

THE USE OF VERSENATE FOR THE DETERMINATION  
OF CALCIUM AND MAGNESIUM IN WATERS  
AND IN PLANT MATERIALS<sup>1</sup>

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Every year this laboratory receives a large number of water samples to be tested for total hardness. The determination for hardness is a common one and three methods are in general use. Both the methods using the gravimetric determinations of calcium and magnesium, and the soda-reagent method are time consuming. The gravimetric method is probably the most accurate, while values obtained by using the soda-reagent method are slightly low in comparison. A third method, the soap method, is more rapid but the results obtained are only approximate. The versenate method (1), described in this study, is a newer method which is rapid and said to be accurate. The versenate method was used for the determination of total hardness in water samples and for separate determinations of calcium and magnesium in both water and plant samples.

**Methods and Materials**

The organic acid, ethylenediaminetetracetic acid, is known commercially as "versene" (1) or "sequestrene AA" (2). A standard solution of the disodium salt (disodium dihydrogen versenate) of this acid is used as the titrating agent for calcium and magnesium in the unknown sample. The sample is adjusted to a pH of about 10 by an ammonium chloride-ammonium hydroxide buffer solution. An indicator solution of a complex organic dye, F-241, is used and the end point indicated by the color change from wine red to blue.

A portion of the water sample is first titrated with the versenate solution, the result being the sum of the calcium and magnesium present in the sample. Calcium is then precipitated from a separate portion of the sample, filtered,

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and the filtrate titrated with the versenate solution. This second titration will give the amount of magnesium present. Calcium is obtained by the difference in the two titrations.

Plant materials were first ashed, dissolved, the silica filtered off, and the above procedure followed on the filtrate.

### Results

The versenate method was first used on several synthetic waters (distilled water plus calcium and magnesium salts) with excellent recoveries of both calcium and magnesium. The gravimetric and versenate methods were then used on natural water samples: two from Brookings and one each from Canton, Aurora and Lake Preston. The comparative results are shown in Figure I. The heights of the sections are proportional to the amounts of calcium and magnesium measured in parts per million (p.p.m.). The left section represents the result obtained gravimetrically, while the right section gives the result obtained by using the versenate method.

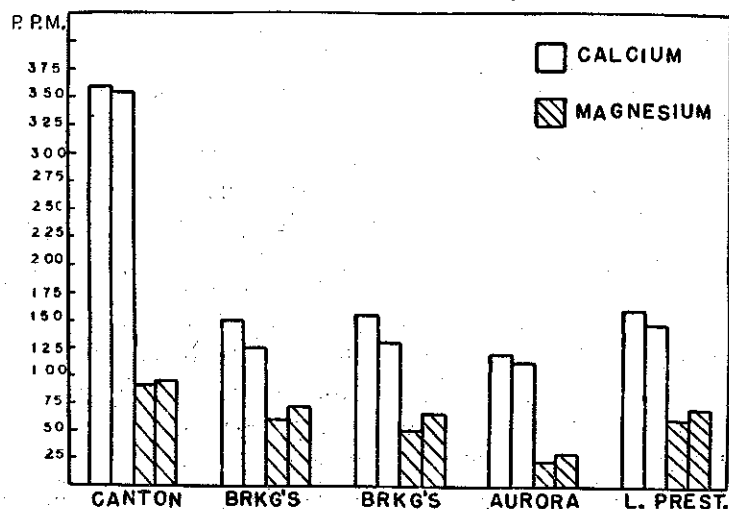


Fig. 1. Calcium and Magnesium Content of Natural Waters.

The plant materials used in this study were: western wheatgrass from two locations, alfalfa hay, dehydrated alfalfa, a mixed turkey feed, and blue grama grass. The results are shown in Figure II.

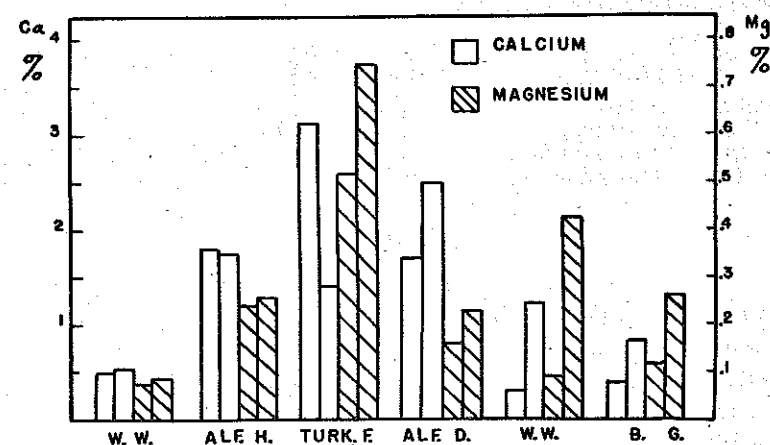


Fig. II. Calcium and Magnesium Content of Plant Materials

W.W. = Western wheatgrass hay.  
 ALFH = Alfalfa hay.  
 Turk.F. = Turkey feed.  
 ALF.D. = Dehydrated alfalfa meal.  
 B.G. = Blue grama grass hay.

The heights of the sections are proportional to the amounts of calcium measured in per cent and the amount of magnesium measured in tenths of a per cent. The left section again represents results obtained gravimetrically while the right represents results obtained by the versenate method.

A new indicator CuVer, was used in place of F-241 which had been withdrawn from the market. The results, using this new indicator, are shown in Table I. The calcium and magnesium contents of the natural waters are given in parts per million. In plant materials the values are given in terms of percent.

TABLE I

Calcium and Magnesium Content of Natural Waters  
and Plant Materials.

	Gravimetric Method		Versenate Method	
	Ca	Mg	Ca	Mg
<b>Water Samples</b>				
Aurora -----	117.92	37.0	115.57	38.88
Cottonwood, Minn. ----	73.61	26.1	75.51	27.40
Brookings -----	160.20	47.18	158.6	51.12
<b>Plant Materials</b>				
Western wheatgrass --	.29	.09	1.46	1.80
Dehydrated alfalfa ----	1.72	.16	3.56	.82
Blue grama grass -----	.38	.12	1.44	.93

### Discussion

In water samples the versenate method results are in closer agreement with those obtained gravimetrically than in plant materials. In all water samples the magnesium content by the versenate method is higher than the value obtained gravimetrically. This seems to indicate that an ion or ions (3) in addition to magnesium are being titrated by the versenate solution. In nearly all the plant samples considerable trouble was experienced with either the indicator, the end point or both. This appears to be the cause for the poor agreement between results obtained in plant materials. Two plant samples, however, did give comparable results for calcium and magnesium with the versenate and gravimetric methods.

### Summary

A new method, the versenate method, for determining total hardness in waters was studied. The method is satisfactory for the determination of total hardness. The method was also used to determine the calcium and magnesium contents of plant materials and water samples. The method does not seem to be adapted to plant materials.

Further studies should be made on possible interfering ions and other indicators for the titration which might give more accurate end points.

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