

THE DETERMINATION OF CALCIUM IN HEAVY MAGNESIUM CARBONATE USING GLYOXAL BIS (2-HYDROXYANIL)

BY M. A. LEONARD

From the Analytical Development Group, Standards Department, Boots Pure Drug Co. Ltd., Nottingham

Received May 22, 1962

The selective and sensitive colour reaction between calcium ions and glyoxal bis (2-hydroxyanil) has been applied to the determination of 0.1 to 0.5 per cent of calcium in heavy magnesium carbonate. The method, which is simple and rapid, gives results which compare well with those by flame photometry.

SMALL percentages of calcium in materials such as magnesium carbonate or magnesium oxide may be determined by flame photometry more conveniently than by the calcium sulphate precipitation method of the British Pharmacopoeia. Where flame photometers are not available, however, it was thought that the very sensitive colour reaction of calcium ions with glyoxal bis(2-hydroxyanil) might be utilised (Goldstein and Stark-Mayer, 1958).

This reagent reacts with calcium, but not magnesium, to form a bright red complex in strong alkali. Interference from other ions may be suppressed, where necessary, by the addition of carbonate, cyanide or sulphide. Quantitative methods for calcium have been described by Williams and Wilson (1961) and Florence and Morgan (1961); these are based on extraction of the red complex with chloroform and *s*-octanol respectively. Umland and Meckenstock (1960) have examined the reaction in both a single phase system (water : methanol) and a two phase system (extraction from water with chloroform : hexanol). Kerr (1960) has studied the reaction in a single phase mixture (water : ethanol : butanol).

These spectrophotometric methods were examined and that of Kerr chosen. Solvent extraction methods suffer in that the complex appears to exist in the organic layer as a sol, and once this layer is separated from its aqueous partner the colour becomes very unstable. Kerr's method also reduces the necessary manipulations.

When much magnesium was present, however, the use of a sodium hydroxide/sodium borate buffer, as in Kerr's method, was found unsatisfactory owing to the formation of magnesium hydroxide. It was found preferable to dispense entirely with a buffer solution and add sufficient *N* sodium hydroxide solution to give optimum sensitivity and stability under the conditions involved.

The assay was also modified to include a blank determination on "calcium free" magnesium carbonate. Initial experiments were made on the effect of alkali concentration and of standing time on the colour development. The position of maximum absorption of the blank solution shifts to shorter wavelengths with time irrespective of the amounts of alkali used. The extinction moreover increases not only with time but

also as the concentration of sodium hydroxide increases. But with 2.8 per cent v/v sodium hydroxide the blank solution has a constant extinction value at 520 $m\mu$ up to 2 hr. after mixing. With the assay solution (containing 20 μg : Ca^{++}) the same concentration of alkali gives curves varying with time but coincident between 480 and 560 $m\mu$ up to 30 min. after mixing. At 520 $m\mu$ curves for both the calcium containing solutions and the "blank" reagent solutions show the greatest difference in extinction. The greatest sensitivity in an assay therefore is expected to be at this wavelength.

It should be observed that at high sodium hydroxide concentrations and on prolonged standing, decomposition of the reagent occurs and it is no longer able to form a characteristic calcium complex.

These initial findings formed the basis of the assay.

TABLE I
RECOVERY EXPERIMENT
0.5 g. "calcium free" magnesium carbonate + x mg. of calcium

Wt. calcium taken x (mg.)	Per cent calcium	Number of determinations	Average wt. of calcium found (mg.)	Standard deviation
0.20	0.04	8	0.19	0.02
0.40	0.08	7	0.41	0.01
0.80	0.16	10	0.81	0.09
1.00	0.20	7	1.01	0.04
1.20	0.24	2	1.21 1.23	— —

Recommended Method

Apparatus. Extinction values were measured in 2.0 cm. cells with a battery operated Unicam S.P. 600 visual range spectrophotometer.

Reagents. Glyoxal bis(2-hydroxyanil) 0.5 per cent w/v in methanol.

Solvent mixture. Equal volumes of 95 per cent ethanol and n-butanol.

Calcium standard solution. Dissolve dry Analar calcium carbonate (1.00 g.) in N hydrochloric acid (25 ml.), boil to expel carbon dioxide, cool and dilute to 1 litre with distilled water. Dilute 10.0 ml. of this concentrated standard solution to 1 litre with distilled water (1 ml. \pm 4.0 μg . calcium).

Magnesium carbonate "calcium free". Dissolve Analar magnesium sulphate ($7\text{H}_2\text{O}$) (24.6 g.) in water (200 ml.) and add dilute sodium hydroxide solution until a precipitate just forms. Heat to 80° and add with stirring a hot solution of sodium carbonate (10.6 g.) in water (200 ml.). Allow the mixture to cool, filter off the precipitate, wash well with water and dry at 110°.

Prepare a standard curve as follows. Dissolve "calcium free" magnesium carbonate (0.5 g.) in 0.5N hydrochloric acid (22.5 ml.), boil the solution for 5 min. to remove carbon dioxide and make up to 250 ml. with water. Place 5.0 ml. of this solution in a series of 8 25-ml. volumetric flasks. Add 0 to 7 ml. calcium standard solution; 7 to 0 ml. of water; 0.70 ml. N sodium hydroxide solution; 0.25 ml. of glyoxal bis(2-hydroxyanil) reagent solution; and 10.0 ml. of ethanol:butanol mixture. Add

DETERMINATION OF CALCIUM

water to 25 ml. Mix the solutions well, allow to stand for 15 min. and then centrifuge at 2,000 r.p.m. for 3 min. Measure the extinction of the supernatant liquids at 520 $m\mu$ against that of the liquor in an identical experiment but containing no calcium.

Treat heavy magnesium carbonate (0.5 g.) in the same manner as the calcium free magnesium carbonate in the preparation of the standard curve. Day to day reproducibility of the standard curve is poor and therefore standards should be set up at the time of each assay. Should the sample contain an excessive amount of calcium a smaller aliquot must be taken and adjusted to 5.0 ml. with the "calcium free" magnesium carbonate solution.

TABLE II
ANALYSIS OF COMMERCIAL SAMPLES OF HEAVY MAGNESIUM CARBONATE

Sample	By proposed method		Per cent calcium found by	
	Wt. (mg.) of Ca found per 0.5 g.	Per cent calcium	Flame photometry	
			B.P. method	
1	1.12	0.22	0.17	0.14
2	1.35	0.27	0.26	0.22
3	2.40	0.48	0.48	0.40
4	0.86	0.17	0.20	0.14
5	2.36	0.47	0.50	0.44
6	0.96	0.19	0.22	0.16
7	1.05	0.21	0.20	0.18

RESULTS AND DISCUSSION

The standard curve passes through the origin and shows a very slight positive curvature. Sensitivity at the 20 $\mu\text{g.}$ level is 0.023 extinction units per $\mu\text{g.}$ calcium.

Recovery experiments were made on 0.5 g. samples of "calcium free" magnesium carbonate containing known additions of calcium from the concentrated stock solution. A survey of these results is given in Table I. The method has been applied to routine samples of magnesium carbonate and results obtained compared with those by alternative procedures (Table II).

Results obtained agree well with those by a flame photometric procedure but are higher than those by the official method. The present method is rapid and simple, and although the precision is only about ± 10 per cent in the worst case, this is considered adequate for the determination of calcium in heavy magnesium carbonate. Where a flame photometer is not available the method should form a useful alternative to the lengthy procedure of the British Pharmacopoeia.

REFERENCES

- Florence, T. M. and Morgan, J. (1961). Australian Atomic Energy Commission Report AAEC/E-60.
 Goldstein, D. and Stark-Meyer, C. (1958). *Analyt. Chim. Acta*, **19**, 437-439.
 Kerr, J. R. W. (1960). *Analyst*, **85**, 867-870.
 Umland, F. and Meckenstock, K. (1960). *Z. anal. Chem.*, **176**, 96-110.
 Williams, K. T. and Wilson, J. R. (1961). *Analyt. Chem.*, **33**, 244-245.

The paper was presented by THE AUTHOR.