissolve 12,4 g of H_3BO_3 and 2,925 g of NaCl and make up to 1 litre with distilled water; solution B: dissolve 4,765 g of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ and make up to 250 ml with distilled water; mix 85 ml of solution A and 15 ml of solution B to get a buffer of pH 7,6.
3. Sodiumdiethyldithiocarbamate 2 % in distilled water. Prepare fresh daily.
4. Masking reagent: dissolve 8,4 g of KOH and add 125 ml of $\text{C}_6\text{H}_{15}\text{NO}_3$ (triethanolamine) and make up to 500 ml with distilled water.
5. Extracting solution: dissolve 0,2 g of 8-hydroxyquinoline (oxine) in chloroform and make up to 100 ml with chloroform. Prepare fresh daily.
6. N-butylamine.

5. Procedure

Add to 25 ml or less of a neutral sample (containing up to 20 gamma of Mg) in a 150 ml separating funnel successively 10 ml of tartrate solution (no. 1), 10 ml of boric acid buffer (no. 2), 5 ml of sodiumdiethyldithiocarbamate solution (no. 3) and make up to about 50 ml. Extract with 25 ml of chloroform and discard the organic phase. Rinse the water phase with about 10 ml of chloroform and again discard the organic phase. Next add 10 ml of masking agent (no. 4), 1 ml of n-butylamine (no. 6) and 10 ml of extracting solution (no. 5). Shake and separate the organic phase, add a knife point of Na_2SO_4 (siccum) and measure the extinction of the samples and of a 10 gamma Mg-standard against a simultaneously treated reagent blanc at 380 nm.

With this procedure Beer's law is followed up to at least 20 gamma of Mg. Every series of determinations should include a reagent blanc and a standard. For the same reason the whole series should be shaken mechanically at the same time. With our shaking machine (150 movements per minute; path length 9 cm) every separation takes 3 minutes.

If the coloured organic layer is kept in diffuse daylight no changes in the measurements are observed during at least 20 minutes as compared with samples kept in dark.

If 5 ml of extracting solution is used the sensitivity of the method increases with about 75 % but the reproducibility impaires somewhat.

In our work the method has to be used with samples which are 1 n in ammoniumnitrate or sodiumsulphate. As long as the standard has the same salt concentration no influence is observed from 2,5 m.e. of ammoniumnitrate or 20 m.e. of sodiumsulphate (in 50 ml total volume). However 5 m.e. of ammoniumnitrate diminishes the sensitivity of the method considerably.

6. Interferences

Within experimental error no influence can be detected from 250 gamma quantities of Mn, Fe, Cu, Zn, Co, Ni, Ca and Al. In variance with UMLAND and HOFFMANN a slight Ca influence is observed if 500 gamma or more of Ca is present. This error may however (partly) be due to a Mg contamination of the calciumcarbonate salt used for the checking of this interference.

LITERATURE

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