2. Hydroxylamine may be determined in the presence of glucose if the ratio, hydroxylamine : glucose, is not greater than 1:20.

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THE DETERMINATION OF CALCIUM BY THE CONVERSION OF THE OXALATE TO THE CARBONATE

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The usual method of determining calcium by precipitating the oxalate and igniting to the oxide has the disadvantages that it requires, in ordinary practice, ignition in platinum to a very high temperature, making it impracticable to use a porcelain Gooch crucible for filtering; and the oxide must be weighed promptly to prevent its taking up moisture and carbon dioxide. The decomposition of the oxalate to the carbonate by heating at a lower temperature, either with or without the addition of ammonium carbonate, has sometimes been recommended but it gives inaccurate results for the reason that at a temperature where the oxalate decomposes rapidly, the dissociation of the carbonate becomes appreciable. It is evident, however, that if the latter dissociation could be entirely prevented the quantitative conversion to the carbonate could be accomplished and the method would have some advantage over the determination as oxide.

The dissociation pressures of calcium carbonate determined by Johnston,[1] are as follows.

T, °C.	500	600	700	800	850	900	950	1000
p, mm.	0.11	2.35	25.3	168	373	773	1490	2710

It is evident from these data that calcium carbonate should be entirely stable and suffer no decomposition where heated in an atmosphere of carbon dioxide at any temperature not exceeding 890°. When heated in air, however, decomposition will begin at a much lower temperature since the partial pressure of carbon dioxide in the air is negligible.

We have found that by heating the oxalate at a temperature ranging between 675° and 800° in a current of dry carbon dioxide, the oxalate is decomposed rapidly and completely, yielding the carbonate, and this furnishes a very satisfactory method of determination which, so far as we are aware, has not previously been used.

Experimental Part

Transparent cleavage crystals of Iceland spar served as a source of calcium. The sample contained a trace of ferrous carbonate equivalent to 0.04% of ferric oxide. The material was powdered and dried at 100° before use.

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[1] Johnston, THIS JOURNAL, **32,** 938 (1910).

Ammonium oxalate was prepared by neutralizing oxalic acid with ammonia and recrystallizing the product obtained. It left no weighable residue on ignition.

To obtain a suitable temperature range for heating the oxalate, the porcelain Gooch crucible (30 cc. capacity) used in filtering the oxalate and covered with a Rose crucible cover, rested in a 15cc. porcelain crucible which was heated with the full flame of a Bunsen burner. Under these conditions potassium iodide (m. p., 685°) melted readily in the Gooch crucible and potassium chloride (m. p., 790°) did not melt after long heating.

A preliminary experiment showed that Iceland spar remained constant in weight, within the errors of weighing, after long ignition in a current of carbon dioxide in the apparatus described above. Ten samples of the spar were next dissolved and precipitated as oxalate in the usual manner. The precipitates were filtered on Gooch crucibles and heated to constant weight in a current of carbon dioxide as described above. The heating was gradual at first, to dry the precipitate, and the current of carbon dioxide continued after heating until the crucible was nearly cold. We found that the decomposition of the oxalate to carbonate was complete, and constant weight could be obtained by heating for 15 minutes at the full heat of the burner.

TABLE I

DETERMINATION OF CALCIUM AS CALCIUM CARBONATE

No.	$CaCO_3$ taken, g.	$CaCO_3$ found, g.	CaO, %	Variance from calcd. (56.03%)
1	0.5678	0.5682	56.07	+0.04
2	.5776	.5785	56.11	+ .08
3	.4485	.4491	56.10	+ .07
4	.4758	.4771	56.18	+ .15
5	.5282	.5297	56.19	+ .16
6	.4618	.4623	56.09	+ .06
7	.4051	.4046	55.96	− .07
8	.5258	.5273	56.19	+ .16
9	.4318	.4321	56.07	+ .04
10	.5251	.5257	56.09	+ .06

The average variation from the calculated percentage is +0.075 or about 1 part in 700. The calcium carbonate formed by ignition always contained a minute amount of carbon coming from the decomposition of the oxalate. The amount is so small that it affects the results but slightly. Determination of calcium oxide by heating the spar in a small platinum crucible to constant weight over the blast gave, in three determinations, 56.08, 56.12 and 56.14%, an average deviation of +0.08% from the calculated value.

Three determinations as sulfate were also made as a check, and the results are given below. The first two were made by precipitating the sulfate in the presence of alcohol in the usual manner, and the third by dissolving the carbonate in hydrochloric acid and evaporating with sulfuric acid, finally heating to redness in a platinum crucible.

$CaCO_3$ taken, g.	$CaSO_4$ found, g.	CaO found, %	Variance from calcd., %
0.6407	0.8737	56.17	+0.14
.7179	.9783	56.13	+ .10
.6770	.9201	55.98	− .05

SUMMARY OF THE RESULTS

CaO found by	Carbonate method	Ignition of spar	Detn. as sulfate	Calcd.
%	56.105	56.11	56.09	56.03

Hinrichsen[2] determined the atomic weight of calcium by igniting an Iceland spar similar to the sample used by us. It contained 0.03% of ferric oxide. Using, in all his determinations, over 130 g. of the spar he found 56.068% of calcium oxide, including the trace of ferric oxide.

Summary

Calcium may be determined accurately as the carbonate by igniting the oxalate in a current of carbon dioxide under suitable temperature control. The method gives results as good as or better than the method depending on the conversion of the oxalate to oxide. It has the advantages over the oxide method that the carbonate can be weighed without danger of taking up moisture or carbon dioxide, and the precipitate of oxalate can be filtered on a porcelain Gooch crucible, thereby saving time in filtration and avoiding the use of a platinum crucible for ignition.

On account of the accuracy and speed of the method, the writers believe that it may often be substituted to advantage for the rapid method of determining calcium by titrating the oxalate with permanganate.

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THE ADSORPTION OF SULFIDES BY COLLOIDAL CHROMIUM HYDROXIDE

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In Sneed's method[1] of qualitative analysis for the hydrogen sulfide group mercuric sulfide is dissolved with the sulfides of arsenic, antimony and tin, contrary to the usual custom. The reagent used is a solution of sodium hydroxide and the sulfides of sodium. The sodium hydroxide prevents hydrolysis of the soluble compound, $Hg(SNa)_2$, and the consequent precipitation of mercuric sulfide. The method calls for the later addition of ammonium chloride which so represses the ionization of the base that hydrolysis of $Hg(SNa)_2$ then takes place, thus permitting the precipitation and separation of mercuric sulfide at the proper time.

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[2] Hinrichsen, *Z. physik. Chem.*, **39**, 311 (1901).

[1] Sneed, THIS JOURNAL, **40**, 187 (1918).