

c being the concentration of the acid, and α and β constants characteristic for the individual acids. The velocity increases with increasing acid strength.

This empirical equation is compatible with the assumption that the addition of an acid molecule is catalyzed by the presence of acid molecules of the same or different kind, taking into account the progressive dissociation of double acid molecules into single molecules as the dilution increases. The reaction can be considered as a case of general acid catalysis.

3. The velocity of addition of picric acid is directly proportional to its concentration.

4. The velocity of addition of phenol to diazoacetic ester is strongly catalyzed by the presence of carboxylic acids, the catalytic effect increasing with increasing acid strength. The equation

$$l = GK^x$$

which has previously been shown to hold true for general acid catalysis in aqueous solution also applies approximately in the presence case, the exponent x having the limiting value of unity. Picric acid is much less active than required by the above equation.

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[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, HARVARD MEDICAL SCHOOL]

THE DETERMINATION OF CALCIUM BY ALKALIMETRIC TITRATION. I

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Among the possible volumetric methods for the determination of small amounts of calcium, after precipitation as the oxalate, alkalimetric titration of the oxide should have certain definite advantages over oxidation with permanganate, which is now used almost exclusively for this purpose. The end-point in the titration of pure calcium oxide is so sharp that, if no errors are introduced in the precipitation and washing of the calcium oxalate or in its subsequent conversion to the oxide, a method based upon this principle should be accurate to 0.002 mg. of calcium. The permanganate titration method, on the other hand, according to the most extensive investigation so far published,¹ is subject to an error of 0.006–0.008 mg. in the analysis of samples containing between 0.2 and 0.5 mg. of calcium.

Of the various objections that have been raised against the determination of small amounts of calcium by permanganate oxidation of the oxalate precipitate, only two appear to be of much importance. These are (1) the fact that the precipitate must be washed with water (or dilute ammonia), in which its solubility is appreciable, and (2) the mechanical loss involved in centrifuging the calcium oxalate, which except perhaps in

¹ Van Slyke and Sendroy, *J. Biol. Chem.*, **84**, 217 (1929).

the case of fluids containing protein tends to float on the surface of the liquid. The necessity of washing with a liquid in which the precipitate is noticeably soluble has led to the introduction of a wide variety of empirical procedures which, whether by design or not, tend to compensate for the loss of calcium oxalate by leaving behind a little of the precipitating agent,² but methods in which the balancing of errors is so large a factor can hardly be expected to give identical results in the hands of every analyst. The mechanical loss of calcium oxalate can be avoided to a large extent by removing the supernatant fluid with a siphon, but apparently this device does not in practice lead to greater accuracy, probably because it is incompatible with the use of strictly uniform technique in washing the precipitate.

In the determination of calcium by titration of the oxide it is possible to avoid the weak points of the permanganate procedure and at the same time to retain the features of the standard gravimetric methods upon which their accuracy rests: *viz.*, (1) separation of the calcium oxalate by filtration, and (2) washing with ammonium oxalate solution, in which the solubility of the precipitate is practically nil. Jansen³ has proposed a method of this kind for quantities of calcium in the neighborhood of 1 mg., but reports errors of at least 0.008 mg. in the analysis of known solutions. In other hands this method has given still less satisfactory results,⁴ and is now rarely used. It is not in the ordinary sense a micro method, but a combination of standard textbook procedures designed for the analysis of samples containing 50 or 100 mg. of calcium and used without essential modification for the determination of much smaller quantities. The filter paper, for example, is out of all proportion to the size of the precipitate, and its presence materially complicates the subsequent steps of the analysis.⁵

Suction filtration on a small mat of paper pulp⁶ is one way in which this defect might be overcome. Some risk of loss, however, is involved in the transfer of a very small precipitate from a filter of this type, by purely mechanical means, to the platinum dish in which it is to be ignited. The

² For the literature see, for example, Bär, *Endokrinologie*, 1, 90 (1928).

³ Jansen, *Z. physiol. Chem.*, 101, 176 (1917-1918).

⁴ Cf. Heubner and Rona, *Biochem. Z.*, 135, 248 (1923).

⁵ Ignition of the calcium oxalate to carbonate has likewise been suggested, as a means whereby the precipitate may be separated by centrifugation, and the ignition and titration subsequently carried out without transferring the material [Lebermann, *Münch. med. Wochenschrift*, 71, 1392 (1924); Trevan and Bainbridge, *Biochem. J.*, 20, 423 (1926)]. The objections to centrifugation, already mentioned, limit the usefulness of this procedure. Furthermore, the difficulty of dissolving the carbonate in hydrochloric acid is so great that Trevan and Bainbridge recommend phosphoric acid in its place, and hence are forced to use an end-point which is by no means sharp. Hendriks, who appears to have subjected this method to a much closer scrutiny than its originators, finds it far from accurate [*ibid.*, 23, 1206 (1929)].

⁶ See, for example, Fiske, *J. Biol. Chem.*, 46, 288 (1921).

alternative procedure of transferring the precipitate dissolved in nitric acid has been tried repeatedly, but the results obtained by titrating the residue left after evaporating the nitric acid solution and igniting have not been satisfactory. Apparently the oxide formed by the decomposition of fused calcium nitrate is so compact that it will not dissolve readily in a moderate excess of standard acid, or else the product is not pure calcium oxide. In any event reconversion of the nitrate to oxalate before ignition is an effective remedy, which at the same time considerably diminishes the total time required for the analysis and brings the error regularly within the anticipated limit (Table I). If the dried calcium nitrate is evaporated with a few drops of a solution of oxalic acid, the oxide formed by ignition of the final residue is much less compact, and dissolves in the course of a few minutes even if the excess of acid added is not more than 0.1 cc. of 0.02 *N*. The undissolved particles of oxide are, moreover, intensely stained by the indicator (methyl red), so that no difficulty is experienced in deciding when solution is complete.

Experimental

Solutions of calcium nitrate were prepared by dissolving calcium carbonate (Kahlbaum's "zur Analyse") in a slight excess of nitric acid. Accurately measured samples of these solutions were evaporated to dryness on the water-bath in a small platinum dish. The dry calcium nitrate residue was treated with 0.5 cc. of 2.5% oxalic acid (base-free), and the contents of the dish were again evaporated to dryness and then carefully ignited over a micro-burner. The cooled residue in each instance was dissolved in an excess of standard hydrochloric acid (0.02 or 0.1 *N*, according to the amount of calcium present), added 1 cc. at a time from a calibrated Ostwald pipet, and the solution was titrated back to the turning point of methyl red with 0.02 *N* sodium hydroxide (free from carbonate and silicate) from a calibrated micro-buret of 5 cc. capacity with 0.02 cc. graduations. Toward the end of the titration the alkali was added in 0.005 cc. portions.

TABLE I
TITRATION OF CALCIUM OXIDE

0.5 cc. of 2.5% oxalic acid was used to convert the calcium nitrate to the oxalate before ignition.

Calcium present, mg.	Calcium found, mg.	Error, %	Calcium present, mg.	Calcium found, mg.	Error, %
0.200	0.202	+1.0	1.000	1.000	0
0.200	0.198	-1.0	1.000	1.002	+0.2
0.200	0.198	-1.0	1.990	1.986	-0.2
1.000	1.000	0	1.990	1.990	0

Summary

A method is described for converting calcium nitrate to the oxide in a form which can be readily analyzed by alkalimetric titration. Since small

calcium oxalate precipitates, which have been separated by filtration and washed with ammonium oxalate solution, can thus be transferred to a platinum dish with the aid of nitric acid before conversion to the oxide, certain defects inherent in the customary permanganate oxidation methods can be avoided.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

ADSORPTION BY SILICA FROM NON-AQUEOUS BINARY SYSTEMS OVER THE ENTIRE CONCENTRATION RANGE

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An interferometric method for measurement of adsorption by carbon from binary organic liquid systems was described in earlier papers from this Laboratory.² It was shown that, in every case investigated, the curve representing adsorption over the entire concentration range was S-shaped. The component having the higher adhesion tension against carbon was adsorbed to the greater extent. The component of lower adhesion tension was, however, preferentially adsorbed if present in sufficiently low concentration. An equation was derived which was based on the assumption that adsorption of each component of a binary liquid system follows the Freundlich equation. The equation $H\Delta x/m = ax^n(1-x) - b(1-x)^d x$ thus obtained was used to calculate the preferential adsorption over the concentration range.³

It is quite well known that carbon adsorbs better from aqueous solutions than from organic liquids, while silica adsorbs better from organic liquids.⁴ Carbon has been shown to have a high adhesion tension against non-polar organic liquids and a relatively low adhesion tension against certain polar organic liquids and water;⁵ the converse is true for silica.⁶ From

¹ Du Pont Fellow in Chemistry, 1927-1928.

² Bartell and Sloan, *THIS JOURNAL*, **51**, 1637 (1929); **51**, 1643 (1929).

³ The symbols used in this paper are the same as those of earlier papers

H = total number of millimoles in the solution

x = mole fraction solute at equilibrium

Δx = mole fraction change due to adsorption

m = weight of adsorbent

c_0 = initial concentration

c = final concentration

Δc = change in concentration due to adsorption

N = total weight (in grams) of solution

a , n , d and b are constants

⁴ Patrick and Jones, *J. Phys. Chem.*, **29**, 1 (1925).

⁵ Bartell and Osterhof, *Ind. Eng. Chem.*, **19**, 1277 (1927).

⁶ Bartell and Miller, *ibid.*, **20**, 738 (1928).