some appearance of a deviation from this rule. Sample No. 1 was selected as being very hard and apparently resistant to weathering, nevertheless it contains 1 per cent. of phosphoric anhydride, which is more than the average for good limestone. However, the "oxygen consumed" is not large. In samples 5 and 6, taken from a road in process of construction, the material of which was considered very good, the "oxygen consumed," while not excessive, is distinctly larger than in most of the selected gray rock, and the phosphoric acid is over 0.5 per cent., or slightly above the average. However, the uniform character of this stone is shown by the close agreement betwen the figures obtained from the selected piece, No. 5, and the average sample, No. 6. On this account the favorable opinion as to its quality may be considered to have been confirmed by this test.

CONCLUSION.

The conclusion would seem justified that the limestone which consumes much more than 0.3 per cent. of oxygen and at the same time contains as much as 1 per cent. of phosphoric acid, more especially if it contains also several per cent. of clay, will disintegrate rapidly upon exposure to air and moisture and will be undesirable for road building or other exposed construction.

While this method of analysis has not been tried upon other rocks than the Trenton limestone, it is probably of much more general application, especially that part of it which takes into account easily oxidizable constituents of rocks.

The writer is indebted to Mr. S. D. Averitt of this laboratory for assistance in the determinations of phosphoric acid and sand and the weighing of the total insoluble matter.

KENTUCKY AGRICULTURAL EXPERIMENT STATION,
LEXINGTON, KY., September 30, 1902.

[CONTRIBUTIONS FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE DETERMINATION OF ATMOSPHERIC CARBON DIOXIDE BY THE WALKER METHOD.

BY A. G. WOODMAN.

Received October 30, 1902.

DETERMINATIONS of carbon dioxide in atmospheric air or in the air of rooms, where results must be obtained with a considerable degree of accuracy, are usually made by the well-known

Pettenkofer method in some form or other. While this method is convenient and for a long time has been the favorite, it is now quite generally recognized that it contains inherent sources of error which can be obviated only by the use of complicated apparatus and extreme skill in manipulation. That the method can be employed to obtain results of the highest degree of accuracy, has been shown by Letts and Blake[1] in an exhaustive study of the question. The refinements found necessary, however, place their modification out of consideration for ordinary use. A method which is comparatively simple and at the same time accurate has been proposed by Walker.[2] This method may be briefly outlined as follows:

To a definite volume of air, usually 1 to 2 liters, is added a measured amount of standard barium hydroxide, care being taken to avoid contact of the solution with the air. After the absorption of the carbon dioxide, the solution is filtered under reduced pressure through asbestos and the clear barium hydroxide received into a known excess of standard hydrochloric acid. The absorption vessel is rinsed out with water free from carbon dioxide. The excess of acid is then determined by titration with barium hydroxide.

The principal errors of the Pettenkofer method in its usual modifications, *viz.*, contact of the absorbing solution with the carbon dioxide of the air or the exhaled breath, action of the caustic alkali on the glass of the container, and the presence of small amounts of the precipitated barium carbonate, are thus avoided.

The work which has been carried out has been mainly the determination of most suitable conditions, such as the necessary time for absorption, the most suitable filtering media, etc. A series of tests on air free from carbon dioxide and on mixtures of known amounts covering a wider range than those described by Walker, has also been made. It will be unnecessary to detail all the preliminary experimental work made to acquire familiarity with the apparatus and facility in manipulation. Much work which was found later to be of little value will be omitted entirely from the discussion. The analytical work has been of necessity

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[1] *Proc. Royal Dublin Soc.*, **9**, 107 (1900).

[2] *J. Chem. Soc.*, **77**, 1110 (1900).

carried on with considerable interruption and has extended over some time.

REAGENTS AND APPARATUS.

The standard solutions used have been N/50 hydrochloric acid, and barium hydroxide, approximately N/100, its exact strength relative to the acid being found daily by titration. It was found advantageous to use solutions of this strength, somewhat more dilute than those recommended by Walker, on account of the increased accuracy with air nearly free from carbon dioxide. The decreased range of usefulness is readily compensated by the employment of smaller samples of the impure air.

The preparation of the acid requires no special comment, it being standardized by gravimetric determinations as silver chloride and preserved in a hard glass bottle in the usual manner. The barium hydroxide, which was made up in quantities of 8 liters at a time, was preserved with especial care. The hard glass bottle containing it, placed on a high shelf so that the measuring apparatus could be filled directly by gravity, was heavily coated on the inside with barium carbonate. This was found as efficient as the paraffin used by Letts and Blake which seemed to have a tendency to flake off with changes in temperature. The bottle was closed by a rubber stopper with two holes, one of which carried the siphon tube dipping to the bottom of the bottle and supplying the measuring burette, while the other carried a fairly large glass T (Fig .1). From one-half the horizontal arm of this projected a glass tube carrying the device for protecting the solution. This device is shown drawn on a somewhat larger scale in the same sketch. The horizontal tube entered the T-tube far enough to support the apparatus. Connection was made by a closely fitting rubber tube. The longer tube, reaching nearly to the bottom of the test-tube, carried a fairly good sized "calcium chloride tube" which contained soda-lime, enclosed in the usual manner by plugs of cotton. The test-tube contained 5 to 10 cc. of dilute (about N/50) caustic potash colored with phenolphthalein, the whole serving to indicate the efficiency of the soda-lime. From the other end of the horizontal arm of the T projected in the same way a long tube bent at right angles fitting by a rubber stopper into the top of the burette, thus making the whole a closed system.

much after the manner of Blochmann.[1] Any air entering the bottle when the solution is drawn from the burette or when the burette is filled again must have come through the protecting apparatus. This will be found efficient, if care is taken in the selection or preparation of the soda-lime.[2]

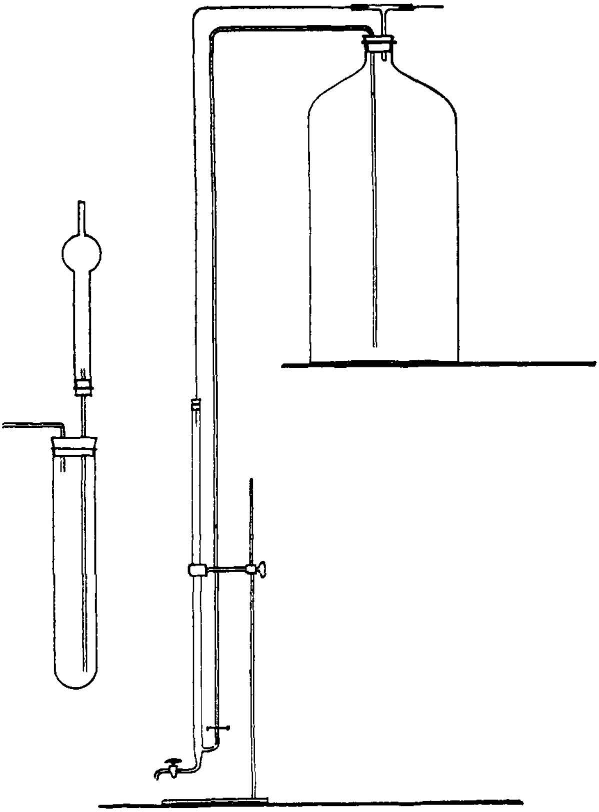

Fig. 1.

The burette used for the barium hydroxide was a glass-stoppered one, differing somewhat from the ordinary form. The lower portion below the graduations was narrowed and bent at right angles. This horizontal part was fitted with an ordinary glass stop-cock. This gave no trouble when kept well vaselined.

[1] *Ann. Chem.* (Liebig), **237**, 39 (1887).

[2] Directions for preparing a good quality of soda-lime are given by Benedict and Turner, this Journal, **21**, 396 (1899).

The tip of the burette was kept covered with a little rubber cap when not in use to prevent clogging from the formation of carbonate. The apparatus could easily be arranged with a special pipette for the delivery of a definite charge of baryta solution but this was not considered worth while for the purpose of testing the method. It was not found necessary to coat the inside of the tubes or the measuring apparatus with paraffin. The solution was always drawn from the burette and replaced by fresh if it had stood for any time. The apparatus as described was found to be remarkably efficient for the preservation of barium hydroxide. While determinations of the strength of the solution by titration against the hydrochloric acid were made every day, it was found as a matter of fact that the solution underwent no appreciable change during a month or so.

The bottles used for the collection of samples were of hard glass, some of 2-liters capacity, others of 1-liter, the exact volume being determined in each case to a cubic centimeter. Some of the bottles were fitted with glass tubes and stop-cocks as described by Walker; in others the stop-cock was replaced by a bit of rubber tubing and a Mohr pinch-cock which answers the purpose quite well though not so conveniently as the glass stop-cock. The bottles were used both plain and coated with paraffin.

The apparatus used for filtering off the barium carbonate, being made from material at hand, differed somewhat from that recommended by Walker. It may therefore need a word of explanation.

To the base of a ring-stand was firmly clamped an ordinary filter-bottle of about 250 cc. capacity closed by a rubber stopper with two holes. Through one of these passed a tube leading to the suction pump, through the other the tube of a Gooch filtering funnel, the upper part of which was cut off so that the remainder above the constriction was about an inch long. The tip projecting into the bottle was bent so that the liquid should flow down the side and not spatter. A rather close coil of stout platinum wire placed above the narrow portion served as a support for the asbestos filter or could be removed if it was desired to use cotton instead. In the upper part of the tube was tightly fitted a rubber stopper through which passed a narrow glass tube extending to within one-eighth inch of the asbestos layer and provided above the stopper with a stop-cock. Connection was made with the short tube of the inverted bottle by means of a rubber tube.

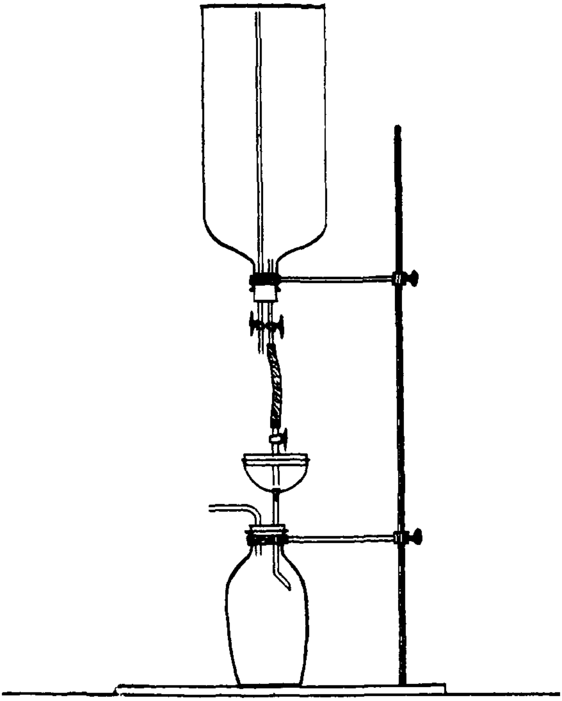

Fig. 2.

All rubber stoppers and connections with which the solutions could possibly come in contact were cleaned by boiling in a 5 per cent. potash solution, washed, and boiled in dilute bichromate and sulphuric acid mixture, rubbed thoroughly and washed until free from acid.

NOTES ON THE PROCEDURE.

The procedure adopted follows in its general outlines that of Walker but since it was found at an early stage of the work that success depended on a close observance of details in manipulation it might be well to mention the precautions found useful.

Collection of Samples.—With such small bottles, this is an easy matter. Any method may be used which secures a complete exchange of the air and prevents contamination with the breath.

It is better for this reason to draw the air out of the bottle than to force it in. For the present purpose, samples for comparison were collected by aspirating the air at a rapid rate through several bottles connected tandem, the air entering through the longer tube and leaving by the shorter one so as to sweep the bottle out completely. The air was drawn through usually for fifteen to thirty minutes, then the bottles allowed to remain connected for a time that the air might be equally distributed. No samples were collected at a temperature higher than that at the time of analysis and they were always allowed to come to the higher temperature of the laboratory so that there was always an outward pressure when the bottle was opened. It is, of course, unnecessary to use dry bottles for collecting the samples.

Absorption of the Carbon Dioxide.—It was found best instead of trying to force the alkali solution entirely below the level of the stop-cock by squeezing the rubber tip, to pinch it and then insert a bit of glass rod about an inch long as a plug to keep out the air. The absorption was usually carried on for thirty minutes.

Filtering off the Barium Carbonate.—25 cc. of the hydrochloric acid was used and the bottle was rinsed with 100-150 cc. of prepared "wash water"—made as suggested by Walker, by adding 1 cc. of a 10 per cent. barium chloride solution and 3 drops of phenolphthaleïn, then titrating with barium hydroxide to a faint permanent pink. Rinsing three times, using 25-30 cc. of wash water each time, was generally sufficient. One advantage of paraffined bottles is that they drain more completely and hence the washing is more readily performed. The preparation of this wash water was usually carried out during the absorption and the water kept in stoppered flasks. Some of the water should also be used to wash down the filter tube.

Equally good results were obtained by using 100 cc. of distilled water which had had air free from carbon dioxide passed through it in a fairly rapid stream for two hours and then been preserved out of contact with the air. This was usually done on a considerable quantity which was kept in a hard glass bottle and drawn off through a siphon tube as required for use.

The Titration.—The acid solution was transferred from the filter bottle to a 6-inch porcelain dish for titration. Barium hydroxide was added to the production of a distinct pink color, the solution then returned to the bottle and finally poured again into the dish. One or two drops of the alkali solution usually sufficed to finish the titration.

EXPERIMENTAL.

Standardization of the Barium Hydroxide.—This was the first problem that presented itself. The natural method would seem to be titration directly against the hydrochloric acid, using the indicator used in the actual determination; but since "neutralized water," that is, distilled water in which the dissolved carbon dioxide had been neutralized with baryta, was to be used in the determination, it seemed on the other hand, that the standardization should be carried out under similar conditions as regards dilution. Again, since barium chloride has been added to the wash water to assist in the separation of the barium carbonate and it has passed through a filter, the carbon dioxide may be considered removed. Why, then, should not equally good results be obtained, with less trouble, by determining the amount of carbon dioxide in a given volume of water and applying a correction for the amount of wash water used? Still another method was by the use of "purified water," by which is meant distilled water with the carbon dioxide removed as previously described.

These four methods, then, have been tried: (*a*) Direct standardization; (*b*) using 150 cc. of "neutralized water" to dilute the hydrochloric acid solution; (*c*) applying a correction for the amount of carbon dioxide in the diluent water; (*d*) using 100 cc. of "purified water."

The results are given in Table I, the value calculated being that of the barium hydroxide in terms of the standard acid.

TABLE I.—METHODS OF STANDARDIZATION.

a.	*b.*	*c.*	*d.*
0.5175	0.5225	0.4855	.....
0.5147	0.5170	.....	.....
0.4832	.....	.....	0.4829
0.4832	.....	.....	0.4831
0.4796	.....	.....	0.4794
0.4798	.....	.....	0.4803
0.4924	0.5048	.....	0.4928
0.4948	0.5077	0.4808	0.4945

The values obtained with purified water and by direct standardization were nearly the same and are undoubtedly the correct ones. Distilled water gave values which were too low, even when a correction was made for the carbon dioxide that it contained. The results with neutralized water, on the other hand, which might be expected to agree with those for purified water, were invariably high. This is probably due to the barium carbonate which has not been removed, since experiments made with a small flask exhausted of its air and fitted with stop-cocks and the filtering arrangement gave results identical with the direct standardization.

The method of standardization finally adopted was either the direct method or the use of 100 cc. of purified water, the bottle being rinsed out with 150 cc. of neutralized water, for which no allowance was made. That is to say, none was poured directly into the filter bottle but all that was used passed through the filter.

The Filtering Medium.—Tests were made using asbestos as the filtering medium and also using cotton. It was found rather more convenient to use a bit of absorbent cotton packed into the stem of the funnel tube in place of the platinum coil. A comparison of the two showed that for ordinary work either medium could be employed but that the cotton gave slightly higher results, as might be expected from the results published by Reiset[1] on the filtration of baryta water through paper.

TABLE II.—FILTERING MEDIA.

Source of air.	Filter.	Time. Minutes.	CO^2 in 10,000.
Outdoors	Cotton	30	3.26
"	Asbestos	30	3.18
Room	Cotton	30	4.05
"	Asbestos	30	4.01
"	Cotton	30	4.10
"	Asbestos	30	3.93
"	Cotton	30	3.99
"	Asbestos	30	4.01

Time Necessary for Absorption.—It is possible to carry out the absorption of the carbon dioxide in fifteen minutes, as Walker states, by agitating the bottle almost constantly. In most cases, however, it would be better to continue the absorption for a little longer time, say for twenty to thirty minutes. A longer time than this is unnecessary and in the case of bottles which are not paraffined it is undesirable.

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[1] *Ann. chim. phys.*, [5], **26**, 155 (1882).

TABLE III.—TIME NECESSARY FOR ABSORPTION.

Source of sample.	Time of shaking. Minutes.	CO_2 in 10,000.
Room	15	3.89
"	30	3.99
"	60	3.95
"	60	3.93

Action of the Alkali on the Glass of the Bottle.—The tests which were made confirmed Walker's conclusion that in the short time necessary for absorption the solvent action of the alkali on the glass is negligible.

TABLE IV.—ACTION OF THE ALKALI ON THE GLASS.

Source of sample.	Paraffined bottle?	Time. Minutes.	CO_2 in 10,000.
Room	No	30	3.68
"	"	30	3.63
"	Yes	30	3.75
"	"	30	3.78
"	No	30	4.84
"	Yes	30	4.78
"	"	30	4.81

Tests on Air Free from Carbon Dioxide and on Known Mixtures.—To obtain a rigid test of the method, determinations were made on air free from carbon dioxide and on similar samples to which a known amount of the gas had been added. The blank determinations were made both on the vacuous bottles from a previous determination and on samples in which air free from carbon dioxide was drawn through the bottles until the original air was entirely displaced. This was determined by passing the air from the bottle through a saturated solution of baryta and in no case was the sample used if the clear solution showed any turbidity when the air was drawn through it at a rapid rate for twenty minutes.

In the tests on known amounts of carbon dioxide, the vacuous bottles were also employed. The carbon dioxide, which was generated by heating magnesium carbonate, was measured over mercury in capillary tubes and added through the shorter tube of the bottle.

TABLE V.—TESTS ON AIR FREE FROM CARBON DIOXIDE.

Filter.	Wash water used.	Standardization.	CO_2 in 10,000.
Cotton	Neutralized	Direct	—0.14
"	Purified	"	0.06
"	Neutralized	"	0 00
"	Purified	"	0.18
"	"	Purified water	0.01
"	Neutralized	Direct	0.07
"	Purified	"	—0.02
"	Neutralized	"	—0.06
None	"	"	—0.01
Cotton	"	"	0.01
"	"	"	—0.02
"	"	"	0.01
Asbestos	"	"	—0.02
"	Purified	"	-0.01
"	Neutralized	"	0.01
"	Purified	"	0.00
"	"	"	0.01
"	"	"	0.01
"	Neutralized	"	0.03
"	"	"	—0.07
"	"	"	0.05
"	"	"	—0.01
"	"	"	0.03

TABLE VI.—TESTS WITH KNOWN AMOUNTS OF CARBON DIOXIDE.

Cc. added.	Temperature.	Bar. Inches.	Cc. N. T. P.	Volume found.
0.852	25.8°	29.85	0.752	0.744
0.841	27.0	30.07	0.742	0.715
1.33	25.0	29.97	1.182	1.182
1.28	24.8	29.96	1.139	1.16
2.011	25.0	29.92	1.784	1.802
1.23	25.3	29.92	1.090	1.075
2.221	25.4	29.92	1.967	2.01
2.158	25.3	29.89	1.972	1.945
1.37	21.2	30.24	1.285	1.286
1.325	21.8	30.24	1.240	1.273
2.074	21.8	30.23	1.941	1.922
1.877	23.0	30.18	1.746	1.708
0.878	23.6	30.18	0.815	0.791
0.996	23.6	30.18	0.924	0.919
1.057	22.6	....	0.990	0.996

CONCLUSIONS.

The results obtained confirm Walker's statement that the method is accurate under ordinary circumstances to 0.1 part in

10,000. With careful work and attention to details it should be accurate to a much greater degree than this, certainly to 0.03 part. It can hardly be said, however, that amounts of carbon dioxide varying from 0 to 40 parts in 10,000, can be determined without modification of the method. The barium hydroxide must always be present in considerable excess, a condition which is most readily attained by the use of a smaller sample of bad air. With a little practice, the method was found to be rapid and easy of execution and preferable to the Pettenkofer method.

BOSTON, MASS.,
October 28, 1902.

LIQUID BATHS FOR MELTING-POINT DETERMINATIONS.

BY HEYWARD SCUDDER.

Received November 28, 1902.

A MIXTURE prepared by boiling together for five minutes seven parts by weight of sulphuric acid (sp. gr. 1.84) and three parts by weight of potassium sulphate remains a transparent liquid at ordinary temperatures and can be heated up to 325° without boiling. If the proportions are changed to six parts by weight of acid and four parts of the sulphate the mixture forms a soft mass at ordinary temperatures (though after boiling and then cooling down it will usually remain liquid for half an hour or more) melting from 60°-100° and boiling above 365°. Acid potassium sulphate can be used instead of potassium sulphate. In this case the amount should be calculated to give the same ratio of potassium sulphate to sulphuric acid.

These mixtures are self-clearing and remain permanently white (turning slightly yellowish at about 230°) unless much organic matter gets in. They can be cleared, if brown, by boiling with a few drops of concentrated nitric acid or with a small crystal of potassium nitrate. The vapor is so slightly acid that the capillary can always be fastened to the thermometer by a rubber band, provided the band is 1 to 2 cm. above the surface of the bath. Platinum wire need never be used. In preparing the bath, after the potassium sulphate has melted the two layers should be mixed or explosive boiling may occur.

Most melting-points given accurately are below 325°. The first mixture is therefore suitable for all ordinary purposes. It