

*A new apparatus for the determination of
carbon dioxide.*

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AS most analysts recognize, the method generally used for the determination of carbon dioxide present as carbonate, by decomposition with acid, absorption in soda-lime or soda-asbestos, and weighing as carbon dioxide, is open to several objections; and several suggestions have been made from time to time with the object of avoiding the use of absorption tubes,¹ but none of these have come into general use, generally because of inconvenience in manipulation.

The principal objection to the use of absorption tubes (apart from their general inconvenience and the numerous precautions their use entails) lies in the uncertainty of the blank correction; when a blank experiment is performed, under precisely the same conditions as the actual determination, a small gain in weight of the absorption tubes is almost invariably observed, but in a series of several blank experiments, this gain is frequently very variable, and by no means proportional to the volume of air drawn through the absorbers, unless many precautions are observed. Care must be taken that the air current which is to carry the carbon dioxide is adequately dried after leaving the evolution flask, and thoroughly freed from hydrochloric acid, chlorine, or hydrogen sulphide; further, the actual absorbent collecting the carbon dioxide is liable to lose water to the air-current² and must therefore be followed by an absorption tube containing the same absorbent as was used to dry the air-current before absorption of the carbon dioxide. The absorption tube is usually weighed against

¹ See, for example, the procedures referred to by W. F. Hillebrand and G. E. F. Lundell, *Applied inorganic analysis*. New York, 1929, p. 631, section D.

² Especially if soda-lime is used; this absorbent does not function efficiently if it is too dry.

a similar tube as counterpoise, and hung in the balance case for some time to attain the same conditions of surface moisture as the counterpoise, since drying by heat is obviously inadmissible.

Even when a consistent blank is obtained this cannot be accepted as unquestionably the true correction, for the absorption of the carbon dioxide in the experiment proper will result in some heating of the absorption tube and change in the weight of air and moisture absorbed on its surface, besides a change in buoyancy owing to expansion.¹ If the absorption tube is hung in the balance case for an adequate length of time before weighing this error will be avoided, but it is evident that the time which was found adequate to attain consistent results in a series of blank experiments will not be adequate in the actual determination owing to the slightly different conditions. In many cases, the resultant error will be so small as to be safely neglected, but its existence should not be overlooked when determinations of especial accuracy are sought.

In all the methods that have been proposed in which the use of absorption tubes is avoided the carbon dioxide is absorbed in baryta solution. The barium carbonate produced may be filtered off, dried, and weighed, or filtered off, dissolved in acid, and determined volumetrically or gravimetrically, or a measured volume of standard baryta may be used and the excess determined by titration or by conductivity methods. These procedures all do away with the necessity for drying the gas-stream, though the main bulk of the water should be condensed. In the first two methods the gas-stream need not be freed from hydrogen sulphide or hydrochloric acid;² sulphur dioxide will interfere, but is not often met with in mineral analysis.³ The first two methods, however, involve filtration with exclusion of air, which is in general a troublesome matter, and hence the third procedure has probably been the most used of these methods avoiding the use of absorption tubes. A determination of the unused baryta by conductivity methods is especially attractive where the necessary apparatus is available, for the electrodes can be fitted in the absorption vessel itself and all exposure to the atmosphere

¹ See, for example, J. J. Manley, in Sir Edward Thorpe, Dictionary of applied chemistry. London, 1921, vol. 1, pp. 521-522, sections 12 and 13.

² Sulphuric acid or sulphur trioxide may be present in the gas-stream if carbon is being determined by wet combustion; this will interfere in the first, but not in the second, procedure.

³ Except in the determination of free carbon or organic matter by direct combustion, should sulphides or sulphates be present.

avoided. It is also a fairly simple matter to conduct the titration with exclusion of air. The use of standard baryta solution, however, is liable to lead to difficulties, owing to the solvent action of such solutions on glass; J. Lindner¹ has shown that the amount of silica dissolved in a few days may be very considerable and can lead to considerable errors, proportionately larger with weaker solutions. To obtain accurate results the baryta solution is best freshly prepared for each analysis. The solvent action of baryta solution on glass may also lead to errors in the first two methods described, as the barium carbonate precipitate is liable to carry down barium silicate which had been in colloidal solution.

With suitable precautions the determination by absorption in standard baryta and back-titration (or conductometric determination) can be made very satisfactory, but it is not really suitable for very large or very small amounts of carbon dioxide. The apparatus now to be described is designed to overcome the difficulties of filtration with exclusion of air and so render the gravimetric determination as BaCO_3 or as BaSO_4 practicable. It depends essentially on the fact that so long as an air-current is being passed upwards through a porous filter-plate liquid will not flow down through it. The high-absorption efficiency of a gas-washing apparatus in which the gas-stream is thoroughly subdivided by the use of a porous plate is also utilized.

The decomposition flask *A* (fig. 1) is provided with a three-hole stopper, carrying a tap-funnel *B*, and an inlet tube *C*, preferably provided with a tap; a small condenser is fitted in the third hole of the stopper, and from the upper end of this connexion is made directly to a small wash-bottle² *D*, of a form which can be shut off at pleasure. The wash-bottle *D* has a capacity of at least 40 to 50 c.c., and an internal height of at least 8 cm., preferably 10 to 12 cm.; with a smaller bottle some of the precipitate may be carried over into the connecting-tubes and occasion errors. From the wash-bottle the air-current passes through a small test-tube with side-tube *E*, and upwards through the sintered glass plate of a glass filter-funnel *F*, having a filter-plate 20 to 25 mm. across set in a tube at least 10 cm.,

¹ J. Lindner, Zeits. Anal. Chem., 1933, vol. 95, p. 1.

² The form of wash-bottle described by the author (Min. Mag., 1933, vol. 23, p. 386) is most convenient for this purpose, but the glass spiral must be omitted, as it ceases to function when the carbonate precipitate becomes bulky, and even leads to splashing and loss.

or better, 12 to 15 cm. long; the narrow stem below the filter-plate need not exceed 5 cm. in length; it should dip right to the bottom of the tube *E*, lest a pocket of carbon dioxide be left, while the side-tube of *E* should be well up to the top. The funnel *F* is closed by

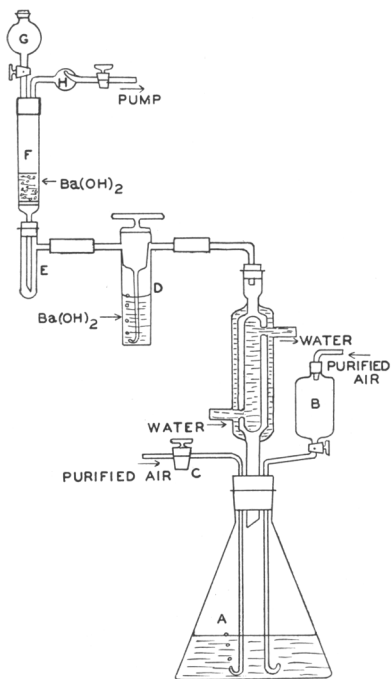


FIG. 1.

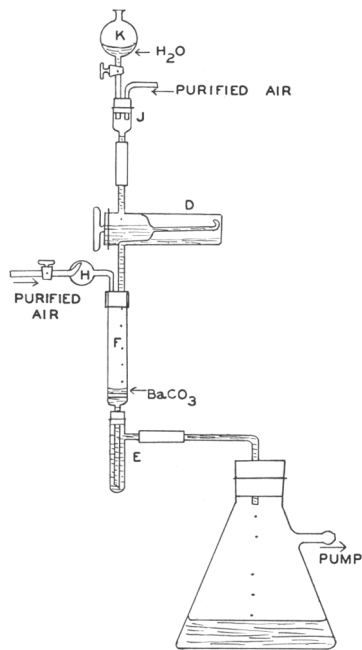


FIG. 2.

Apparatus for determination of carbon dioxide.

a rubber stop-cap (a stopper is less suitable, not being flexible), carrying a small tap-funnel *G* and a connecting-tube with splash-bulb and tap *H*. The connexions between *D* and *E* are made with stout pressure tubing, as thin rubber is not quite gas-tight to carbon dioxide; mercury seals might also be used.

The procedure in use is as follows: the weighed portion of material¹ having been placed in *A*, along with a proper amount of water, and the air displaced by a stream of purified CO₂-free air, about ½ to 1 gram of Ba(OH)₂·8H₂O (depending on the amount of CO₂ to be

¹ This should not contain more than about 0.10 to 0.15 gm. carbon dioxide, unless a larger wash-bottle is used at *D*.

collected) is roughly weighed out, dissolved in about 10 to 15 c.c. of hot water, and filtered direct into the wash-bottle *D*; a second portion of about $\frac{1}{4}$ to $\frac{1}{2}$ gram baryta is dissolved in about 10 c.c. of water and filtered into the tap-funnel *G*. The exit-tube *H* is connected to the vacuum pump and a fairly rapid current of CO_2 -free air drawn through the apparatus; now the top of the funnel *G* is opened and baryta allowed to flow slowly into the funnel *F* (there is no need to remove the stopper of *G*); bubbles should rise freely from all parts of the filter-plate, and the air-current, while considerably checked, should not be too greatly slowed; four bubbles a second may safely rise from the tube of the wash-bottle *D*, this rapid rate being permissible owing to the high efficiency of absorption in the funnel *F*. The air-stream may be allowed to pass for some time to check the efficiency of the purifying train if this is in any doubt; no opalescence or precipitate whatever should be produced in *D* or *F* after 1 or even $1\frac{1}{2}$ hours at the above rate, and a blank experiment should not show any weighable amount of barium carbonate formed. Acid is now added through the funnel *B*, and presently the evolution flask is heated as usual. The main part of the carbon dioxide is absorbed in *D*, but some passes on and is collected in *F*; as barium carbonate precipitates in *F* it gradually chokes the pores of the filter-plate, and in order to keep up the speed of the air-current, the vacuum has to be increased;¹ the air-current must not be allowed to stop or the plate in *F* becomes wetted and the current cannot then be started again, or only with difficulty.

When the carbonate has been wholly decomposed and the carbon dioxide all carried forward by the air-stream the tap of wash-bottle *D* is closed, then the tap of *H*; *D* is disconnected, and the side-tube of the small tube *E* is connected by a bent tube to a 200 c.c. filtering-flask; *H* is disconnected from the vacuum pump, which is connected to the filtering-flask, while *H* is connected instead to the air-purifying train. It is now a simple matter to filter off the barium carbonate precipitate in the funnel *F* and wash it with water introduced through *G*, while totally excluding atmospheric carbon dioxide. This done, the stop-cap on *F* is detached and any splashes on its inside, or into the splash-trap of *H*, are quickly washed into *F* with a little water,

¹ It is solely for this reason that the wash-bottle *D* is interpolated to collect most of the CO_2 ; if it is known that the material being used does not contain more than about 10 mg. of CO_2 , *D* may be omitted and the CO_2 collected wholly in *F*, greatly simplifying the subsequent procedure.

filtered off, and washed once or twice. Then the tap-funnel *G* is removed, and the wash-bottle *D* inserted in its place; on replacing the stop-cap the bottle *D* will be on its side (fig. 2). There is no danger from atmospheric carbon dioxide during this interchange, since the barium carbonate in *F* has already been washed free from baryta, and *D* remains safely closed. The other side-tube of *D* can now be connected to a small adaptor *J*, with a two-hole stopper carrying a tap-funnel *K* and a connexion to the purified air supply. On starting the vacuum pump, with the tap of *H* closed and *D* opened, the liquid and precipitate in *D* can readily be transferred to *F*, and rinsed out and washed with water introduced through *K*, with total exclusion of atmospheric carbon dioxide. The flexibility of the stop-cap on *F* greatly assists in the rinsing out of the precipitate; if a stop-cap is not available the rubber connexions between *D* and *J* and between *E* and the filter flask should be made fairly long, so that *D* and *F* can be inclined slightly and gently shaken without disconnexion at any point.

The washed barium carbonate in *F* can now be dried and weighed as such,¹ or dissolved in acid on the funnel for precipitation as BaSO_4 ; the latter course should, of course, be adopted if there is any possibility of the barium carbonate containing sulphate (sulphites would be oxidized to sulphate by the air-stream in the alkaline solution). A certain amount of barium carbonate always remains adherent to the inside of wash-bottle *D*, and there may be traces inside the stop-cap fitted to *F* and in the splash-bulb of *H*; all these are rinsed out with a little acid, and their barium content precipitated as sulphate, filtered off on a small filter,² ignited, and weighed.

With such minerals as scapolite decomposition by hydrochloric acid is always imperfect, and L. H. Borgström³ proposed to employ a mixture of hydrofluoric and hydrochloric acids for their decomposition (a glass flask can still be used, but of course will not last

¹ Although the area of the glass filter-funnel *F* is as great as that of an absorption tube the errors due to absorbed air and moisture are much less, since the funnel is dried in an oven and cooled in a desiccator; if allowed to stand at least $\frac{3}{4}$ to 1 hour in the desiccator the weight of such a funnel remains constant to 0.1 or 0.2 mg. during several dryings and weighings. The effective error is further reduced by the large factor BaCO_3 or $\text{BaSO}_4:\text{CO}_2$. But for the highest accuracy solution and precipitation as BaSO_4 is probably preferable.

² But little washing will be needed as there will be no foreign salts present.

³ L. H. Borgström, Zeits. Anal. Chem., 1914, vol. 53, p. 685.

for many experiments). With this addition there will, of course, be a possibility of hydrofluoric acid passing forward to the absorption bubbler or tubes,¹ and this will be counted as carbon dioxide whatever method is used, since barium fluoride is insoluble in water and baryta solution, but soluble in acid. Borgström failed to find any definite evidence of hydrofluoric acid reaching the absorption tubes, but his blank correction was rather large and somewhat irregular, so that traces might have been missed. The author has tested the matter, and finds that with 6 to 8 c.c. of strong hydrofluoric acid in a total volume of 100 c.c. liquid there are sometimes traces of fluorine carried forward, but often the condenser retains the whole. It will, however, be advisable, when hydrofluoric acid is used to facilitate the attack on refractory carbonate-bearing minerals, to dissolve the barium carbonate, plus any barium fluoride, in acid and precipitate as BaSO_4 ; in the filtrate the fluorine is then determined colorimetrically and a correction made.

As already mentioned, if not more than about 10 mg. of carbon dioxide is to be collected the wash-bottle *D* is omitted and the whole of the carbon dioxide collected in *F*. If the carbon dioxide to be collected is still smaller in amount the funnel *F* and the whole apparatus may be decreased in size, and 1 mg. or even 2 mg. of carbon dioxide may be successfully collected in 1 c.c. of baryta in a funnel 3 cm. high above the filter-plate, with a 1 cm. filter-plate, provided care is taken with the regulation of the air-stream. The method is thus available for micro-analysis.² It will also be evident that a similar arrangement can be adapted for the determination of carbon dioxide in air.

In order to test the method a number of experiments were made³ with pure calcium carbonate, to which certain additions were made in some experiments, to test the effect of other volatile acids. The results, shown in the following table, indicate that the method is eminently satisfactory, the only inaccurate results obtained being when a carelessly performed filtration left some BaCO_3 in the solution at the start of the analysis.

¹ The purifying train normally used with the absorption-tube method cannot be relied on to trap HF.

² Compare W. Reich-Rohrwig, Zeits. Anal. Chem., 1933, vol. 96, p. 315. (Absorption tubes used.)

³ The experiments were carried out by Mr. S. E. Ellis of the Mineral Department.

Analyses of calcium carbonate (CO₂ 43.96 %) using the new apparatus.

	Weight of CaCO ₃ used.	Weight of BaCO ₃ found.	Weight of BaSO ₄ found.	Total CO ₂ found.	CO ₂ theory.
	grams	grams	grams	grams	grams
1 ...	0.2637	0.4892	0.0346	0.1156	0.1159
2 ...	0.2629	0.4817	0.0427	0.1201	0.1156
3 ...	0.2605	0.4740	0.0446	0.1141	0.1145
4 ...	0.2544	0.4877	0.0154	0.1116	0.1118

In no. 2 the Ba(OH)₂ solution was not quite clear initially.

In no. 4 1 gm. H₃BO₃ was added before the HCl.

Summary.—A simple apparatus is described for the collection of carbon dioxide in baryta solution, and the subsequent filtration and washing of the barium carbonate produced with complete exclusion of atmospheric carbon dioxide. No special apparatus is required, the arrangement being set up from ordinary laboratory equipment; the manipulation of the apparatus is simple and much more convenient than the use of absorption tubes. The accuracy attainable is very satisfactory. The apparatus can be adapted for micro-analysis. The effect of volatile acids other than carbonic has been tested experimentally; only hydrofluoric acid is liable to cause any interference, and a method of correcting for this, if necessary, is described.
