[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# THE DETERMINATION OF CALCIUM BY IGNITION OF CALCIUM OXALATE TO CARBONATE IN AIR

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## Introduction

Because of its practical importance the quantitative determination of calcium has received a great deal of attention, and the various methods described in the literature have been made the subject of exhaustive critical study. Winkler[1] has tested and reviewed a number of methods, recommending, as the most reliable, precipitation as oxalate followed by ignition to oxide. Szebelledy,[2] continuing Winkler's work, recommends drying the precipitated oxalate to $CaC_2O_4{:}H_2O$. Ewe[3] compared experimentally ten standard methods, and determined their relative merits.

It is obvious that by using the proper temperature precipitated calcium oxalate, theoretically at least, can be changed quantitatively into any of the following forms: $CaC_2O_4\cdot H_2O$, $CaC_2O_4$, $CaCO_3$ or $CaO$.

Weighing as $CaC_2O_4\cdot H_2O$ always involves the danger of a slight variation in the water content; weighing as $CaC_2O_4$ is objectionable because of its hygroscopicity, and the errors in weighing $CaO$ are too well known to need mentioning.

In spite of its advantages, the ignition of calcium oxalate to carbonate in air has never been satisfactorily studied. The proper temperature range has never been accurately determined, and the conditions given are usually such that the precipitate is partly converted to oxide, which must then be changed to carbonate by treating it with ammonium carbonate and igniting gently. This method was originally proposed by Fresenius[4] and studied by Irby,[5] Fram,[6] Brunck[7] and Canals,[8] the latter four authors contributing but little to the procedure of Fresenius.

In view of the fact that no thoroughly reliable procedure has yet been described, it is not surprising to find in standard books on analysis such obviously incorrect statements as "At 500°, the oxalate begins to decompose, free carbon is liberated and calcium carbonate begins to form,"[9]

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[1] Winkler, *Z. angew. Chem.*, **31**, [I], 187, 203 (1918).

[2] Szebelledy, *Z. anal. Chem.*, **70**, 39 (1927).

[3] Ewe, *Chem. News*, **121**, 53 (1920); *Am. J. Pharm.*, **92**, 401 (1920).

[4] Fresenius, "A System of Instruction in Quantitative Chemical Analysis," 4th ed., John Churchill and Sons, London, **1865**, p. 164.

[5] Irby, *Z. anal. Chem.*, **13**, 56 (1874).

[6] Fram, *Chem.-Ztg.*, **21**, 410 (1897).

[7] Brunck, *Z. anal. Chem.*, **45**, 83 (1906).

[8] Canals, *Bull. soc. chim.*, [4] **23**, 422 (1918).

[9] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 4th ed., **1925**, p. 107.

while some authorities[10] are inclined to believe that while in careful hands the method will give accurate results, it requires much more careful attention than the oxide method, and hence will not commend itself widely.

Recent investigators, Foote and Bradley[11] and de Groot,[12] apparently believed that the only safe procedure was ignition in an atmosphere of carbon dioxide in a Rose crucible.

From Johnston's[13] measurements of equilibrium pressures of the thermal dissociation of calcium carbonate and from the partial pressure of carbon dioxide in air,[14] it can be shown that calcium carbonate is stable in air up to about 520°. Likewise, the oxalate can be completely changed into carbonate by a prolonged ignition at a temperature as low as 430° as was shown by Irby.[5] It is to be expected, therefore, that conditions can be found under which ignition in air will result in complete and rapid conversion of calcium oxalate into carbonate, without any danger of decomposition of the latter into oxide. The purpose of this work was to investigate these conditions and the errors involved because, from the authors' experience, the precipitate is best weighed in this form.

## Experimental

As a standard in this work, Kahlbaum's "Iceland Spar," consisting of 99.95% calcium carbonate with magnesium and ferrous carbonate as main impurities, was used. The composition was checked by ignition of oxalate to oxide and by titration of oxalate with ceric sulfate.[15]

Samples ranging in weight from 0.2 to 0.9 g. were dissolved in 25 cc. of 1:4 hydrochloric acid and the solution was diluted to 200 cc. Calcium oxalate was precipitated from the hot solution by adding to it slowly and with constant stirring twice the theoretical amount of pure ammonium oxalate, dissolved in 25 to 50 cc. of water, after which the solution was made just alkaline to methyl red by adding slowly with constant stirring a freshly filtered solution of 1:5 ammonium hydroxide. The solution was kept hot for two hours, filtered through a porcelain filtering crucible (Type A2),[16] and the precipitate washed, either with hot 0.5% ammonium oxalate solution, or with cold water. The crucible containing the precipitate was dried at 110°, and then ignited.

The ignitions were carried out in a Simon-Müller crucible furnace[17] the temperature of which could be kept constant within less than 5° by maintaining a constant current through the heating coil with an accurate ammeter and a variable resistance in the circuit. This furnace was carefully calibrated in terms of current by means of a calibrated platinum-platinum-rhodium thermocouple, and the temperature-current calibra-

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[10] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, p. 502.

[11] Foote and Bradley, THIS JOURNAL, **48**, 676 (1926).

[12] De Groot, *Chem. Weekblad*, **23**, 456 (1926).

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

[14] *Cf.* Clarke, "The Data of Geochemistry," U. S. Geological Survey Bulletin, 695, 1920, p. 47.

[15] Willard and Young, THIS JOURNAL, **50**, 1333 (1928).

[16] Manufactured by the Staatliche Porzellanmanufaktur, Berlin.

[17] Simon and Müller, *Z. angew. Chem.*, **39**, 1377 (1926).

tion curve was repeatedly rechecked during the process of this investigation. A number of ignitions were also carried out in a large electric muffle, calibrated in a similar way.

Ignitions were carried out at 350, 400, 450, 500, 550 and 600°, using two different samples at each temperature. In this series the crucible with the precipitate was ignited for one hour, cooled in a desiccator and weighed inside a closed weighing bottle, using a similar weighing bottle for counterpoise. It was then ignited for one hour longer, cooled, weighed and the process repeated once more. The results are given in Table I.

TABLE I

IGNITION OF CALCIUM OXALATE BETWEEN 350 AND 600°

| No. | Iceland spar, g. | Temp. of ignition, °C. | Time of ignition, hours | Precipitate, g. | Wt. $CaCO_3$ (theory), g. | Error, mg. |
|---|---|---|---|---|---|---|
| 1 | 0.6174 | 350 | 1 | 0.7594 | 0.6171 | +142.3 |
|  |  |  | 2 | .7374 |  | +120.3 |
|  |  |  | 3 | .7252 |  | +108.1 |
| 2 | .6511 |  | 1 | .8158 | .6508 | +165.0 |
|  |  |  | 2 | .8059 |  | +155.1 |
|  |  |  | 3 | .7940 |  | +143.2 |
| 1 | .8297 | 400 | 1 | .8387 | .8293 | + 9.4 |
|  |  |  | 2 | .8315 |  | + 2.2 |
|  |  |  | 3 | .8302 |  | + 0.9 |
| 2 | .6454 |  | 1 | .6524 | .6451 | + 7.3 |
|  |  |  | 2 | .6454 |  | + 0.3 |
|  |  |  | 3 | .6452 |  | + .1 |
| 1 | .5927 | 450 | 1 | .5926 | .5924 | + .2 |
|  |  |  | 2 | .5924 |  | .0 |
|  |  |  | 3 | .5924 |  | .0 |
| 2 | .6382 |  | 1 | .6382 | .6379 | + .3 |
|  |  |  | 2 | .6381 |  | + .2 |
|  |  |  | 3 | .6379 |  | .0 |
| 1 | .9089 | 500 | 1 | .9087 | .9085 | + .2 |
|  |  |  | 2 | .9086 |  | + .1 |
|  |  |  | 3 | .9086 |  | + .1 |
| 2 | .7721 |  | 1 | .7716 | .7717 | − .1 |
|  |  |  | 2 | .7716 |  | − .1 |
|  |  |  | 3 | .7715 |  | − .2 |
| 1 | .7561 | 550 | 1 | .7540 | .7557 | − 1.7 |
|  |  |  | 2 | .7500 |  | − 5.7 |
|  |  |  | 3 | .7465 |  | − 9.2 |
| 2 | .7967 |  | 1 | .7955 | .7963 | − 0.8 |
|  |  |  | 2 | .7924 |  | − 3.9 |
|  |  |  | 3 | .7887 |  | − 7.6 |
| 1 | .7820 | 600 | 1 | .7556 | .7816 | − 26.0 |
|  |  |  | 2 | .7351 |  | − 46.5 |
|  |  |  | 3 | .7160 |  | − 65.6 |
| 2 | .8432 |  | 1 | .8153 | .8428 | − 27.5 |
|  |  |  | 2 | .7929 |  | − 49.9 |
|  |  |  | 3 | .7783 |  | − 64.5 |

Even at as low a temperature as 400°, a three-hour ignition gives practically quantitative results, if the sample is not too large. At 450 and 500°, respectively, one-hour ignition suffices for quantitative conversion into carbonate, but at 550° and above the results are low due to formation of oxide.

Calcium oxalate ignited in this way gives a product which is perfectly white in color. When, however, the precipitate is filtered through filter paper, which can be completely burned off in a muffle at 500° in thirty minutes, and then ignited for from one to twenty-four hours, the precipitate is gray, and the results are 2 to 3 mg. high, depending on the size of the sample. Ignition of C. P. calcium oxalate as purchased likewise results in the formation of a product which is gray in color.

The formation of this impurity has hitherto been explained on the assumption that the decomposition of oxalate results in the formation of a small amount of carbon.[9]

Since in our procedure no formation of this product took place, no attempt was made to determine its nature. It seems doubtful, however, that this product, so resistant to heating in air, is carbon, and it is suggested that it might be a stable polymer of carbon suboxide formed in decomposition of the oxalate.[18]

The influence of time of ignition at 500° is shown in Table II, which is self-explanatory.

TABLE II

IGNITION OF CALCIUM OXALATE AT 500°

| No. | Iceland spar, g. | Time of ignition | Precipitate, g. | $CaCO_3$ (theory), g. | Error mg. |
|---|---|---|---|---|---|
| 1 | 0.2194 | 30 min. | 0.2192 | 0.2193 | −0.1 |
| 2 | .8812 | | .8821 | .8808 | +1.3 |
| 1 | .5915 | 45 min. | .5913 | .5912 | +0.1 |
| 2 | .8847 | | .8844 | .8843 | + .1 |
| 3 | .7040 | | .7038 | .7037 | + .1 |
| 4 | .4999 | | .4996 | .4997 | − .1 |
| 1 | .3491 | 60 min. | .3487 | .3489 | − .2 |
| 2 | .4913 | | .4913 | .4911 | + .2 |
| 3 | .5014 | | .5010 | .5012 | − .2 |
| 4 | .7079 | | .7076 | .7076 | .0 |
| 1 | .3863 | 18 hrs. | .3862 | .3861 | + .1 |

The recommended procedure for the determination of calcium (in solutions of its pure salts) is as follows. Precipitate the oxalate by adding to the hot acid solution twice the theoretical amount of ammonium oxalate (or oxalic acid), and slowly neutralize with 1:5 ammonium hydroxide, using methyl red as indicator. Let the solution stand on the hot-plate

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[18] *Cf.* Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, **1924**, Vol. V, pp. 904–907.

for two hours, filter through a filtering crucible (or a Gooch), dry at 110° for thirty minutes and ignite in an electric muffle for one hour at a temperature between 475 and 500°. For the separation of calcium from other elements the usual methods are applicable, followed by ignition to carbonate as above.

This method has been used in this Laboratory for the last three years, both in research work and by the students in quantitative analysis, and has given very satisfactory results.

When an accurate thermocouple is not available, the furnace can be adjusted to the right temperature in the following simple way. Silver chloride melts at 455° and lead chloride at 501°; thus the correct temperature can be easily obtained by adjusting the oven to such a temperature that silver chloride will melt, but not lead chloride. The melting point can be detected with the following device. In a small pyrex tube sealed at one end place some anhydrous silver chloride powder (or lead chloride); insert into the tube two electrodes, made by sealing into pyrex tubes short pieces of platinum wire with copper wire leads, so that the ends of the electrodes reach the bottom of the tube containing the powder, but do not touch each other. The electrodes can be kept in place by putting between them and wrapping around them a piece of asbestos paper, so that the whole fits tightly into the glass tube. The "melting point detector" so prepared (see Fig. 1) is placed inside the oven, with the leads going outside and connected in series with two dry cells and a small flash-light bulb. At the melting point the molten mass establishes an electrical connection between the electrodes and the light glows. A fresh detector has to be used each time, since the anode is strongly attacked by chlorine.

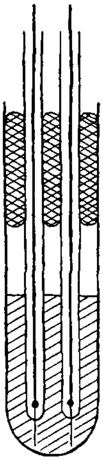

Fig. 1.—Melting point detector.

By the proper choice of material this simple method could be used to adjust the furnace to any desired temperature. It was tested in connection with this work and found to give very satisfactory results.

## Summary

1. Ignition of calcium oxalate in air was studied at 350, 400, 450, 500, 550 and 600°.

2. Between 450 and 500° the oxalate is quantitatively converted into carbonate in one to two hours. This is made the basis of an accurate method for the gravimetric determination of calcium.

3. A simple method is described for adjusting a furnace to a desired temperature by utilizing the melting points of suitable salts.

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