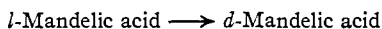


scribed. The variations in the constant are purely sporadic. Mandelic acid racemizes much more readily in sodium hydroxide solution than in acid solution, and in both much more readily than Rochelle salt. There is nothing to show that the racemization of mandelic acid is any other than is represented by the simple scheme



The existence of a complex has been investigated by the methods of hydroxyl-ion concentration and by measurements of conductivity but neither method gives any certain indication of complex formation. Attempts to isolate a complex have failed. It is shown that the racemization of mandelic acid in strong hydrochloric acid is accompanied by a certain amount of decomposition, together with liberation of free chlorine: possibly the decomposition product is phenylacetic acid.

WINNIPEG, CANADA

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[CONTRIBUTION FROM THE ALABAMA EXPERIMENT STATION]

## QUANTITATIVE DETERMINATION OF CALCIUM BY THE MAGNETO-OPTIC METHOD

By EDNA R. BISHOP AND C. B. DOLLINS

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Allison and Murphy have described a magneto-optic<sup>1</sup> method of chemical analysis in which compounds are detected by characteristic light minima produced by the time lag of their Faraday effect. Since very minute traces of a compound will produce its characteristic minima regardless of what other substances may be present, it seemed desirable to study the quantitative possibilities of this method.

**Technique.**—In general, the method consists of finding the smallest amount of material that will produce light minima characteristic of a calcium compound. This will represent a definite concentration of calcium which is determined by using solutions of known concentration and, from this, the amount in an unknown sample is calculated.

The water used is redistilled from Pyrex glass apparatus. Great care is exercised to guard against any possible contamination. Standard volumetric apparatus is used.

The fact that some calcium is dissolved from glass is recognized. The water was always tested before making an analysis and consistently gave no calcium minima. The reproducibility of results and checks with permanganate titration indicate that the amount dissolved is either negligible or constant.

To test the rate of solution of calcium from glass, water redistilled from Pyrex was left standing in a Pyrex beaker under a bell jar and in a 100-cc. normax flask and tested from day to day for calcium chloride. To ensure the presence of chloride without the addition of any calcium the water was exposed to fumes from concentrated hydrochloric acid. The water in the normax flask gave negative results until the fifth day, when the

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<sup>1</sup> Allison and Murphy, *THIS JOURNAL*, 52, 3796 (1930).

minimum of the more abundant isotope was read. The second minimum became visible on the seventh day. The amount of calcium in the water kept in Pyrex was still below the threshold value. Water was evaporated down to one-fourth its volume in a Pyrex beaker, which would not only concentrate any calcium which might be present but increase its rate of solution. This water showed bare threshold minima for calcium chloride. Some singly distilled water which had been standing around a laboratory in a Pyrex flask for two months was examined. Threshold minima were observed but disappeared when the water was diluted with an equal amount of freshly distilled water, showing that the concentration was equal to or greater than 3.74 g. Ca/10<sup>12</sup> cc. of water but less than twice that amount.

Stock solutions are prepared by dissolving a weighed sample in a 100-cc. volumetric flask. Any calcium-free compound may be added to give a desired anion. A series of dilutions is then made by diluting 1 cc. of the stock solution to 100 cc., 1 cc. of the resulting solution to 100 cc., etc., until the most dilute contains 1 part or less of calcium in 10<sup>12</sup> of water. The most dilute solution is examined for calcium chloride or phosphate minima. If the minima are not seen, then each successive increasing concentration is examined until they do appear. Let the concentration in which the minima appear to be 1/10<sup>n+1</sup> of the stock solution. A 10-cc. buret is then filled with 1/10<sup>n+2</sup> solution which is added in 0.5-cc. portions to a cell containing approximately 50 cc. of water and examined for calcium chloride or phosphate minima after each addition until they appear. This gives the concentration range in which to work. An accurate solution is then prepared corresponding to the most concentrated that did not produce minima. By means of a specially calibrated pipet, 49.75 cc. of this solution is placed in a cell and a 10-cc. buret is filled with 1/10<sup>n+2</sup> solution. The solution in the buret is added drop by drop to the cell until each minimum just appears. The volume necessary to detect the minimum of each isotope is read separately and the average of the two readings used. The amount added from the buret will be less than 0.5 cc. so that the final volume in the cell will differ from 50 cc. by less than 0.25 cc. or 0.5%. Therefore the concentration, *c*, at which the minima appear will be the concentration placed in the cell increased by as many tenths as there were twentieths of a cc. added from the buret.

**Sensitivity.**—The sensitivity, *s*, of the apparatus is the lowest concentration of a given element at which its characteristic minima can be detected. In order to determine the sensitivity of the apparatus for calcium, solutions were prepared as follows: 0.8–0.9 g. of calcium acetate was heated in an electric muffle to form the oxide, which was dissolved in hydrochloric acid and diluted to 200 cc. in a volumetric flask. The concentration of calcium in each of two solutions was determined on two 25-cc. aliquots by precipitation of the oxalate and titration with permanganate. These solutions were then analyzed by the magneto-optic method as outlined above. The average of the concentration at which the two minima were read was used as the sensitivity. Thirteen determinations gave values from 3.64 to 3.80 × 10<sup>-12</sup> g. Ca/cc. with an average of 3.74 × 10<sup>-12</sup> g. Ca/cc. for the sensitivity.

**Effect of the Presence of Other Compounds.**—To study the effect of the presence of other compounds on the sensitivity, the three types that were considered most likely to interfere were investigated. To study common ion effect, hydrochloric acid was added. To see if a closely related cation would affect the results, magnesium chloride was added. To investigate any possible competition of anions for the calcium, sulfuric acid, nitric acid and phosphoric acid and sodium ammonium phosphate were added. The compound whose influence was being studied was added in making the 1/10<sup>7</sup> dilution so that it was present in the order of 10<sup>10</sup> times as much as the calcium. None of the compounds studied had any effect on the sensitivity. The results are included in the thirteen values summarized above.

**Sensitivity for Other Calcium Compounds.**—Calcium chloride solutions to which sodium sulfate, nitric acid and sodium ammonium phosphate had been added were determined simultaneously as described above for all four calcium salts.<sup>2</sup> Several determinations showed that the minima due to each of these compounds became visible at the same concentration and that this concentration was identical with that found when only the chloride was present.

The minima read are in each case characteristic of the *compound* or an ion pair acting together. The calcium ion, however, seems to function simultaneously with every anion that may be present and the concentration at which the minima become visible is a function solely of the calcium-ion concentration and independent of the kind of anion with which it functions. All anions were present in excess. There is, however, a difference in the sharpness of the minima and hence the ease with which they can be read. The order of decreasing sharpness is phosphate, chloride, sulfate and nitrate. The nitrate presents the added difficulty of very closely spaced minima.

**Determination of Calcium in Plant Ash.**—A weighed sample (0.05 to 0.1 g.) of dried, ground plant material was ashed in an electric muffle, dissolved in hydrochloric acid, filtered and diluted to volume in a 100-cc. volumetric flask. This sample was then analyzed by the magneto-optic method as indicated above. At first determinations were made as the chloride but in later work sodium ammonium phosphate was added during the dilutions and calcium phosphate minima were read because of their greater sharpness.

The percentage of calcium in the sample is given by

$$\frac{s}{c} \frac{v}{m} 100 = \% \text{ Ca}$$

where  $s$  is sensitivity =  $3.74 \times 10^{-12}$  g. Ca/cc.,  $c$  is concentration with respect to stock solution at which the minima became visible,  $m$  is weight of sample in stock solution in grams and  $v$  is volume of stock solution in cc.

All samples were unknowns to the observer and were designated simply by number. Several determinations were run of each solution. Other portions of each sample were ashed and determined by permanganate titration. The results are shown in Table I.

TABLE I  
PERCENTAGE CALCIUM IN SOME VEGETABLE SAMPLES

Vegetable	Sample no.	Magneto-optic method			Permanganate titration
		No. of detns.	Min.	Max.	
New Zealand spinach	56	4	0.933	1.02	0.973
	63	4	0.942	1.04	
Turnip tops	57	5	1.87	2.12	2.01
	55	4	1.96	2.03	

Since none of the compounds tested affects the determination, it seems probable that this method may be used for the determination of calcium in any type of sample by using appropriate methods of obtaining a calcium

<sup>2</sup> We are indebted to Dr. Fred Allison for furnishing us with the unpublished scale readings of calcium phosphate, namely, 23.20 and 23.52.

phosphate or chloride solution. The size of sample weighed could be reduced to advantage by the use of a micro-balance. Great care is necessary to prevent calcium contamination. The time necessary to make one determination after the stock solution is prepared varies from two to four hours and requires considerable practice and skill in manipulation of the apparatus. This method is recommended for those cases where the amount of calcium is too small to determine by the usual chemical methods.

We wish to express our appreciation to Dr. Allison for the use of his apparatus and for the many courtesies he has extended to us throughout the work.

### Summary

A quantitative method for the determination of calcium by the magneto-optic method has been outlined.

The sensitivity of the apparatus to calcium is  $3.74 \times 10^{-12}$  g. Ca/cc. when the minima are read for either phosphate, chloride, sulfate or nitrate. This varies slightly with the observer.

Of these minima, the phosphate is the most satisfactory to read and the chloride is second.

The presence of excess chloride, nitrate, sulfate, phosphate, magnesium, sodium, or ammonium does not affect the results.

Duplicates will check each other and values obtained with permanganate titration within 10%.

AUBURN, ALABAMA

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

## THE EFFECT OF AMMONIA ON THE POSITIVE ION EMISSIVITY OF IRON, NICKEL AND PLATINUM

BY A. KEITH BREWER

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In a recent article<sup>1</sup> it was shown that adsorbed gases in certain cases affect the photoelectric threshold of metal surfaces in a manner identical to that occasioned by adsorbed alkali ions. To illustrate, the emission characteristics of iron in 5 mm. of ammonia at 80° are identical to iron 0.02 covered with K<sup>+</sup> ions; on the other hand, ammonia has only a small effect on the emissivity of platinum.

An obvious interpretation of these results is that some of the adsorbed ammonia molecules are dissociated into ions by the electrical forces at the iron surface and that the change in work function is due to the presence of the positive ions so formed. This interpretation is not necessarily the only one, however, since it is within the range of possibility that a layer of

<sup>1</sup> A. Keith Brewer, *THIS JOURNAL*, 54, 1888 (1932).