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METHODS FOR THE DETERMINATION OF THE CARBON DIOXIDE EVOLVED FROM EFFERVESCENT SYSTEMS

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ABSTRACT

Different methods for determining the carbon dioxide evolved from effervescent systems are described. In addition, a comparison between some of them is carried out when a stoechiometric mixture of L-tartaric acid and sodium bicarbonate reacts.

The methods compared are: gravimetric, volumetric and gasometric.

The gravimetric methods can be direct or indirect. The direct ones are based on taking in the carbon dioxide by a sorbent substance. The increase of weight after the absorption represents the CO_2 evolved. In the indirect gravimetric methods the

amount of carbon dioxide is determined by substraction of the weight of the sample after and before the effervescent reaction.

The volumetric methods are based on an acid-base titration. In the method used, the carbon dioxide released reacts with barium hydroxide. The excess of barium hydroxide is titrated with oxalic acid. It is possible to calculate then the carbon dioxide produced in the reaction from the volume of oxalic acid used.

In the gasometric methods the volume of gas is directly determined by the displacement of a solution when the gas is released.

The gasometric method seems to be the most efficient among the studied ones.

INTRODUCTION

The effervescent preparations are products partially or fully soluble in water in which the dissolution is accelerated by the carbon dioxide released when the organic acid and the carbonate contained in both react.

$$\text{R-COOH} + \text{XHCO}_3 \xrightarrow{H_2O} \text{R-COOX} + CO_2 + H_2O$$

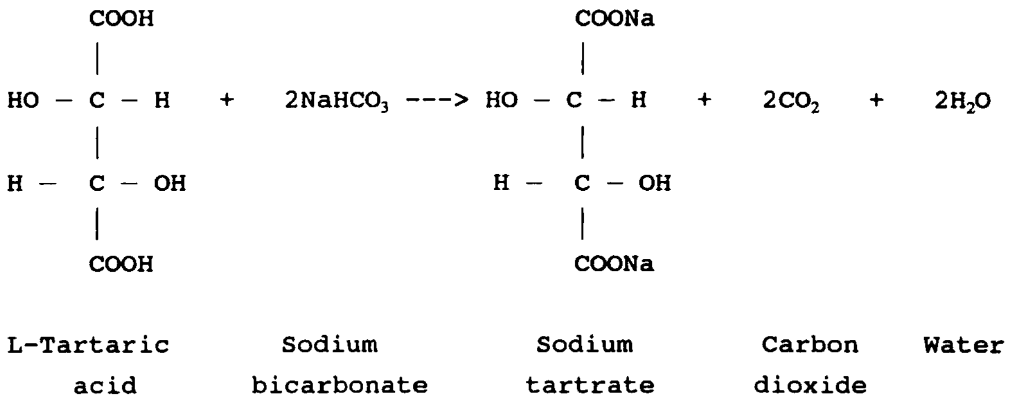
In the formulation studies, it is necessary to determine the rate of reaction of these systems. For this purpose, the amount of one of the products originated can be determined. Amongst them, the obvious compound to measure is the carbon dioxide.

As interesting as the studies previously mentioned, or even more, are those on stability. A great reactivity loss, especially because of moisture which catalizes the starting point of the reaction, means a deterioration in the physical stability. This worsens the organoleptic characteristics and furthermore, it usually produces lower chemical stability.

The procedures used to determine the carbon dioxide can be classified in five main groups:

- Gravimetrics
- Manometrics
- Volumetrics
- Gasometrics
- Spectrophotometrics

The aim of this work is to compare several of these methods and find out the most practical and accurate. Thus, the carbon dioxide released when a stoechiometric mixture of L-tartaric acid and sodium bicarbonate react has been determined in each one.



$$\begin{array}{c} COOH \\ | \\ HO - C - H \\ | \\ H - C - OH \\ | \\ COOH \end{array} + 2NaHCO_3 \text{ ---> } \begin{array}{c} COONa \\ | \\ HO - C - H \\ | \\ H - C - OH \\ | \\ COONa \end{array} + 2CO_2 + 2H_2O$$

The L-tartaric acid and the sodium bicarbonate used are in accordance with the N.F. XVII and the U.S.P. XXII, respectively.

GRAVIMETRIC METHODS

These can be classified into direct and indirect methods.

The direct gravimetric methods are based on the adsorption of the carbon dioxide by a sorbent substance. The weight increase of such substance represents the amount of CO_2 released during the reaction.

In this work, the method proposed by the NF XVII[1] for testing the carbon dioxide absorbency of the soda lime has been modified. The same method has been described by Bermejo[2], Kolthoff et al.[3] and Willard et al.[4] to determine carbonates by direct gravimetry. Fig. 1 shows the setting-up of the device used.

The procedure is as follows:

- Fill the lower transverse section of the U-shaped drying tubes 1-4 with some loosely packed glass wool. Place about 5 g silicagel (drying agent) into one arm of the tube and accurately weigh the tubes and the contents. Introduce then 9.5 g to 10.5 soda lime into the other arm of the tube and weigh again accurately.
- Fill tube 5 with silicagel.
- Put some loosely packed glass wool on the top of

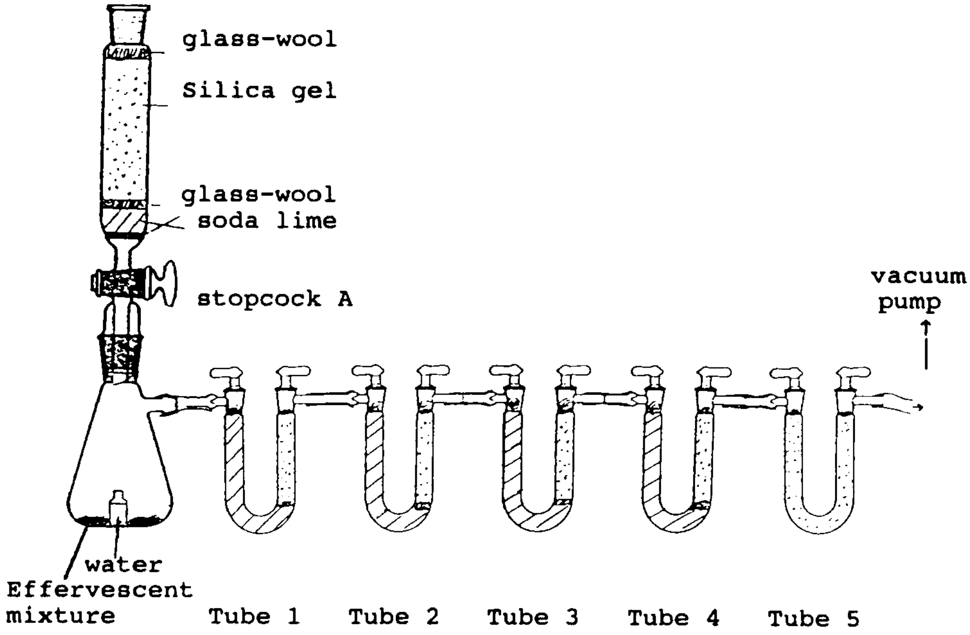


FIGURE 1

the tubes and insert the stoppers in their open arms. Connect them in a way that the side of the silicagel faces the pump.

- Cover the filter flask with the separating funnel and open both the stop-cock A and the stoppers of the tubes.
- Switch on the pump for 10 minutes. Then close the stoppers, disconnect the tubes and weigh individually 1-4. Add the four determinations (Wo).
- Connect again the tubes in the same order.
- Remove the funnel and place 0.7924 g sodium bicarbonate and 0.7075 g tartaric acid on the bottom of the filter flask, weighed with an accuracy of 0.01 mg.
- Fill a 10 ml glass vial with freshly boiled and

cooled water and place it on the bottom of the filter flask.

- Cover the filter flask with the funnel and open stop-cock A as well as those of the tubes.
- Switch on the vacuum pump and shake the filter flask gently to let the water pour over the sample.
- Stop the pump after ten minutes, close the stoppers, disconnect the tubes and weigh 1-4 again. Add up the four determinations (Wf).
- Calculate in grams the weight of CO_2 evolved by substracting Wf from Wo and the percentage in relation to the theoretical value:

$$\% = \frac{Wf - Wo}{0.4152} \cdot 100$$

In the <u>indirect gravimetric methods</u>, the amount of carbon dioxide released is determined by substraction of the sample weight after and before the effervescent reaction.

A classical method, described by Bermejo[5] is the gravimetric titrations of carbonates using the Schroedter alcalimeter.

Anderson et al.[6] recorded the effervescent reaction with a high sensitive balance. Brossa et al.[7] and Cuenya et al[8-9] designed several devices in order to make the weighing process easier.

In this work, the Schroedter alcalimeter (Fig. 2) is used in the following method:

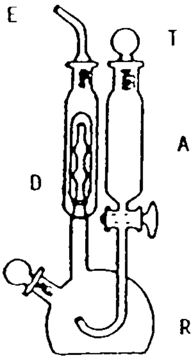


FIGURE 2

- Fill the drying container D with concentrated sulphuric acid till a third of its height.
- Stopper the evolving tube E and fill container A with 10 ml water.
- Introduce 0.7024 g sodium bicarbonate and 0.7075 g tartaric acid into chamber R, weighed with an accuracy of 0.01 mg. Weigh (Wo).
- Remove stopper T and add the water contained in A over the sample, drop by drop.
- When the effervescent reaction is finished, remove the stopper from tube E and connect it to the vacuum pump. In order to release the portion of carbon dioxide dissolved in the water, maintain the vacuum gently for 10 minutes.
- Replace stoppers E and T and weigh the whole device (Wf).
- Calculate in grams the weight of CO_2 evolved and the percentage in relation to the theoretical value:

$$\% = \frac{Wo - Wf}{0.4152} \cdot 100$$

The second of the indirect gravimetric methods used is based on that utilized by Anderson et al.[6] with the following technique (Fig. 3):

- Place 0.7924 g sodium bicarbonate and 0.7075 g tartaric acid into a 100 ml polypropylene beaker, weighed with an accuracy of 0.01 mg.
- Fill a 10 ml glass vial with freshly boiled and cooled water and put it on the bottom of the filter flask.
- Stopper the beaker with a high density polyethylene circular cover which has a rectangular slot (2.9 x 0.6 cm) in the center. Weigh (Wo).
- Shake the beaker gently to pour the water in the vial over the sample. Two hours later, weigh again (Wf).
- Calculate as in the alkalimetric method.

In order to verify the real need of the cover, the same method has been tested with no use of it.

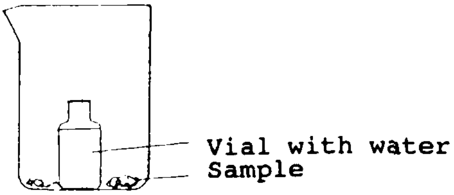


FIGURE 3

MANOMETRIC METHODS

They are based on the relationship between the volume of carbon dioxide released and the pressure generated in the closed system where the reaction is produced.

Anderson et al.[6] designed a device for effervescent tablets which uses this principle.

VOLUMETRIC METHODS

These methods are based on an acid-base titration.

The British Pharmaceutical Codex[10] describes one of these procedures for effervescent mouth-wash tablets. This technique had been used by Hepburn[11] in 1926 for the determination of carbon dioxide in carbonates. Hadgraft and Smith[12] use the same procedure in their studies for potassium salts effervescent tablets.

Edwards et al.[13] modified this methodology in 1935 to be applied to the analysis of baking powders and self-raising flours.

One year later Cornell[14] described a similar method, official in Australia since 1924, for the same kind of products.

Fig. 4 shows the setting-up of the device used in the British Pharmaceutical Codex[10]. In this work, the technique has been modified as follows:

- Transfer 0.2641 g sodium bicarbonate and

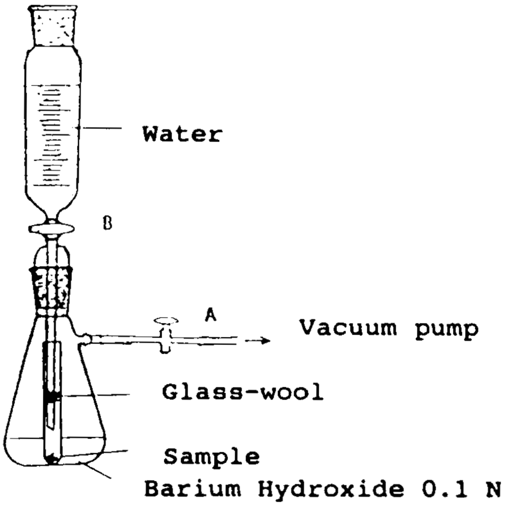


FIGURE 4

0.2358 g tartaric acid, weighed with an accuracy of 0.01 mg, to a test tube and insert a loose plug of glass wool about half way down the tube.

- Place the test tube in a filtering flask containing 75 ml of 0.1 N barium hydroxide.
- Cover the filtering flask with the separating funnel introducing the stem into the test tube.
- Fill the funnel with 30 ml water.
- Connect the pump and reduce the pressure as much as 20 mm mercury. Then close the exit tube.
- Add 10 ml water from the funnel.
- After 16 hours titrate the excess of barium hydroxide with 0.1 N oxalic acid using phenolphthalein solution as indicator.
- Repeat the procedure omitting the sample.
- The difference between both titrations represents the amount of barium hydroxide required

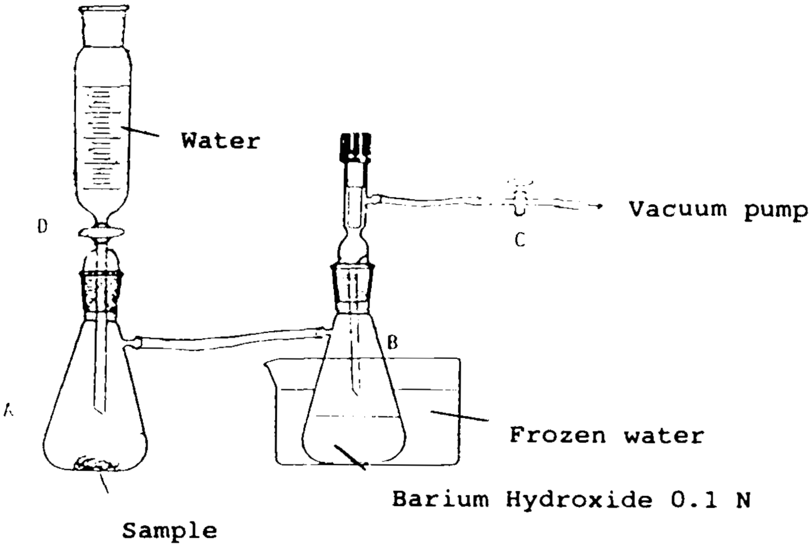


FIGURE 5

for the sample. Each ml. 0.1 N barium hydroxide is equivalent to 0.002201 g CO_2.

- Calculate the percentage of carbon dioxide released in relation to the theoretical value:

$$\% = \frac{g\ CO_2\ \text{released}}{0.1384\ g} \cdot 100$$

A modification of this technique is used by Cornell[14] whose device is shown in figure 5.

The sample is placed in flask A and the amount of 0.1 N barium hydroxide in flask B, both containers connected by a rubber tube. Titration of the excess of barium hydroxide is made only after 45 minutes.

GASOMETRIC METHODS

These methods determine directly the volume of gas produced in the effervescent reaction.

Rattray[17] applied one of these methods in the case of effervescent tablets in 1932.

The method used in this work is based on that of the Association of Official Agricultural Chemists[18], used in baking powders.

Recently the USP XXII[19] has modified both this device and the methodology in order to determine the content of carbonate in the sodium bicarbonate.

Faguet et al.[20,21] and Joachim et al.[22,23] had already applied this same technique in the field of the effervescent preparations.

Fig. 6 shows the equipment used. The procedure is as follows:

- Displacement solution: Dissolve 100 g sodium chloride in 350 ml water. Add 1 g sodium bicarbonate and 2 ml methylorange and then enough hydrochloric acid (1+2) to get only acid (decided pink). Stir until CO_2 is removed. This solution is used in the gas measuring tube and in the levelling bulb.
- Open stopcock A and use the levelling bulb to bring the displacement solution to the zero position (position B).
- Close the stopcock A and put 0.2641 g sodium bicarbonate and 0.2358 g tartaric acid into the round flask, weighed with an accuracy of 0.01 mg.
- Introduce a vial filled with 10 ml water into the flask.

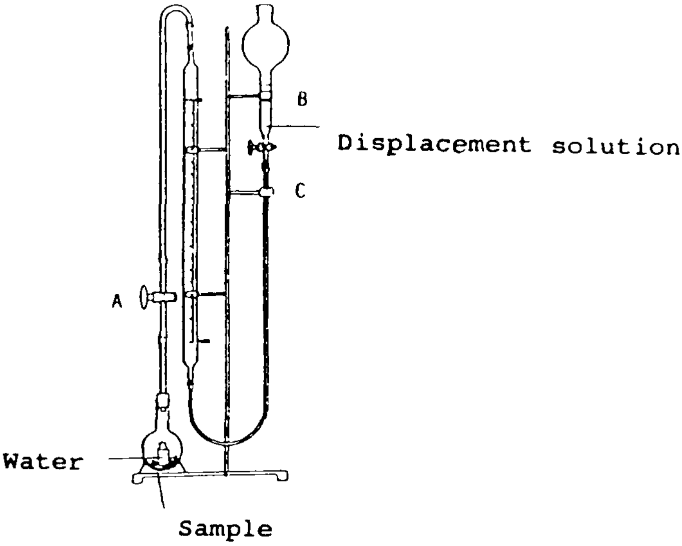


FIGURE 6

- Connect the flask to the device and open stopcock A. After 1 minute, no modification in the level of the displacement solution must be produced.
- Descend the levelling bulb to the position C in order to reduce the pressure in the apparatus. After 1 minute shake the flask gently to pour the water over the sample. Let the effervescence develop for 5 minutes.
- Shake the flask while the level of the displacement solution decreases.
- Place the levelling bulb in the position B and let it stand for 5 minutes. Record the volume read in the graduated tube which corresponds to the carbon dioxide produced.

- Calculate the percentage in relation to the theoretical value:

$$\% = \frac{V\ CO_2\ \text{evolved}}{70.45818\ \text{ml}} \cdot 100$$

COLORIMETRIC METHODS

These methods are based on the reaction between the CO_2 produced and an indicator system which modifies the colour intensity when the pH changes. Absorbance is determined and compared with a standard.

Landis[24] describes one of these methods to determine carbon dioxide in blood. The acid/base indicator is dissolved in a solution of carbonate/sodium bicarbonate at pH 8.85. The absorbance is measured at 430 mm.

Abd El Khalek and Abd El Azim[25] used a 1% w/v sodium bicarbonate solution with phenolphthalein.

RESULTS AND DISCUSSION

Table I summarizes the results obtained using different methods. The average of five determinations is shown besides the standard deviation (s) and the coefficient of variation (c.v.). Furthermore, the necessary time for every determination has been calculated.

TABLE I

Results obtained with the different methods used.

Method	Mean %	s %	c.v. %	Total time approx.
Direct Gravimetric	91.72	3.270	3.560	20 min
Polypropylene glass	114.80	1.830	1.590	2 h
Anderson	110.97	3.430	3.088	2 h
Alkalimetric	93.34	1.103	1.182	10 min
BPC Volumetric	95.98	0.359	0.374	32 h
Modified Cornell	49.54	0.782	1.600	45 min
Gasometric	97.22	1.588	1.633	12 min

The gravimetric method seems to be valid but it maybe lacks enough accuracy or precision. One of the most important disadvantages is the low comfort of the device and the great number of necessary weights to carry it out.

The results obtained by the direct gravimetric methods demonstrate that in some way, the water evaporates in the effervescent reaction and therefore, its weight is added to the carbon dioxide produced.

Using a blank is not a solution. In this case the water evaporation is very low because the effervescent reaction is not produced.

The method used by Anderson et al[6] is excellent to study the kinetics of the reaction during the first minutes but it is not very effective to get to know the total amount of carbon dioxide produced.

In the alcalimetric method, the water is taken by the sulphuric acid and thus, the determination is more accurate and exact.

This procedure is very easy although the device is difficult to clean and dry, which represents a big drawback to proceed to succesive determinations.

The volumetric method of the British Pharmaceutical Codex is exact and accurate. However, it takes a long time. With this kind of methods, it seems necessary to invest a long time to be sure that the total liberation of CO_2 has been produced. That could be the reason for the low recovery in the method of Cornell, which uses only 45 minutes. The low coefficient of variation seems to be in accordance to this argument.

The results obtained by the gasometric method are excellent. They are the closest results to the theoretical values and with a very small variation. Moreover, determinations are very quick and the device is easy to clean. So this method seems the most suitable in the case of multiple determinations.

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