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Application of Microdiffusion Methods for the Determination of Carbon Dioxide in Solid Carbonates

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A new absorption device is recommended as a modification of the Cavett apparatus. Its application for the determination of carbon dioxide in solid carbonates is discussed. Barium carbonate has been used as a test substance. Determinations of carbon dioxide were carried out by decomposing the samples with hydrochloric acid, absorbing the evolved gas in barium hydroxide solution and re-titrating the excess alkali with standard hydrochloric acid solution to a thymolblue end-point. Carbon dioxide has been determined in the range of 0.3—3 mg. with relative standard errors of 18—2%, respectively. Estimations have been made with quantities of carbon dioxide as low as 70 μg . The results of carbon dioxide determinations in a precipitate of the system uranyl nitrate — barium chloride — sodium carbonate — water are shown.

Microdiffusion methods were frequently used for the determination of various organic and inorganic substances in biological materials, body fluids etc. The main feature of these substances is that they can be liberated as a gas and can be absorbed in a favourable reagent by diffusion.

A well known microdiffusion device is the Conway apparatus¹. It is very simple, but has — according to some authors — several disadvantages.

Milton and Duffield² recommended a number of micro-estimation procedures using the Cavett apparatus³. One of the methods listed is the estimation of carbon dioxide in blood.

Considering the simplicity and rapidity of the procedure, as well as the satisfactory accuracy of microdiffusion analysis, it would be of interest to extend its use to inorganic materials, e.g. inorganic solid carbonates. The subject of our special interest are the analyses of the precipitates obtained in the system $\text{UO}_2(\text{NO}_3)_2$ — BaCl_2 — Na_2CO_3 — H_2O ⁴. For this purpose the Cavett apparatus was somewhat modified and the analytical procedure was developed.

DESCRIPTION OF THE ABSORPTION DEVICE

The Cavett apparatus, recommended by Milton and Duffield for microdiffusion analysis, consists of a wide-mouthed Erlenmeyer flask of 50 ml. capacity, fitted with a ground-in stopper carrying a small cup. The principle of the determination is to decompose the sample in the inner cup and to absorb the evolved gas in the absorbing solution, placed on the bottom of the Erlenmeyer flask.

As the action of a HCl solution upon solid carbonate is immediate, the decomposing reagent must be added to the substance in an entirely closed system, to avoid considerable gas escape. This condition cannot be fulfilled in the Cavett apparatus. Besides, interferences by the absorption of atmospheric CO_2 can be avoided if the analysis is performed in an inert-gas atmosphere. For these reasons a modified apparatus with greater possibilities is recommended. Fig. 1 shows this apparatus.

It is made of Duran-50 glass (Jena) and consists of an absorption vessel containing the absorption liquid (5), and a cup containing the sample to be estimated (6). The sample is inserted into the cup in a weight crucible, which may have a bottom made of sintered glass (8), for direct analysis of precipitates.

The sample-cup (6) is mounted on the tube of a funnel (1), containing the reagent required for the liberation of the gas. The inert gas is introduced into the absorption vessel by connecting tube (3) to the gas-source. Aperture (7) serves both for adding the absorption liquid and for re-titrating the excess alkali.

Both apertures are tightly closed by ground covers, and greased. Stoppers are avoided for the sake of cleanliness of the inside of the vessel. During the reaction the covers are held in place by spring clips, fastened to the flask and cover.

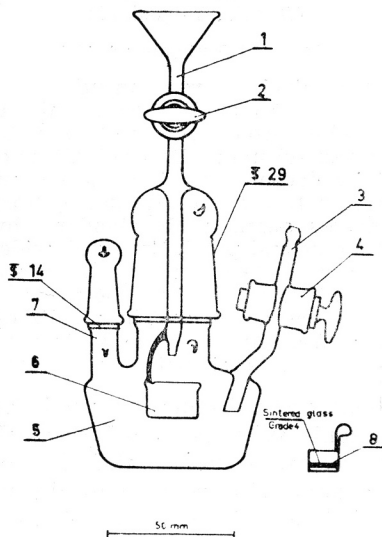


Fig. 1. Device for microdiffusion analysis. 1. funnel containing the decomposing solution, 2., 3. and 4. stopcocks, 3. tube for the introduction of the inert gas, 5. absorption vessel, 6. sample cup, 7. tube for inserting the absorbent and for re-titration, 8. microcrucible with bottom of sintered glass.

EXPERIMENTAL

BaCO_3 (Merck p. a.) was used as a test substance for the following reasons: its comparatively high molecular weight and well defined chemical composition permit estimations of small quantities of CO_2 . The non-hygroscopic character of the substance minimizes the weighing errors of the samples. The samples were dried at 115°C to constant weight.

Method of determination

The principles of the method, decomposition of the material with HCl , absorption of the evolved CO_2 in a $\text{Ba}(\text{OH})_2$ solution and re-titration of the excess alkali with a standard HCl solution, are well known and widely used. Belcher *et al.*³ gave a brief survey of errors possibly occurring in the estimation of CO_2 in this way. Two considerable systematic errors, the escape of gas during the addition of the reagent and the absorption of atmospheric carbon dioxide are avoided by the construction of the apparatus. Both the absorption reaction and the re-titration are carried out in an atmosphere of CO_2 -free nitrogen.

In order to avoid occlusion of basic components by the precipitated BaCO_3 , and too high internal gas pressures, the absorption reaction was carried out at room temperature, heating the absorption vessel at the end, just to complete the reaction.

During the reaction the absorbens was stirred magnetically to increase the rate of absorption.

Re-titration. The visual end-point detection was difficult owing to the adsorption of the indicator on the surface of the precipitate. Thymolphthalein² and thymolblue indicator solutions were compared.

Figure 2 shows the result of the comparison. Two samples of BaCO_3 were analysed in the usual way and the $\text{Ba}(\text{OH})_2$ solution was re-titrated potentiometrically in the presence of thymolphthalein or thymolblue. The pH-values at which the colour of the indicator changes are marked on the diagram. It is evident that the point at which the first colour-change of thymolblue is noticed indicates the inflection of the titration curve correctly. Besides, owing to the adsorption of the indicator on the precipitate, the detection of the thymolphthalein end-point (colour-change from blue to uncoloured) is somewhat uncertain.

For this reasons thymolblue was used in further work.

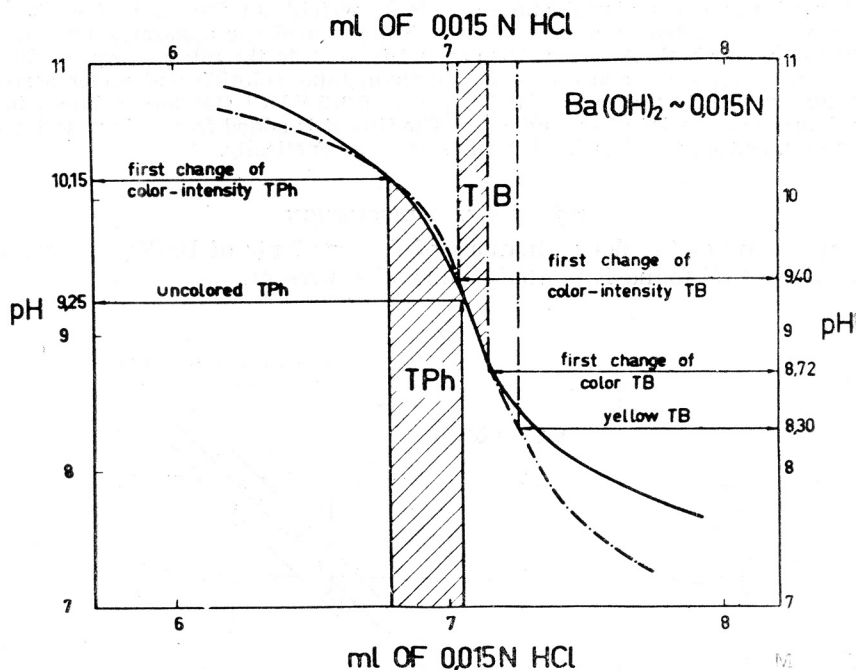


Fig. 2. Potentiometric titration curves of 0.015 N $\text{Ba}(\text{OH})_2$ solution with 0.015 N HCl solution in the presence of solid BaCO_3 . The regions of colour-change of thymolphthalein and thymolblue are marked.

Reagents

- 1) 0.015 N $\text{Ba}(\text{OH})_2$ standard solution.

A clear solution was prepared by filtration through a sintered glass filter into a Pyrex automatic burette provided with a soda asbestos tube. The burette was filled using CO_2 -free nitrogen. Under these conditions the solution remained clear for about two weeks. Standardization of the solution was performed by running blanks. A little solid BaCO_3 was added to the blank solution, in order to minimize titration errors i. e. to simulate the conditions under which analyses are performed.

- 2) 0.015 N HCl standard solution
- 3) 1 N HCl solution
- 4) 0.04% solution of thymolblue (Riedel-de Haën indicator).

Procedure

Put a weight sample containing 0.3–3 mg. CO_2 into the sample cup (6), and insert the magnetic stirrer into the absorption vessel (5). Close all apertures, keeping open stopcocks (2) and (4). Connect tube (3) to the source of CO_2 -free nitrogen and allow nitrogen to flow through the vessel for 10 min. Then lift the cover from tube (7) and insert the capillary of the burette containing $\text{Ba}(\text{OH})_2$ standard solution. Under a steady stream of nitrogen add 10 ml. of the solution. Close aperture (7) and put on springs to keep the covers in place. Open stopcock (4) for a moment to equalize the inner and outer pressure, and let 1–2 drops of 1 N HCl from funnel (1) fall into the sample cup (6). The inner pressure immediately rises due to the CO_2 evolved and further addition of HCl becomes impossible. Stir the system magnetically 10–20 min. until the inner pressure reaches a minimum (no more bubbles should be formed in the sample cup) and add 1–2 additional drops of HCl solution. The reaction is completed when further addition of HCl solution does not affect the inner pressure. The reaction time is between 20–60 min., depending upon the amount of CO_2 , the characteristics of the material and the sample weight. In the case of BaCO_3 , the reaction was completed within 20–30 min. Finally, heat the apparatus for ten min. at 35°C in a water bath. After cooling connect tube (3) to the nitrogen source, lift the cover from aperture (7), add 4–5 drops of thymolblue solution and under a stream of nitrogen re-titrate the excess $\text{Ba}(\text{OH})_2$ with 0.015 N HCl standard solution to the first colour-change point of the indicator. The titrant is added from a burette through aperture (7). During the titration stir the system magnetically.

RESULTS AND DISCUSSION

The results of the determinations of CO_2 contents of BaCO_3 are given in Fig. 3 where CO_2 found is plotted against CO_2 present.

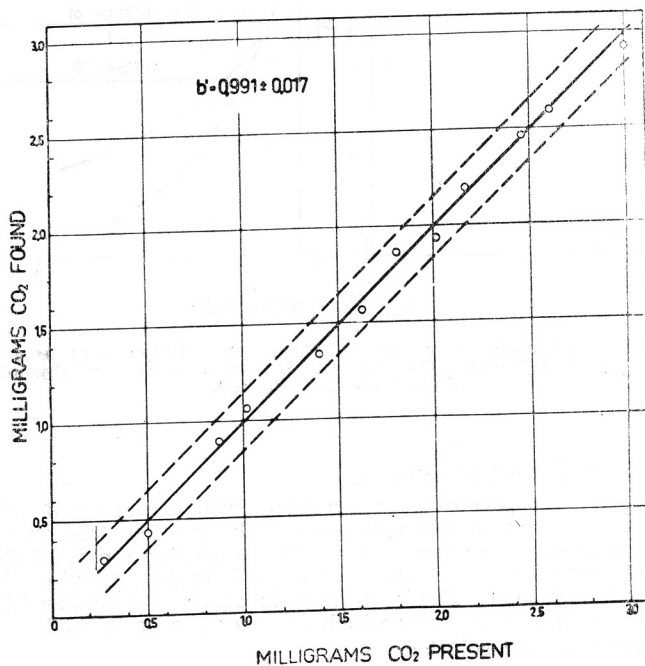


Fig. 3. Regression of milligrams of CO_2 found upon milligrams of CO_2 present and 99% confidence limits for predictions of CO_2 found.

The CO_2 present was calculated from the weight of the substance. Fig. 3 shows the linear regression and the 99% confidence limits.

Fig. 4 shows the standard error (curve 1) and the relative standard error (curve 2) as a function of CO_2 present.

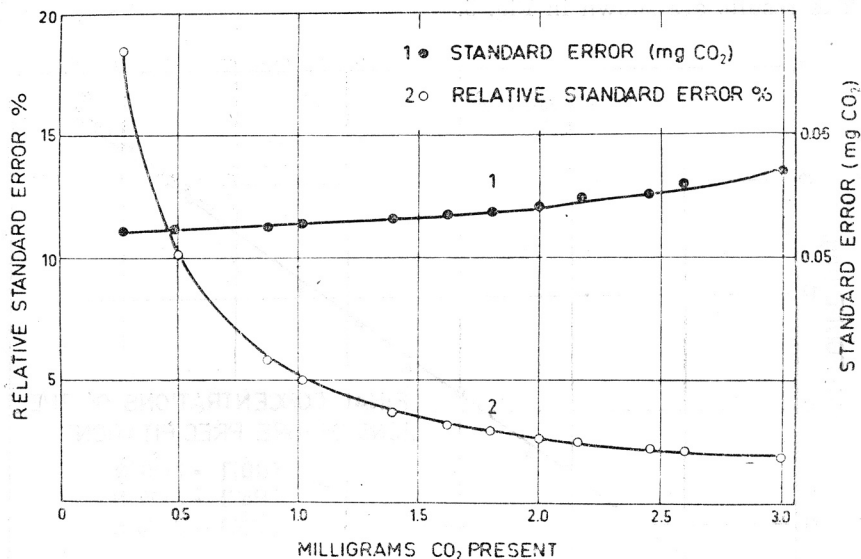


Fig. 4. Standard error (curve 1) (mg. CO_2) and relative standard error (curve 2) of CO_2 found in relation to milligrams of CO_2 present.

By changing the conditions the method might be used for the determination of even smaller amounts of CO_2 .

Table I shows some of the results, obtained by using a 0.004 N $\text{Ba}(\text{OH})_2$ solution as the absorbing liquid and a 0.004 N HCl solution as the re-titrating reagent.

TABLE I
Results of CO_2 determinations in solid BaCO_3

mg. BaCO_3 taken	mg. CO_2 calculated	mg. CO_2 found	difference in %
0.320	0.071	0.070	- 1.4%
0.400	0.089	0.076	-15 %
0.479	0.107	0.114	+ 7 %
0.532	0.119	0.121	+ 2 %
0.745	0.166	0.160	- 3.6%
0.943	0.210	0.202	- 4 %

Another way to increase the sensitivity of the method when analysing materials containing small amounts of CO_2 is to use larger quantities of material. As an example the results obtained when analysing a typical precipitate in the system $\text{UO}_2(\text{NO}_3)_2 - \text{BaCl}_2 - \text{Na}_2\text{CO}_3 - \text{H}_2\text{O}^4$ are shown. The precipitate was obtained by mixing equal volumes of $\text{UO}_2(\text{NO}_3)_2 + \text{BaCl}_2$ solution and Na_2CO_3

solution. The final solution of the precipitating ions was $2 \times 10^{-3} N$ in $UO_2(NO_3)_2$, $4 \times 10^{-3} N$ in $BaCl_2$ and $3 \times 10^{-3} N$ in Na_2CO_3 .

The precipitate being formed after mixing was dried to constant weight at $110^\circ C$.

The results are shown in Fig. 5.

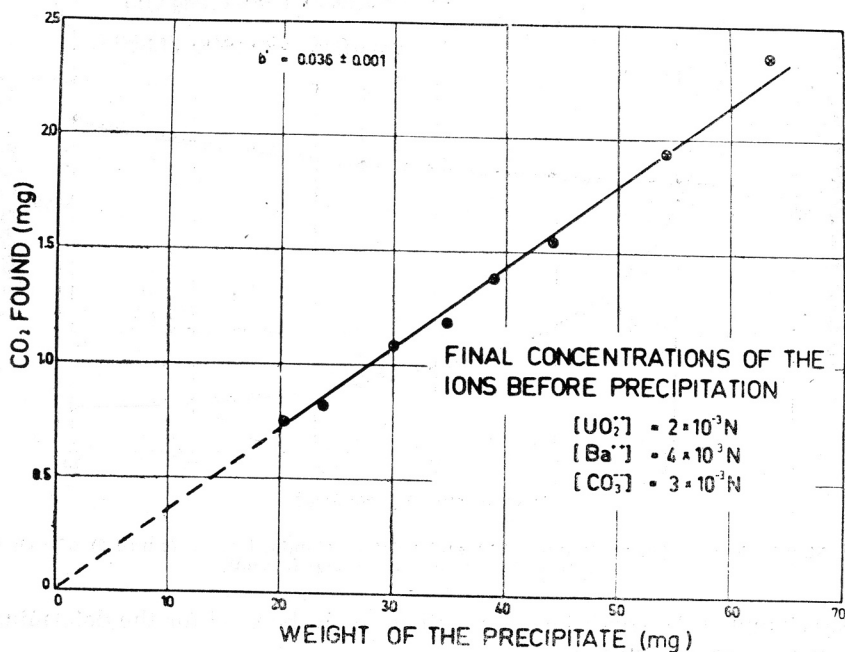


Fig. 5. Regression of the results of the determinations of CO_2 (mg. of CO_2 found upon mg. of the precipitate) in the system: $2 \times 10^{-3} N UO_2(NO_3)_2$, $4 \times 10^{-3} N BaCl_2$, $3 \times 10^{-3} N Na_2CO_3$.

Statistical analysis has proved that the intercept of the straight line is not significant. The slope was found to be $b = 0.036 \pm 0.001$. Hence the percentage of CO_2 in the sample is $3.6 \pm 0.1\%$ CO_2 .

CONCLUSION

The described method can be used with satisfactory result for serial determinations of CO_2 in solid inorganic materials. In serial work the procedure takes about 45 minutes per sample. Sulfides interfere owing to their similar behaviour.

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IZVOD

Primjena mikrodifuzione metode za određivanje ugljičnog dioksida u krutim karbonatima*H. Füredi*

Opisana je aparatura za analizu plinovitih supstanci, koja je modifikacija Cavett-ove posude. Prikazana je mogućnost primjene te aparature za određivanje ugljičnoga dioksida u krutim karbonatima. Za provjeravanje metode upotrebljen je *p.a.* barijev karbonat. Ugljični dioksid je analiziran razaranjem uzoraka sa solnom kiselinom. Nakon toga je nastali plin absorbiran u otopinu barijeva hidroksida, a višak barijeva hidroksida retitriran sa solnom kiselinom poznatoga normaliteta uz timolno modrilo kao indikator. U području od 0,3—3 mg CO₂ određivan je ugljični dioksid s relativnom standardnom pogreškom od 18 do 20%. Prikazani su rezultati određivanja ugljičnoga dioksida u talogu sistema uranil nitrat — barijev klorid — natrijev karbonat — voda.

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