An Apparatus for the Determination of Small Quantities of Carbonate

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Jensen ¹ in 1931 described a new method for the determination of carbonate. The original apparatus was, however, owing to its large volume, rubber tubings and rubber stoppers, not suitable for smaller quantities than that corresponding to 30 mg of carbon dioxide. Since a reliable method for the determination of smaller amounts of carbonate was lacking, the apparatus described in the present paper has been constructed. By replacing rubber by glass, and by diminishing the volume from approx. 600 to approx. 50 ml, the lower limit has been reduced to about 0.2 mg carbon dioxide.

PROCEDURE

The sample is placed in vessel A (Fig. 1), the pipette P filled with hydrochloric or sulfuric acid, and a measured amount of 0.1 *N* barium hydroxide (containing 50 g BaCl₂·2H₂O per litre in order to depress the solubility of barium carbonate) is introduced into the vessel B. A drop of 0.01 % phenolphthalein is added to vessel B. Before the system is closed the mercury level must stand in the upper position in order to avoid the formation of a pressure greater than 1 atm. After the vessels have been connected, the hydrochloric acid is led into vessel A by opening the stopcock S. By means of an up-and-down movement of the mercury level, the air in the apparatus is circulated in the direction shown by the arrows. The two vessels containing solution act as valves. 40—50 beats per minute are suitable. When all the carbon dioxide has been expelled from the solution in vessel A and absorbed in the barium hydroxide in vessel B, the latter solution is back titrated with 0.1 *N* hydrochloric acid from a Rehberg burette ² connected to the apparatus.

Fig. 1. The apparatus.

The necessary stirring during the titration is obtained by the air circulation. The same procedure is repeated without sample. The difference in the amount of 0.1 *N* hydrochloric acid used is equivalent to the carbonate in the sample.

EXPERIMENTAL

The amount of 0.1 *N* hydrochloric acid used in blank experiments is shown in Table 1. By extrapolation, one finds that the amount of 0.1 *N* hydrochloric acid corresponding

Table 1.

Approx. 0.1 <i>N</i> barium hydroxide ml	0.1 <i>N</i> hydrochloric acid used ml					Mean ml
0.250	0.255	0.255	0.257	0.258	0.255	0.256
0.500	0.538	0.541	0.542	0.537	0.538	0.539
0.750	0.822	0.819	0.818	0.823	0.820	0.820

to 0 ml of barium hydroxide is -0.023 ml. The content of carbon dioxide in the air in the apparatus is therefore equivalent to 0.023 ml of 0.1 *N* hydrochloric acid.

The influence of the time of circulation on the expulsion and absorption of carbon dioxide is shown in Table 2. It can be seen that a circulation time of 15–20 minutes is sufficient in most cases.

Table 2.

Time of circulation minutes	Potassium carbonate		found added
	added mg	found mg	
1	1.039	0.200	0.193
2	1.021	0.740	0.724
4	1.113	1.000	0.898
8	1.270	1.256	0.989
16	1.211	1.217	1.005
32	1.191	1.200	1.007
2	5.58	1.89	0.338
4	5.47	4.84	0.885
8	5.59	5.59	1.000
16	5.34	5.33	0.998

STANDARDIZATION OF 0.1 N HYDROCHLORIC ACID

The titration acid can be standardized in many ways, but it would appear to be most convenient to standardize against potassium, sodium, or calcium carbonate, exactly as used in the actual analysis. In the above experiments potassium carbonate was used. For control, the acid was standardized also against borax with methyl orange as indicator. The difference was negligible.

SOURCES OF ERROR

A change in the carbon dioxide content of the air in the laboratory will, of course, influence the results, and should, therefore, be avoided by means of ventilation of the room. If hydrochloric acid is used to expel the carbon dioxide care must be taken that the concentration in vessel A is not stronger than 3 *N*. Already at 4 *N* the amount of hydrogen chloride passing over into the barium hydroxide will be measurable.

The content of salts of volatile acids other than carbonates in the sample is another possible source of error. Fluosilicic acid, which may be formed from fluorides in the sample and silicon from the glass, is, for instance, able to pass over into the barium hydroxide. This error can be overcome by making vessel A of plexi-glass. It is not possible, however, to give a general method of overcoming all possible errors, but rather each case has to be considered separately.

EXAMPLES

Results of some analyses are shown in Table 3.

Table 3.

Substance	Sample wt. mg	0.1 N hydrochloric acid used		Carbon dioxide in the sample	
		in blank ml	with sample ml	mg	%
Hydroxylapatite containing carbo- nate I	76.3	0.540	0.112	0.942	1.234
	74.0	0.541	0.125	0.915	1.237
Do II	51.8	0.290	0.101	0.416	0.803
	49.9	0.286	0.104	0.400	0.802
Rock phosphate	43.8	0.987	0.037	2.090	4.77
	38.1	0.994	0.168	1.822	4.78

After the described apparatus was constructed, the attention of the author was drawn to the fact that Blom and Lund ³, in a modification of the original apparatus, have also used the two vessels as valves in connection with an injection syringe.

SUMMARY

An apparatus for the determination of carbonate in amounts corresponding to 0.2—2.0 mg of carbon dioxide has been described. Experiments showing the use of the apparatus have been given.

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