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ON THE DETERMINATION OF CARBON DIOXIDE BY ABSORPTION.

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OF all the methods for the determination of carbon dioxide the absorption method is the most reliable and most correct. It is however not easy to obtain good results with an absorption apparatus. The inexperienced generally get varying results; after some practice the results become uniform, but either always too high or too low. The application of a corresponding correction may be used with advantage in such cases, but one must admit that this is a makeshift only. As long as the causes for the excesses or shortages are unknown, the influence of such causes can not be estimated, and therefore one is always uncertain whether the applied correction actually compensates the error.

I therefore decided to seek the causes. If I could not remove them, I would at least measure their influence. The correction which was so far found by merely empirical methods could then be calculated from the obtained data. Thus the method would be brought beyond dispute, at least from the scientific standpoint.

The method and the apparatus which I shall discuss in the following are those described by Fresenius.<sup>1</sup> Before going into details, I may briefly remind the reader of them. The carbon

<sup>1</sup> Quant. Anal. I, page 449, and II, page 308.

dioxide is developed by boiling with a dilute acid. A mixture of carbon dioxide, air and water vapor is generated, from which the latter is removed first. From the remaining gas mixture carbon dioxide is absorbed. These operations are performed by a current of air free from carbon dioxide. Consequently the apparatus has to provide for

- (1) an air purifying device,
- (2) a developing apparatus,
- (3) a drying apparatus,
- (4) an absorption apparatus,
- (5) an aspirator.

Each of these parts must do its work perfectly, if good results are to be obtained. This can be easily accomplished as to the air purifying and the drying apparatus by making them amply large. The evolution flask can be rather small with substances which do not foam, but with foaming substances like baking powder the size of the flask must be chosen according to the practical requirements. For our work a capacity of 300 cc. is sufficient.

The absorption apparatus occasions some difficulty. Its size is limited by the capacity of the analytical scale. We use U tubes filled with soda-lime and calcium chloride as recommended by Fresenius. My experience is that these tubes contain generally too little calcium chloride, whereby losses are caused. Soda-lime loses some moisture in a current of air dried by calcium chloride. In order to retain the moisture a considerable length of calcium chloride must be provided at the end of the second U tube. Fresenius prepares both tubes alike and exchanges them after the first use in order to have the fresher filling in front the second time. I do not think that this is the best plan. My opinion is that each tube has to serve a particular purpose, and should consequently have a special outfit. In the first tube carbon dioxide is to be absorbed and therefore it must be filled mainly with soda-lime. The second tube has to answer two different requirements. Firstly it has to act as a safety tube to catch any residue of carbon dioxide not absorbed in the first tube. If it is considered that these traces naturally are in a highly dilute state, it seems indispensable that in order to

retain them with safety a powerful absorbent must be employed, in other words, a fresh filling. Secondly it has to absorb the moisture which during the operation has been given off by the soda-lime in both tubes. This can be attained only if the current of air passes a rather long column of calcium chloride before leaving the tube. To meet these requirements the second tube is filled half with soda-lime and half with calcium chloride.

As already mentioned, the first absorption tube receives mainly a filling of soda-lime. Only at the end at which the current of air enters a layer of calcium chloride is provided in order to absorb any moisture which may rise from the soda-lime in this direction.

This manner of filling the two absorption tubes has proved very satisfactory. Experience teaches very soon how much carbon dioxide can be absorbed by the first tube with safety and how often the filling must be renewed. We found that with our soda-lime twenty grams of filling can take up one gram of carbon dioxide. The filling of the second tube, which consists of about ten grams of soda-lime and ten grams of calcium chloride, needs renewing but seldom. As we work its weight increases at each determination very constantly by about five milligrams, whether the quantity of carbon dioxide be large or small or a blank determination be made. This proves that the small increase is caused entirely or almost entirely by moisture. When after repeated use the total increase amounts to about two-tenths gram it is observed that the increase diminishes and at the same time the results are low. Therefore we renew the filling as soon as the total increase amounts to one-tenth gram.

The aspirator is another part to which in my opinion not enough attention is paid. As will be shown later in this article, the aspirator must allow a perfect regulation of the air current and must show the quantity of air used. Both are easily attained by employing a Mariotte's bottle.

As to the manner in which the method is to be carried out, the following points seem to be worth noting. It is evident that the current of air must not exceed a certain rapidity if the absorption is to be complete in all parts of the apparatus. As the absorption of carbon dioxide by soda-lime takes place according

to general experience very easily and quickly, there is practically no danger of loss. Long columns of calcium chloride in the drying tubes secure proper absorption of moisture in this part. It remains only to make the absorption of moisture in the second weighed tube perfect. In my opinion it is impossible to give on this point any definite rules which can be followed in all cases. On the contrary the maximum rapidity admissible must be found by experiments, not only for each apparatus but also for each new lot of absorbents, as especially the commercial soda-lime has a varying content of moisture.

In order to find the allowable rapidity of the air-current one may proceed practically as follows: The apparatus is charged exactly as for an analysis except that the carbonate is left out; in other words, a blank experiment is made. The aspiration is started with a rapidity of fifty cubic centimeters per minute. After two liters of air have passed it is interrupted. If the absorption tubes show a loss in weight the experiment must be repeated with less rapidity, say forty cc. per minute, and in this manner must be continued until the weight of the tubes is constant. If the work has been done with due precaution it will now be found that the first tube has lost just as much as the second has gained. If this is not the case it is a sure indication that the result is due to a compensation of errors.

The ascertained maximum of rapidity of the air-current must not be exceeded in determinations; a slower rate is unobjectionable. It may be mentioned here that the calcium chloride in the second tube must be of the same quality as that in the drying apparatus, which is also evident from the remarks made by Fresenius.<sup>1</sup>

Further it is manifest that a certain quantity of air must be aspirated in order to transfer all carbon dioxide from the evolution flask and the drying apparatus to the absorption tubes. The common directions on this point, as for instance two air-bubbles a second for half an hour, and similar rules, are too indefinite, and in fact do not suffice. On the contrary the required quantity of air must be determined for each apparatus. This is done simply by liberating about a half gram carbon

<sup>1</sup> Quant. Anal., 1, 72.

dioxide in the evolution flask, aspirating a certain quantity of air, for instance one-half liter, weighing the tubes and repeating the aspiration until the weight of the tubes remains constant. As a precautionary measure some addition is to be made to the minimum thus found.

In order to regulate the current of air and to keep it constant some skill is required. The aspirator must not be put in operation before the air in the apparatus comes to equilibrium, which generally is the case after the liquid in the evolution flask has boiled a few minutes. The flame is then reduced just far enough to keep the liquid slightly boiling. Now the aspirator is connected and the water allowed to run off until it comes to a standstill. Now is the time to open the cock between the evolution flask and the air purifying apparatus. Immediately the outflow from the aspirator starts and becomes constant after a few seconds. By aid of watch and measuring cylinder the speed is soon regulated.

We make it a rule to aspirate with but half the allowable rapidity until the main quantity of carbon dioxide is absorbed, *i. e.*, until the soda-lime tube has recooled; from then to the end of the operation the full speed is used. It may be said that in our work these speeds are respectively ten cc. and twenty cc. per minute.

The flame remains burning during the whole time of aspiration. If the flame were extinguished the air in the evolution flask would cool and contract, making a regulation of the air-current impossible.

Another point often overlooked is the presence of carbon dioxide in distilled water and laboratory air. There is too much in both to neglect. The whole apparatus, including the evolution flask, must be filled with air free from carbon dioxide and the distilled water must be freed from it by boiling with a little acid. In pouring the water into the evolution flask air must not be allowed to enter.

Finally, corrections for changes of temperature and air-pressure are indispensable, as the tubes and their contents occupy a rather large volume.

In regard to accuracy of our results little remains to be desired. Blank determinations give a gain or loss of not more

than two-tenths mg., and determinations of carbon dioxide in clear crystals of Iceland spar give, if one gram is employed, results which vary from 44.01 to 43.96 per cent. The explanation for these slight variations may be found partly in the inexactness of the weighings, of which four must be made for every determination, and partly in the quantity of moisture condensed on the surface of the tubes, which varies according to the moisture in the surrounding air.

It may be well to append a sketch of the apparatus as modified by me. Great care has been taken to draw all parts in proper proportion. The ratio is 1 : 12.

Some explanations in regard to details may follow :

*a.* Air-purifying cylinder, filled with soda-lime. At the top is cotton to keep back soda-lime dust.

*b.* Cock to regulate the air-current.

*c.* Capillary tube to offer resistance to the air current in case cock *b* is opened too far.

*d.* Funnel tube, closed at the bottom by a perforated rubber stopper into which

*e.* a glass tube is fitted. This arrangement, in connection with cock *b*, is a substitute for a three-way cock, but has the advantage that the regulating part, *i. e.*, "*b*" does not become wet and is not exposed to heat.

*f.* Evolution flask.

*g.* Cooler. Consists of a glass tube around which a lead pipe is wound. It was adopted by us on account of varying water pressure. It stands sudden changes of pressure very well.

*h.* Drying tube filled with coarse calcium chloride.

*i.* A little pumice stone prepared with copper sulphate.

*k.* Drying tube filled with fine calcium chloride.

*l.* Cock to close drying apparatus when not in use.

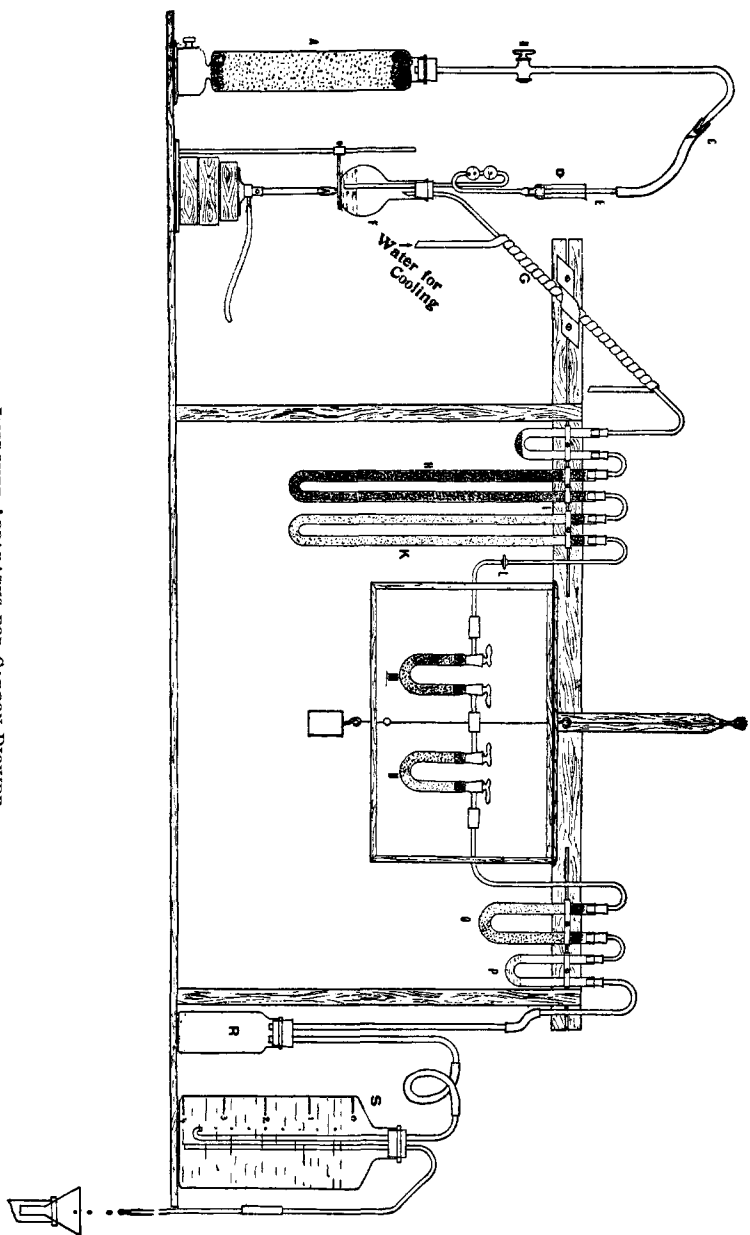
*m* and *n.* Absorption tubes, filled as described above. They are put in a glass case to protect them from dust. The connections are made by perforated rubber stoppers.

*o.* Guard tube, containing calcium chloride and soda-lime.

*p.* Indicator tube.

*r.* Safety bottle, to receive water which may be sucked back from

*s.* The aspirator.



IMPROVED APPARATUS FOR CARBON DIOXIDE.