

## ARTICLES

# Simple Chemical Method for the Determination of Carbon Dioxide in Air

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**Abstract**—A method was proposed for the direct determination of carbon dioxide in air using a sorption tube specially constructed for this purpose. The method is based on measuring the volume of air consumed for the neutralization of a known amount of barium oxide hydrate in the tube by carbon dioxide contained in air. The equivalence point is detected by the minimum electrical conductance of the barium hydroxide solution. To verify the accuracy of the method, a technique based on the use of a calibration mixture of air with the CO<sub>2</sub> concentration varying by the inverse exponential law was developed. The method is suitable for the determination of CO<sub>2</sub> in air in a wide concentration range and for the verification and calibration of indirect methods for the determination of CO<sub>2</sub>. With an insignificant decrease in accuracy, the equivalence point can be detected by the change in the color of phenolphthalein. This significantly simplifies the method and allows its wide use in practice, e.g., in laboratory works in environmental science or for demonstration purposes in educational organizations.

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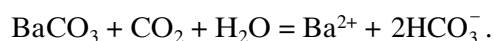
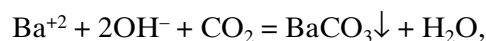
The determination of carbon dioxide in air was always an important practical problem. It became particularly important in recent decades because of the studies of the greenhouse effect [1]. However, because of the low concentration of CO<sub>2</sub> in air (normally about 0.03 vol %), its accurate determination is a rather difficult problem. Errors in the determination of CO<sub>2</sub> by many methods reported in the literature are so large that they exceed its normal concentration in the atmosphere [2, 3]. The majority of methods are suitable only for the determination of increased concentrations of CO<sub>2</sub> in air, e.g., for the estimation of the degree of gas contamination of rooms in plant workshops, the concentration of CO<sub>2</sub> in vegetable stores, in fires, etc. Methods based on chemical, physicochemical, and physical principles are used for the determination of CO<sub>2</sub> in air [4]. The concentration of CO<sub>2</sub> in aqueous solutions is frequently determined using enzymatic reactions [5, 6].

Because of difficulties in the direct detection of the equivalence point for the interaction of low concentrations of CO<sub>2</sub> with reagents, the two-step titration method is most frequently used among chemical methods for the determination of CO<sub>2</sub>. Within this method, first an aliquot portion of a solution of barium hydroxide of known concentration is partially neutralized with carbon dioxide contained in a known volume of air, and next residual Ba(OH)<sub>2</sub> is titrated with a reference solution of acid [7, 8]. The two-step character of the method complicates the work and decreases its performance and the accuracy of determination.

Known instrumental methods [4], such as determination by the change in the electrical conductance of

water on its equilibrium saturation with CO<sub>2</sub> in the electroconductometric method, by the release of heat on the neutralization of alkali in the thermochemical method, or by the absorption of infrared radiation in infrared gas analyzers, have an advantage, which consists in a significant decrease in time consumption in serial determinations. However, these methods are indirect, because they require control at regular intervals with the use of calibration gas mixtures containing a known concentration of CO<sub>2</sub>. In addition, the instrumentation of these methods is rather expensive; hence, these methods cannot be called simple.

In this work, we propose a chemical method for the determination of CO<sub>2</sub> in air, which differs from the method mentioned above by a lower cost and simple implementation, being highly competitive with them in accuracy. The method is based on the detection of the equivalence point in the neutralization of an aqueous solution of Ba(OH)<sub>2</sub> by CO<sub>2</sub> contained in air by measuring the electrical conductance of the solution. The accurate detection of the equivalence point in this case is caused by the fact that CO<sub>2</sub> interacts with Ba(OH)<sub>2</sub> in two reactions proceeding successively [9]:



From the equations of the reactions, it follows that, at the first step of CO<sub>2</sub> absorption, barium and hydroxyl ions are removed from the solution because of the formation of a barium carbonate precipitate, which leads to a decrease in the electrical conductance of the solu-

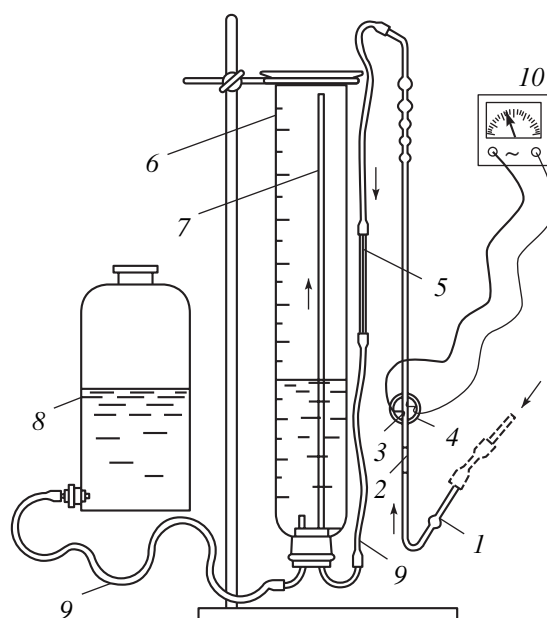
tion. At the second step, as the  $\text{BaCO}_3$  precipitate transforms into  $\text{Ba}(\text{HCO}_3)_2$  and the latter dissociates into  $\text{Ba}^{2+}$  and  $\text{HCO}_3^-$  ions, the electrical conductance of the solution increases. Therefore, the minimum electrical conductance will be observed on attaining the equivalence point between the amount of absorbed  $\text{CO}_2$  and the initial amount of  $\text{Ba}^{2+}$  cations in the solution. Evidently, it is easy to detect this point by measuring the electrical conductance of the solution and, thus, to determine the amount of  $\text{CO}_2$  consumed for the formation of  $\text{BaCO}_3$ . The high initial concentration of  $\text{Ba}(\text{OH})_2$  in the solution and the high affinity of residual carbonic acid for the  $\text{Ba}^{2+}$  cation provide the complete recovery of low concentrations of  $\text{CO}_2$  from air. All these facts allow the development of a one-step method for the determination of  $\text{CO}_2$  in air.

## EXPERIMENTAL

**Instrument and procedure.** For the implementation of the method, we developed an instrument which provided the simultaneous solution of three problems: (1) the complete absorption of  $\text{CO}_2$  from air by a  $\text{Ba}(\text{OH})_2$  solution, (2) the measurement of the volume of air passed through the  $\text{Ba}(\text{OH})_2$  solution, and (3) the measurement of the electrical conductance of the solution. As seen in Fig. 1, the design of the instrument is extremely simple. It can be assembled at nearly any laboratory possessing experience in operation with laboratory glassware.

The central part of the instrument is a glass tube (inner diameter 2.5–3.5 mm), in which  $\text{CO}_2$  is adsorbed from air. The lower part of the tube is bent and supplied with a spherical cavity so that the resulting leg could contain the required volume of a  $\text{Ba}(\text{OH})_2$  solution (from 40 to 1600  $\mu\text{L}$ ). The upper part is supplied with spherical cavities as bulbs limiting the exit of liquid from the tube. Carbon dioxide is adsorbed at the inner surface of the tube wetted with the column of the  $\text{Ba}(\text{OH})_2$  solution, which moves upward through the tube as air arrives into it. On arriving at spherical cavities in the upper part of the tube, the column of liquid expands and, turning into a film, breaks. The released liquid flows down along the walls towards the arriving air and produces the counterflow absorption effect. It was found experimentally that a tube with a length of 500–700 mm at a flow rate of air of 15–20 mL/min provides the complete absorption of  $\text{CO}_2$ . To restrict the maximum flow rate of air, a glass capillary was inserted between the sorption tube and the graduated cylinder. The length and diameter of the capillary were selected experimentally.

To preclude the effect of expired air on the concentration of  $\text{CO}_2$ , air was taken no closer than one meter from the head of the experimentalist. For this purpose,



**Fig. 1.** Instrument for the determination of  $\text{CO}_2$  in air: (1) sorption tube, (2) aliquot portion of a  $\text{Ba}(\text{OH})_2$  solution, (3) platinum electrodes, (4) enforcement ribs, (5) glass capillary, (6) volumetric cylinder, (7) glass tube inside the cylinder, (8) glass vessel for pressure equilibration, (9) red-rubber hoses, and (10) conductometer. Arrows indicate the motion of analyzed air in the instrument.

a glass or rubber tube of the corresponding length was attached to the lower end of the sorption tube.

The electrical conductance of the solution in the tube was measured with two platinum-wire electrodes sealed in the walls of the tube. To strengthen the part with sealed electrodes, enforcement ribs as two glass loops were soldered to the tube from above and from below. Electrical conductance was measured in the upper part of the column of the solution free from the precipitate as it reached the level of electrodes. A bridge circuit (Wheatstone bridge) [10] operating from acoustic frequency current generated by the phone line or a standard Radelkis Type OK-102/1 conductometer was used for the measurement.

The volume of air passed through the tube was measured with the use of an inverted graduated cylinder filled with water (Fig. 1). Air was fed from the sorption tube into the upper part of the cylinder using a thin glass tube passed through the whole length of the cylinder. Air feed into the cylinder was provided by decreased pressure inside the cylinder due to the weight of the water column. Water displaced from the cylinder was collected in a special vessel connected with the cylinder by a rubber tube.

The volume of air fed into the cylinder was determined as the difference between the levels of water in the cylinder before and after its displacement with air

multiplied by the coefficient  $k$ , which takes into account the volume of the tube inside the cylinder:

$$V_c = V - Vd^2/D^2 = Vk, \quad (1)$$

where  $V_c$  is the true volume of air saturated with water vapor that was fed into the cylinder;  $V$  is the apparent volume of air fed into the cylinder, which was measured by cylinder graduation without taking the volume of the tube inside the cylinder into consideration;  $d$  is the outer diameter of the tube inside the cylinder;  $D$  is the inner diameter of the cylinder; and  $k = 1 - d^2/D^2$ .

Volume was measured on the equalization of pressure in the cylinder and atmospheric pressure by lifting the vessel to align the levels of water in the vessel and in the cylinder.

To eliminate the effect of oscillations of air humidity on the results of measurements, the concentration of  $\text{CO}_2$  was converted to dry air. Because the relative humidity of air in the volumetric cylinder over water is always 100%, the volume of dry air will be equal to the difference between the volume of humid air and the volume occupied by water vapor at the temperature of measurement. For the calculation of the volume of dry air, we used the Boyle–Mariotte law, according to which the following equation can be written for water vapor at a constant temperature:

$$(V_c - V_a)P = V_c p_s,$$

where  $V_a$  is the volume of dry air in the cylinder without  $\text{CO}_2$ ;  $P$  is atmospheric pressure; and  $p_s$  is the pressure of saturated water vapor.

Transforming this equation, we obtain a formula for the calculation of the volume of dry air in the cylinder free from  $\text{CO}_2$ :

$$V_a = V_c(1 - p_s/P) = V_c h, \quad (2)$$

where  $h = 1 - p_s/P$ .

The pressure of saturated water vapor  $p_s$  was found in the handbook [11]. In the range from 20 to 30°C, the value of  $p_s$  varies from 0.024 to 0.043 atm.

Substituting the value of  $V_c$  from formula (1) into formula (2), we obtain an expression for the calculation of  $V_a$ :

$$V_a = Vkh. \quad (3)$$

The detailed formula for the calculation of the experimentally determined concentration of  $\text{CO}_2$  in volume percent converted to dry air was deduced from the following relationship:

$$c = 100V_{\text{CO}_2}/(V_a + V_{\text{CO}_2}) = 100/(V_a/V_{\text{CO}_2} + 1), \quad (4)$$

where  $c$  is the experimentally determined concentration of  $\text{CO}_2$  converted to dry air in volume percent and  $V_{\text{CO}_2}$  is the volume of  $\text{CO}_2$  absorbed from air.

The volume of absorbed  $\text{CO}_2$  for the given temperature was calculated from the concentration and volume

of the  $\text{Ba}(\text{OH})_2$  solution by the Mendeleev–Clapeyron equation:

$$V_{\text{CO}_2} = C_{\text{Ba}(\text{OH})_2} V_{\text{Ba}(\text{OH})_2} RT/P, \quad (5)$$

where  $R$  is the universal gas constant 0.0821 L atm  $\times$  mol<sup>-1</sup> K<sup>-1</sup>;  $T$  is absolute temperature (K);  $P$  is atmospheric pressure (atm);  $C_{\text{Ba}(\text{OH})_2}$  is the initial concentration of  $\text{Ba}(\text{OH})_2$  in the solution (M); and  $V_{\text{Ba}(\text{OH})_2}$  is the volume of the  $\text{Ba}(\text{OH})_2$  solution placed in the sorption tube (L).

Substituting the value of  $V_{\text{CO}_2}$  from formula (5) and the value of  $V_a$  from formula (3) into formula (4), we obtain expression (6) for the accurate calculation of the volume percentage of  $\text{CO}_2$  in dry air from the volume of air displacing water from the cylinder, which was measured by cylinder graduation (1):

$$c = 100/(PVkh/(RTC_{\text{Ba}(\text{OH})_2} V_{\text{Ba}(\text{OH})_2}) + 1). \quad (6)$$

In the case when the concentration of  $\text{CO}_2$  in air is below 0.1 vol %, the difference between the volumes of air with and without  $\text{CO}_2$  can be neglected in calculations. As a result, relationship (4) is simplified:

$$c \approx 100V_{\text{CO}_2}/V_a. \quad (7)$$

Substituting the value of  $V_{\text{CO}_2}$  from formula (5) and the value of  $V_a$  from formula (3) into relationship (7), we obtain a simplified formula for the approximate calculation of the volume percentage of  $\text{CO}_2$  in dry air:

$$c = 100C_{\text{Ba}(\text{OH})_2} V_{\text{Ba}(\text{OH})_2} RT/(PVkh). \quad (8)$$

**Preparation of a calibration mixture with the variable concentration of  $\text{CO}_2$ .** To estimate the accuracy of the method at different concentrations of  $\text{CO}_2$  in air, it is necessary to have standard calibration mixtures. However, commercially available mixtures have insufficient accuracy. Thus, calibration mixtures for the calibration of  $\text{CO}_2$  analyzers produced by the Russian company Praktik-NTs are mixtures of  $\text{CO}_2$  and nitrogen in which the permissible error in the concentration of  $\text{CO}_2$  is  $\pm 0.01\%$  of the total volume of the mixture (State Register no. 3795-87). Taking into account that the normal concentration of  $\text{CO}_2$  in the atmosphere is about 0.03%, it should be accepted that standard calibration mixtures do not exhibit sufficient accuracy for their use in the determination of  $\text{CO}_2$  in atmosphere.

Therefore, we developed our own technique for the verification of the proposed method. The specific feature of this method is that all manipulations with mixture components are performed at atmospheric pressure; hence, there is no need for the use of special instruments for the preparation of gas mixtures.

The problem is that a gas mixture with a low concentration of one of the components can hardly be prepared with the required accuracy in vessels with soft

walls because of the difficulties in measuring volume and a significant permeability of the majority of polymer materials for gases [12]. These mixtures can be rather easily prepared at atmospheric pressure in vessels with hard walls; however, they can hardly be transferred to the place of the reaction without changing the concentration of the microcomponent. The fact is that the displacement of a gas mixture with aqueous solutions from a vessel with hard walls is commonly accompanied by a change in the concentration of the microcomponent because of its uncontrolled dissolution in the displacing solution.

These difficulties can be avoided by replacing calibration mixtures which have a constant concentration of  $\text{CO}_2$  with mixtures with a concentration varying by the inverse exponential law. These mixtures can easily be prepared with the required accuracy and readily calculated theoretically. An air flow with the exponential dependence of the concentration of  $\text{CO}_2$  on the volume of passed air is formed by nearly the same technique as the exponential gradient of salt concentration in an eluent in chromatography [13]. For this purpose, air purified from  $\text{CO}_2$  was passed through a round-bottom flask with a known concentration of  $\text{CO}_2$  (Fig. 2). As purified air arrives at the flask, air is mixed with the contents of the flask gradually diluting it and, as demonstrated below, the concentration of  $\text{CO}_2$  at the outlet is given by the inverse exponential dependence on the passed volume.

To deduce the theoretical dependence of the concentration of  $\text{CO}_2$  on the volume of passed air, we used the differential equation describing this process. If air purified from  $\text{CO}_2$  is delivered to the inlet of a flask with the volume  $V_f$  and some concentration of  $\text{CO}_2$   $c'$  and the contents of the flask are stirred as shown in Fig. 2, the amount of  $\text{CO}_2$  in an infinitely small volume of the mixture  $dV_m$  at the outlet of the flask will be expressed by the product  $c'dV_m$ , and the infinitely small decrease in the amount of  $\text{CO}_2$  in the flask will be expressed by the product  $-V_f dc'$ . As a result, the following equation can be written:

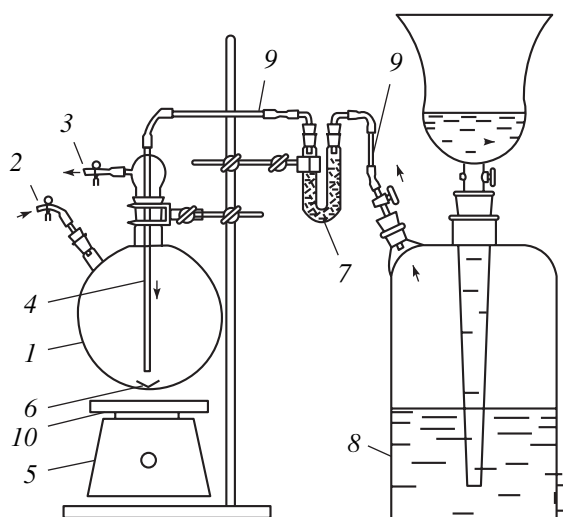
$$c'dV_m = -V_f dc'. \quad (9)$$

Integrating Eq. (9) at the initial conditions  $V_m = 0$  and  $c' = c'_0$ , we obtain the following dependence of  $c'$  on  $V_m$ :

$$\ln c' = -V_m/V_f + \ln c'_0. \quad (10)$$

Because the volume of air saturated with moisture after the removal of  $\text{CO}_2$  in the adsorption tube is measured in the graduated cylinder, the total volume  $V_m$  should be calculated as the sum of the volume of air in the cylinder converted to dry air by formula (3) and the volume of absorbed  $\text{CO}_2$ :

$$V_m = V_a + V_{\text{CO}_2}, \quad (11)$$



**Fig. 2.** Device for the preparation of a calibration mixture with the variable concentration of  $\text{CO}_2$ : (1) mixing flask, (2) nozzle for feeding the initial portion of  $\text{CO}_2$ , (3) nozzle for discharging the variable concentration of  $\text{CO}_2$ , (4) tube for feeding dry air purified from  $\text{CO}_2$  into the flask, (5) magnetic stirrer, (6) rotating tin plate, (7) U-shaped tube with anhydrous calcium chloride, (8) gasometer with a 5% KOH solution, (9) glass connecting tubes, and (10) heat-insulating foam-plastic screen. Arrows indicate the initial  $\text{CO}_2$  feeding and the motion of air in the device.

where  $V_a$  is the volume of air in the cylinder converted to dry air;  $V_{\text{CO}_2}$  is the volume of absorbed  $\text{CO}_2$ .

Because  $V_{\text{CO}_2} = V_c c'/100$ , its substitution into expression (11) and the transformation of the latter gives the following value:

$$V_m = V_a / (1 - c'/100). \quad (12)$$

Substituting the value of  $V_m$  into Eq. (10) and transforming it, we obtain the expression for the concentration of  $\text{CO}_2$   $c'$  as a function of its initial concentration in the flask  $c'_0$  divided by the exponent of the expression involving the volume of dry air  $V_a$ , the volume of the flask  $V_f$ , and the desired concentration  $c'$ :

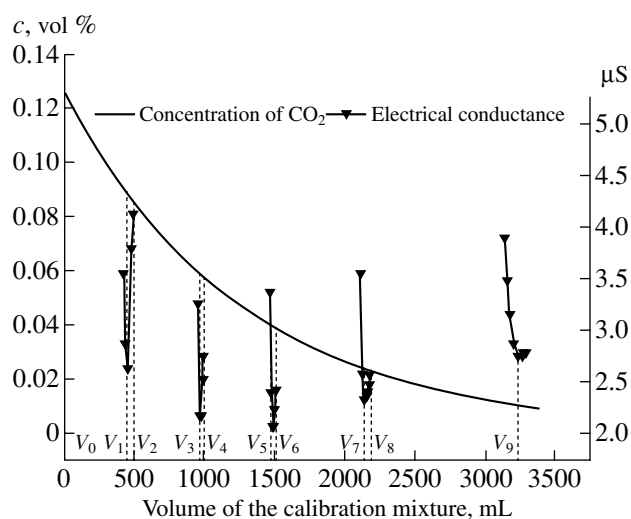
$$c' = c'_0 / \exp[V_a / (V_f(1 - c'/100))]. \quad (13)$$

At low concentrations of  $\text{CO}_2$  in air, e.g., below 0.1%, the value of  $c'$  in the right-hand part of Eq. (13) can be neglected and, as a result, it takes a simpler form:

$$c' = c'_0 / \exp(V_a/V_f). \quad (14)$$

Substituting the value of  $V_a$  according to expression (3) into formula (14), we obtain a formula for the calculation of the concentration of  $\text{CO}_2$  in dry air from the apparent volume of air saturated with moisture, which is measured by cylinder graduation:

$$c' = c'_0 / \exp(Vkh/V_f). \quad (15)$$



**Fig. 3.** Curves of the variation of electrical conductance of aliquot portions of a barium hydroxide solution in the course of their titration in the sorption tube with the calibration mixture of air with the concentration of CO<sub>2</sub> decreasing by the inverse exponential relationship.

The graphical form of relationship (15) is presented in Fig. 3. According to the figure, the volumes of CO<sub>2</sub> in portions of calibration mixture emerging from the flask are determined by the areas under the curve limited by values of the volumes of the mixture in the horizontal axis  $V_0, V_1, V_2, V_3, \dots, V_n, V_{n+1}, \dots$ , etc. Volumes of CO<sub>2</sub> can be calculated theoretically by the integration of expression (15) in the corresponding limits or determined experimentally by the method described in the previous section. By dividing the volumes of CO<sub>2</sub> by the volumes of the portions of the calibration mixture emerging from the flask, we obtain the average concentrations of CO<sub>2</sub> in the volumes expressed by the differences of the volumes corresponding to the integration limits of the segments of the curve. The comparison of the theoretical average concentrations of the volumes of CO<sub>2</sub> with those determined experimentally allows the estimation of the accuracy of the proposed method. The exponential dependence of the concentrations of CO<sub>2</sub> on the passed volume of the calibration mixture assumes a significant change in the average concentrations of CO<sub>2</sub> on going from one fragment of the area under the curve to another. This fact was used for the estimation of the accuracy of the method in a wide range of CO<sub>2</sub> concentrations.

The formula for the theoretical calculation of average concentrations of CO<sub>2</sub> in portions of air emerging from the flask can be obtained not only by the volume integration of expression (15) and the subsequent division of the result of integration by the volume of the emerged portion of air but also by a simpler technique. Namely, the average concentration of CO<sub>2</sub> can be calculated as the product of the volume of the flask  $V_f$  by

the difference between the initial ( $c'_n$ ) and final ( $c'_{n+1}$ ) concentration of CO<sub>2</sub> in the flask divided by the volume of the portion of dry air emerged from the flask. This volume is determined as the difference of the final and initial volumes of air measured by the cylinder graduation multiplied by the coefficients involving the volume of the tube in the cylinder and air humidity according to formula (3):

$$(V_{n+1} - V_n)kh.$$

As a result, the following formula is obtained for the calculation of the average concentration of CO<sub>2</sub>:

$$c'_{av} = (c'_n - c'_{n+1})V_f / (V_{n+1} - V_n)kh. \quad (16)$$

Substituting the values of  $c'_n$  and  $c'_{n+1}$  calculated by formula (15) into Eq. (16) and taking into account that  $c'_0 = 100V'_{CO_2} / V_f$ , where  $V'_{CO_2}$  is the initial volume of CO<sub>2</sub> introduced into the flask, we obtain an expanded formula for the theoretical calculation of the average concentration of CO<sub>2</sub> in portions of air passed through the sorption tube:

$$c'_{av} = 100V'_{CO_2} [\exp(-V_n kh / V_f) \quad (17)$$

$$- \exp(-V_{n+1} kh / V_f)] / [(V_{n+1} - V_n)kh].$$

For the more accurate calculation of average theoretical concentrations of CO<sub>2</sub> within the integration limits  $V_n$  and  $V_{n+1}$ , we first determined the values of  $c'_n$  and  $c'_{n+1}$  by approximate formula (15) and next divided the values of  $V_n$  and  $V_{n+1}$  in formula (17) by  $1 - c'_n / 100$  and  $1 - c'_{n+1} / 100$ , respectively, according to formula (12). As a result, the formula for the calculation of accurate values of average theoretical concentrations of CO<sub>2</sub> takes the form

$$c'_{av} = 100V'_{CO_2} \{ \exp[-V_n kh / (V_f(1 - c'_n / 100))] - \exp[-V_{n+1} kh / (V_f(1 - c'_{n+1} / 100))] \} / \{ [V_{n+1} / (1 - c'_{n+1} / 100) - V_n / (1 - c'_n / 100)] kh \}. \quad (18)$$

Correspondingly, for the calculation of average experimental values of the concentrations of CO<sub>2</sub>  $c'_{av}$  obtained on the basis of the data on the titration of Ba(OH)<sub>2</sub> with the calibration mixture in the sorption tube, the values of  $V$  in formulas (6) and (8) must be replaced by the difference  $V_{n+1} - V_n$ .

**Reagents and conditions of determinations.** For the absorption of CO<sub>2</sub>, we used a nearly saturated solution of Ba(OH)<sub>2</sub> prepared from a domestic compound of the chemically pure grade and filtered from BaCO<sub>3</sub> impurities. The exact concentration of Ba(OH)<sub>2</sub> in the solution was determined by titration with standard solutions of hydrochloric or sulfuric acid with the detection of the equivalence point with a potentiometer.



The solution was stored in a tightly closed flask. In the determination of  $\text{CO}_2$ , the exact volume of the solution was taken with a calibrated pipette or a syringe (Hamilton) and placed in the lower leg of the sorption tube. After that, it was diluted to the required volume with water so that the concentration of  $\text{Ba}(\text{OH})_2$  was within 0.1–0.02 M.

Initial  $\text{CO}_2$  for the preparation of a mixture of air with the initial concentration of  $\text{CO}_2$   $c'_0$  in the flask was obtained by the neutralization of edible sodium hydrogen carbonate with a 30% solution of sulfuric acid directly in the gasometer. The concentration of impurity gases in initial  $\text{CO}_2$  was determined by placing the open end of a pipette filled with  $\text{CO}_2$  into a concentrated solution of potassium hydroxide (20–30%). The solution of potassium hydroxide rose through the pipette until  $\text{CO}_2$  was completely absorbed. On attaining equilibrium, the volume of the pipette free from alkali indicated the concentration of neutral impurity gases. Commonly it was within 0.5–5%. On the basis of the obtained data, the true volume of  $\text{CO}_2$  introduced into the system  $V'_{\text{CO}_2}$  was calculated. Initial  $\text{CO}_2$  was introduced with the necessary precautions into a mixing flask of the device for preparing a calibration mixture using a calibrated medical syringe. The volume of the flask was determined from the difference in its weight before and after filling with water. To decrease the sorption of  $\text{CO}_2$  and water at the walls of the flask, the inner surface of the flask was treated with a 1% solution of dimethyldichlorosilane in benzene, next dried in a drying oven, repeatedly washed with distilled water, and again dried for a day. To remove  $\text{CO}_2$  traces, the flask was evacuated before admitting air purified of  $\text{CO}_2$ .

Air free from  $\text{CO}_2$  was prepared by keeping atmospheric air in a gasometer over a 5% solution of KOH of the analytical grade at least for an hour. To remove water vapor from air, at the outlet of the gasometer it was passed through a U-shaped tube filled with anhydrous  $\text{CaCl}_2$ . For use in experiments, air was displaced from the gasometer by filling it through a funnel with a 1% KOH solution.

To ensure the complete absorption of  $\text{CO}_2$  in the sorption tube and, thus, to eliminate the error in the determination of its concentration, the flow rate of air through the system was limited to 20 mL/min at the initial steps and decreased to the minimum (<1 mL/min) at the equivalence point. The decrease in the flow rate of gas to the required values on approaching the equivalence point was attained by the vertical displacement of the equilibrating vessel to bring the level of water in it closer to the level of water in the volumetric cylinder corresponding to the end of the reaction.

Calculations and the construction of plots were performed by the Origin program.

## RESULTS AND DISCUSSION

Figure 3 presents five curves of the dependence of the electrical conductance of the  $\text{Ba}(\text{OH})_2$  solution on the volume of the calibration mixture passed through the sorption tube and containing  $\text{CO}_2$  with the concentration varying by the inverse exponential law.

From the shapes of the curves, it is seen that, with increasing volume of the calibration mixture, the electrical conductance of the solution decreases and reaches the minimum at the point of equivalence of absorbed  $\text{CO}_2$  and the amount of  $\text{Ba}(\text{OH})_2$  in the tube. Further absorption of  $\text{CO}_2$  leads to the dissolution of resulting  $\text{BaCO}_3$  with the formation of  $\text{Ba}^{2+}$  ions and hydrogen carbonate. As a result, the electrical conductance of the solution begins to increase.

The volumes of the calibration mixture passed through the sorption tube that correspond to the equivalence point were determined by the position of the minimum in electrical conductance curves.

For the concentration range from 0.01 to 0.11%, the experimental and theoretical values of the average concentrations of  $\text{CO}_2$  in portions of gas were calculated by approximate formula (8) and by formula (17) without regard for the volume of  $\text{CO}_2$ , respectively. The results of calculations are presented in Table 1. For clearness, the same data is presented as a plot in Fig. 4a. As follows from Table 1, the difference between the theoretical and experimental values of the concentrations of  $\text{CO}_2$  in the entire range of measurements is no more than 2% of the initial specified concentration  $c'_0$ . It is also seen in the figure that the values of concentrations calculated from the experimental data closely fit the theoretical straight line.

Even better results were obtained in the determination of the concentration of  $\text{CO}_2$  in the range from 0.1 to 0.9%. Average experimental concentrations were calculated by exact formula (6). Average theoretical concentrations were calculated by formula (18) involving corrections for the volume of  $\text{CO}_2$ . As seen in Table 2, the difference between the experimental and theoretical data in this case is no more than 1% of the initial specified concentration  $c'_0$ . Visually in Fig. 4b, this is seen as the nearly complete coincidence of the experimental points with the theoretical straight line.

In plots, the theoretical values of concentrations based on the initial parameters of the preparation of the calibration mixture are used as reference. However, the observed discrepancy between the theoretical and experimental values is equiprobably contributed by both errors of the method and errors in the preparation of the calibration mixture, which cannot be attributed to the method. Therefore, the actual accuracy of the determination of the concentration of  $\text{CO}_2$  by the proposed method can be higher.

The sensitivity of the method was sufficient to find the permeability of silicone-rubber hoses for atmo-

**Table 1\*.** Experimental ( $c_{av}$ ) and theoretical ( $c'_{av}$ ) values of average concentrations of CO<sub>2</sub> in portions of the calibration mixture determined in the concentration range from 0.01 to 0.11 vol % (see Fig. 4a)

$V_{\text{Ba(OH)}_2}$ , mL	$V_n$ , mL	$V_{n+1}$ , mL	$c_{av}$ , vol/vol%	$c'_{av}$ , vol/vol%	$\Delta$ , %
0.100	0	450	0.1095	0.1074	1.6
0.070	500	970	0.0734	0.0742	-0.6
0.050	995	1495	0.0493	0.0512	-1.5
0.040	1513	2146	0.0311	0.0336	-1.9
0.035	2188	3238	0.0164	0.0179	-1.2

\* Values of  $c_{av}$  and  $c'_{av}$  in vol % were calculated by formulas (8) and (17), respectively. In these calculations,  $k = 0.993$ ,  $h = 0.966$ ,  $T = 299.2$  K,  $c_{\text{Ba(OH)}_2} = 0.1875$  M,  $P = 0.974$  atm,  $V_f = 1320$  mL,  $V'_{\text{CO}_2} = 1.662$  mL,  $R = 0.0821$  L atm mol<sup>-1</sup> K<sup>-1</sup>,  $V = V_{n+1} - V_n$ , and  $\Delta$ , % =  $(c_{av} - c'_{av})V_f/V'_{\text{CO}_2}$ .

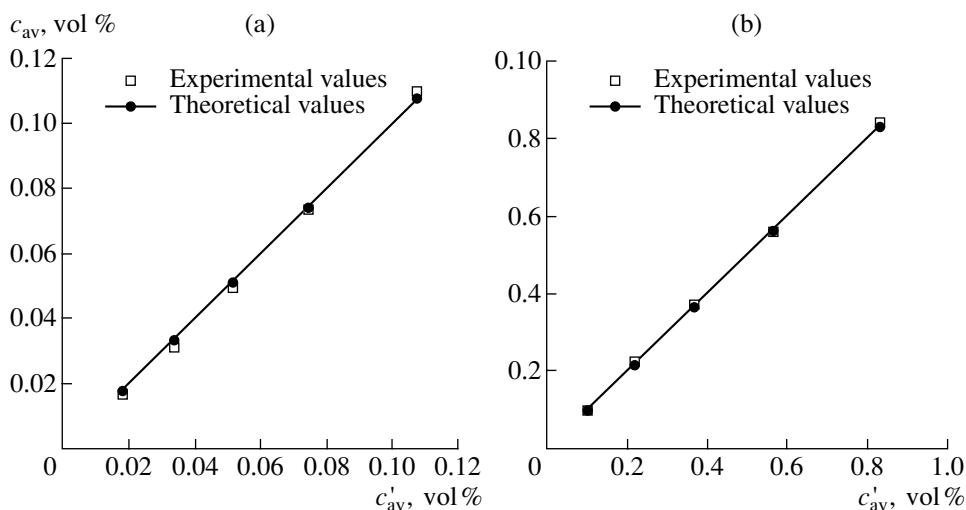
**Table 2\*\*.** Experimental ( $c_{av}$ ) and theoretical ( $c'_{av}$ ) values of average concentrations of CO<sub>2</sub> in portions of the calibration mixture determined in the concentration range from 0.1 to 0.9 vol % (see Fig. 4b)

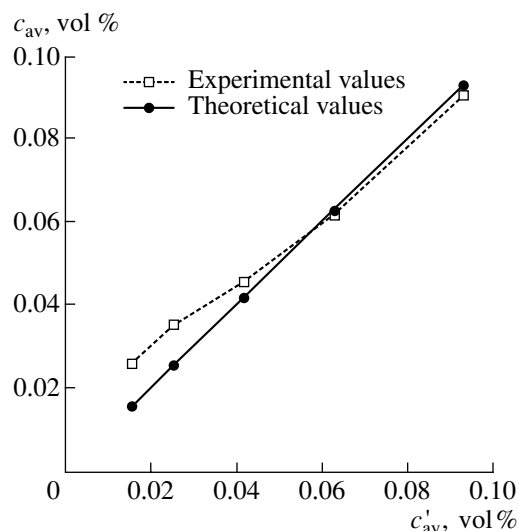
$V_{\text{Ba(OH)}_2}$ , mL	$V_n$ , mL	$V_{n+1}$ , mL	$c'_n$ , vol/vol%	$c'_{n+1}$ , vol/vol%	$c_{av}$ , vol/vol%	$c'_{av}$ , vol/vol%	$\Delta$ , %
0.817	0	465	0.9852	0.7012	0.8433	0.8342	0.92
0.619	500	1030	0.6835	0.4638	0.5606	0.5650	-0.44
0.462	1060	1655	0.4538	0.2937	0.3728	0.3667	0.61
0.360	1700	2480	0.2841	0.1606	0.2216	0.2160	0.57
0.262	2530	3830	0.1548	0.0598	0.0968	0.0998	-0.30

\*\* Values of  $c'_n$  and  $c'_{n+1}$  in vol % were calculated by formulas (15). Values of  $c_{av}$  and  $c'_{av}$  in vol % were calculated by formulas (6) and (18), respectively. In these calculations,  $k = 0.993$ ,  $h = 0.972$ ,  $T = 296.2$  K,  $c_{\text{Ba(OH)}_2} = 0.1875$  M,  $P = 0.984$  atm,  $V_f = 1320$  mL,  $V'_{\text{CO}_2} = 13$  mL,  $R = 0.0821$  L atm mol<sup>-1</sup> K<sup>-1</sup>,  $V = V_{n+1} - V_n$ , and  $\Delta$ , % =  $(c_{av} - c'_{av})V_f/V'_{\text{CO}_2}$ .

spheric CO<sub>2</sub>. As a result of the penetration of CO<sub>2</sub> from air through hose walls into the system at concentrations of CO<sub>2</sub> in the system lower than room concentration and the removal of CO<sub>2</sub> from the system at concentra-

tions higher than room concentration, the plot of the dependence of the experimental concentration of CO<sub>2</sub> substantially deviates from the theoretical straight line, as seen in Fig. 5. As the concentrations of CO<sub>2</sub> in the

**Fig. 4.** Comparison of average experimental values of the concentration of CO<sub>2</sub> with theoretical values in portions of the calibration mixture in the concentration ranges (a) from 0.01 to 0.11 vol % (data from Table 1) and (b) from 0.1 to 0.9 vol % (data from Table 2).



**Fig. 5.** Discrepancies between the experimental and theoretical values of average concentrations of  $\text{CO}_2$  in portions of the calibration mixture as a result of the diffusion of  $\text{CO}_2$  through the wall of silicone-rubber connecting tubes.

system and in room air (0.057 vol %) become equal, the experimental curve crosses the theoretical curve. It was also demonstrated that the rate of  $\text{CO}_2$  exchange with the environment increases proportionally to the length of the silicone-rubber hose. The replacement of hoses with glass tubes and the use of glass tubes for joining hoses of ordinary red rubber eliminated the error in the determination caused by the permeability of silicone-rubber hoses.

In the cases when accuracy characterized by a relative error higher than 5% is not required, the phenolphthalein indicator can be used instead of electrical conductance measurements for the determination of the equivalence point in the neutralization of  $\text{Ba}(\text{OH})_2$  in the sorption tube. The accuracy of the determination of  $\text{CO}_2$  increases if a color-calibrated reference is used for the detection of the change in the color of the indicator.

Thus, the proposed method is attractive because of its simplicity and can be used for the direct determination of the concentrations of  $\text{CO}_2$  in air in all cases when the required accuracy is above 1–2 vol %. The fact that the method provides the concentration of  $\text{CO}_2$  without adjustment by calibration mixtures allows its

use for the control and calibration of instrumental methods with an error higher than the specified accuracy limits. The replacement of electrical conductance measurements in the determination of the equivalence point with its detection with phenolphthalein allows the use of the method in educational organizations for laboratory works and demonstration purposes.

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#### REFERENCES

1. Wood, R.A., Keen, A.B., Mitchell, J.F.B., and Gregory, J.M., *Nature*, 1999, vol. 399, p. 572.
2. Demidov, A.V. and Mokhov, L.A., *Uskorennye metody opredeleniya v vozdukh vrednykh i paroobraznykh veshchestv* (Rapid Methods of Determining Harmful and Vaporous Compounds in Air), Moscow: Medgiz, 1962.
3. Luk'yanycheva, V.I., Ponomarenko, E.A., Fomicheva, N.G., et al., *Zavod. Lab.*, 2003, vol. 69, no. 8, p. 17.
4. *Spravochnik khimika* (A Chemist's Handbook), Nikol'skii, B.P., Ed., Moscow: Khimiya, 1987, vol. 4.
5. Hall, N.P., Cornelius, M.J., and Keys, A.J., *Anal. Biochem.*, 1983, vol. 132, p. 152.
6. Forrester, R.L., Wataji, L.J., Silverman, D.A., and Pierre, K.J., *Clin. Chem.*, 1976, vol. 22, p. 234.
7. Bykhovskaya, M.S., Ginzburg, S.L., and Khalizova, A.D., *Metody opredeleniya vrednykh veshchestv v vozdukh* (Methods for Determining Harmful Substances in Air), Moscow: Meditsina, 1966.
8. Minkh, V.A., *Metody gigienicheskikh issledovaniy* (Methods of Hygienic Studies), Moscow, 1961.
9. Nekrasov, B.V., *Osnovy obshchei khimii* (Basic General Chemistry), Moscow: Khimiya, 1967.
10. Karandeev, K.B., *Metody elektricheskikh izmereniy* (Methods of Electrical Measurements), Moscow: Khimiya, 1974.
11. *Spravochnik khimika* (A Chemist's Handbook), Nikol'skii, B.P., Ed., Moscow: Khimiya, 1966, vol. 1.
12. Reitlinger, S.A., *Pronitsaemost' polimernykh materialov* (Permeability of Polymeric Materials), Moscow: Khimiya, 1974.
13. *Liquid Column Chromatography*, Deyl, Z., Macek, K., and Janak, J., Eds., Amsterdam: Elsevier, 1975, vol. 1.