

## METHOD IN DETAIL

I—Weigh out a 2 gram sample of raw material (or clinker) or a 0.5 gram sample of treater dust and add to the former 0.5 g. of ammonium chloride and to the latter 0.25 g. of ammonium chloride. Transfer to a mortar, mix thoroughly and grind. Transfer the contents of the mortar to a 20 cc. platinum crucible, the bottom of which has been covered with a generous layer of calcium carbonate—about 2 grams. Cover contents of crucible with about 2 grams of calcium carbonate and proceed with heating and sintering as in the J. Lawrence Smith method.

After the mass has been slaked in a small casserole, place on the hot plate and heat to boiling. Filter into a flat-bottomed porcelain dish and wash the precipitate 3 or 4 times with very hot water. Add to the filtrate an excess of acetic acid (5 to 10 cc.) and evaporate on a steam bath until no odor of acetic acid remains. Take up with a little hot water, using the precaution to wash the sides of the dish *thoroughly*. Now add from 10 to 15 cc. of cobalt reagent (see below) and evaporate on steam bath to pasty consistency. Remove from bath and when precipitate has *cooled*, take up with about 30 cc. of *cold water*, breaking up precipitate thoroughly.

Filter through an asbestos padded Gooch crucible and wash precipitate once with *cold water*.<sup>1</sup>

Wash contents of crucible into a 400 cc. beaker (containing an excess of standard *N/5* potassium permanganate solution)<sup>2</sup> with hot water and dilute to 250 cc.

Place on steam bath for about 15 minutes or until a decided black color appears. Acidulate with 10 cc. 1 : 1 sulfuric acid. With a standard pipette (10 cc.) neutralize the excess potassium permanganate with *N/5* oxalic acid solution, the potassium permanganate equivalent of which has been determined. When the final solution has cleared, titrate with standard potassium permanganate solution.

COBALT-NITRITE SOLUTION—(1) Dissolve 220 g. of sodium nitrite in 400 cc. of water.

(2) Dissolve 113 g. of cobalt acetate in a mixture of 300 cc. of water and 100 cc. of glacial acetic acid.

(3) Mix the above solutions and place under vacuum over night. Filter and dilute to 1000 cc. Keep the solution in a dark bottle. Never use a solution over two weeks old.

II—When determining “water-soluble” potash by this method, weigh 10 g. of the material into a 600 cc. beaker, cover with about 250 cc. of water and boil for 30 minutes. Pour into a 500 cc. flask. Cool to room temperature. Make solution to mark. After shaking well, filter a portion of the solution through a dry paper. Draw off 50 cc. (1 gram equivalent) and place in a platinum or porcelain dish. Then proceed as in the above method, beginning with “Add to the filtrate an excess of acetic acid (5 to 10 cc.) and evaporate on steam bath until no odor of acetic acid remains.”

<sup>1</sup> Water poured from a beaker causes less disturbance in the crucible and gives better results.

<sup>2</sup> 10 cc. for each 1 per cent  $K_2O$  equivalent in the sample.

## ILLUSTRATION—RESULTS ON SAMPLE OF RAW MATERIAL

DATA—20 cc. Permanganate originally used;  
10 cc. Oxalic acid used to neutralize excess Permanganate;  
10 cc. Oxalic acid found to equal 11.2 cc. Permanganate;  
5 cc. Permanganate used to neutralize excess Oxalic acid.  
Now (20 cc. + 5 cc.) — 11.2 cc. (Oxalic acid equivalent)  
= No. of cc. of Permanganate used to complete titration.  
Therefore (No. of cc. of Permanganate)  $\times$  Factor  
= per cent  $K_2O$ .

CALCULATION OF  $K_2O$  FACTOR—

$\frac{\text{CaO Factor}}{2} : 0.0056 = X : 0.00171$ , where  $X = K_2O$  factor.

Regular *N/5* Permanganate is used where the calcium oxide factor is based on 0.5 gram. To calculate the  $K_2O$  factor to 1 gram, one-half of the calcium oxide factor must be used in the above proportion.

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## DETERMINATION OF CARBONATES IN LIMESTONE AND OTHER MATERIALS

By J. F. BARKER

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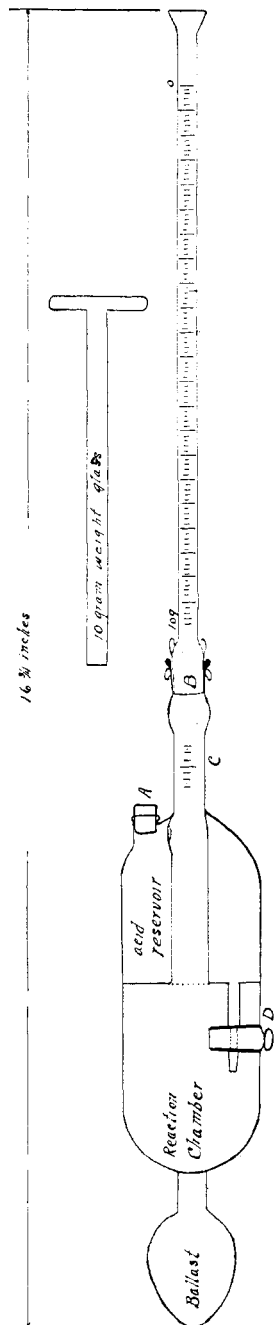
Results obtained in the determination of carbonates by the apparatus herein described compare favorably with results from the use of any standard laboratory method. The advantage of this method over others is that no mechanical balance or scale is required and there are no long calculations to be made. Anyone with some aptitude for accuracy can, with this instrument, make as reliable a determination in home or office as a skilled chemist in a well-equipped laboratory using complicated apparatus.

The invention depends upon the principle of the hydrometer, which takes account of the law that when an object is immersed in a liquid it is buoyed up by a force equal to the weight of the liquid displaced by the object. In this apparatus the carbon dioxide gas set free from the sample decreases the weight; and the rise of the graduation scale tube above the water records the percentage of carbonates from which the gas was released.

## PROCEDURE

To analyze a sample of limestone for carbonates, measure out 40 cc. of HCl (sp. gr. 1.15), using a small graduate; pour this into the acid reservoir through the opening *A*. With graduated stem disconnected hang a 10-g. weight at *B*. The hydrometer should then float in a cylinder of water and be immersed to some point at *C*. Remove the 10-g. weight and introduce pulverized limestone until instrument is immersed to exactly the same point. Now connect up graduated stem and add water a drop at a time, through the funnel-shaped top, until immersed to zero point. Raise hydrometer out of water and open stopcock *D* until acid drops slowly into reaction chamber, decomposing the limestone. As the reaction proceeds the instrument rises slowly and at the conclusion the point on stem at the surface of the water gives the per cent of calcium carbonate equivalent to the carbon dioxide in the sample. This figure is the *calcium carbonate equivalent* so often mentioned in connection with limestone analyses.

A Fahrenheit thermometer accompanies each instrument and is hung inside the floating cylinder. Its reading is taken before and after each determination to allow for any error due to change in temperature. To the figure for calcium carbonate equivalent add 0.5 for each degree rise, or subtract 0.5 for each degree fall in temperature between the two readings. This temperature change need seldom amount to more than a fraction of a degree.



HYDROMETER FOR DETERMINATION OF CARBONATES IN LIMESTONES AND OTHER MATERIALS

corrections were found necessary and subsequent instruments have been so graduated that their readings need no correction save for change in temperature occurring during the progress of the determination.

Each outfit of this apparatus includes a glass cylinder

for floating the hydrometer, a small Fahrenheit thermometer, 500 cc. of hydrochloric acid (sp. gr. 1.15), a 50 cc. graduate, a small dropping pipette and a scoop for convenience in transferring the sample. The manufacturer's price for a single outfit, it seems now, will be less than \$10.00.

APPLICATION OF THE METHOD

For analyzing carbonates other than limestone and similar materials, this instrument is fitted with a graduated stem which reads percentage of carbon dioxide, an arrangement which greatly extends its use. It will be found especially suited to determining the comparative strengths of baking powders and considering speed and accuracy is more suitable than any other device now employed for that purpose.

The method is adapted for use in all chemical laboratories, college, experiment station, or commercial laboratories. However, it is devised for use outside of chemical laboratories, also. Limestone companies can employ it to check up on every carload of their goods, or to locate the stone in their quarry most suitable for grinding. County agricultural agents will use it to keep posted on the quality of limestone being sold in their territory and to determine the composition of local limestone deposits. Many an individual farmer or some member of his household will no doubt wish to own the apparatus.

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DEGREE OF ACCURACY

The following table of results illustrates what may be expected as to degree of accuracy. They represent all of the determinations made by one person, a boy without laboratory training and who has never studied chemistry. The standard method mentioned is by use of the Parr carbon apparatus.

CALCIUM CARBONATE EQUIVALENTS		
Limestone No.	Author's Method	Standard Method
200	80.0	80.0
201	81.5	81.8
220	78.5	78.6
221	71.0	71.1
223	78.5	78.7
224	83.0	84.0
226	83.5	82.9
230	83.5	83.2
240	99.5	99.0
244	98.5	98.5
254	97.5	97.7
256	89.0	88.9
257	95.5	95.8
Calcite	99.5	..

SOME DETAILS

To those who care to examine the method critically it should be said that sources of error have been eliminated until the method is accurate to the degree that the graduated stem can easily be read: this means about 0.25 per cent. The limestone can be weighed to an accuracy of 0.02 g. The weight of CO<sub>2</sub> remaining in the apparatus tends to offset the loss due to moisture escaping with the gas, but the difference, together with any other possible sources of error, has been accounted for in the graduation of the reading stem.

This graduation was first determined theoretically and then tested by checking against pure calcite. Small

CARBONATION STUDIES: I—A MECHANICAL STIRRER FOR CARBONATION DIRECT IN THE BOTTLE

By HARRISON E. PATTEN AND GERALD H. MAINS

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In connection with an attempt to distinguish between naturally charged or bottle-fermented wines, and artificially carbonated wines, the need was felt for a machine which would enable one to carbonate direct in the bottle, and in a measure to control the purity of the carbon dioxide gas.

After extended experiments the machine described below was devised.<sup>1</sup>

A detachable stirring-head enables one to pass carbon dioxide (or other gas) through a side tube into the bottle containing liquid to be impregnated. This liquid is agitated by tines rotated by a shaft attached by pulley and belt to a motor. The complete assembly is shown in Fig. I.

DETAILS OF CONSTRUCTION

The stirring-head (Fig. II) consists of a stirrer with clock spring tines *AA*, and shaft *B* rotating in a shaft-chamber, *F*. The upper end of the stirrer-shaft *B* is fitted with a pulley, *H*, serving to connect it by belt to a source of power, and the shaft-chamber through which *B* runs is machined into a stuffing-box packed with oil-soaked lampwick which can be screwed tight to place by means of a hexed screw-collar, *Q*, thus rendering the joint between the shaft and shaft-chamber gas-tight. An opening below the stuffing-box joint leads into the side-tube *J*, so that there is free gas connection between the sleeve *C* and the

<sup>1</sup> See U. S. Patent 1,216,722.