LVIII.—*Carbon Dioxide. Its Volumetric Determination.*

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CARBON dioxide appears to have been first recognised as a regular constituent of the atmosphere by MacBride in 1764 (*Experimental Essays*), and he estimated the amount gravimetrically after drawing a measured volume of air over caustic alkali, a process which, with some modifications, still remains the standard. It was not, however, until Pettenkofer described his well known volumetric process for its estimation before this Society, in 1857, that its measurement as an index of the respiratory impurity of enclosed spaces became practically available. Since then many chemists have been attracted by the subject, and, in looking over the Chemical Society's Journal, we find over 120 papers or abstracts of papers bearing on this subject; and among the contributors are many illustrious chemists. As a rule, some modification of Pettenkofer's process has been used for estimating the carbon dioxide in the air of rooms, and the older gravimetric method for the air of open spaces; but, among special processes, the following may be mentioned. Wanklyn suggested a

"nephelometric method," imitating a cloud of barium carbonate; Dupré and Hake used a similar process, but with oxyacetate of lead; Winter Blythe absorbs by sodium hydroxide, and then estimates by Schrotter's carbon dioxide apparatus; Angus Smith used manganate of sodium, and observed the change to permanganate. He also suggested as a household test his minimetric method, which depends on the formation of a cloud in a given volume of lime water. It is, however, very difficult to exclude all adventitious carbonates, and this considerably detracts from the value of any test in which the absence of carbonates in the reagents is assumed. Kapussten (*J. Chem. Soc. Abstr.*, 1880, 420) used alcoholic soda solution, and noted the amount of water required to dissolve the carbonate.

In 1884, Blockman (*Ber.*, 1884, **17**, 1017, 1019) suggested phenolphthalein as an indicator, lime water as an alkali, and a 500 c.c. flask in place of the larger vessel of Pettenkofer. He showed that the test could be made either by adding the solution to a measured quantity of air until decolorised, or by using a fixed quantity of alkaline solution, re-filling the flasks with air, and agitating as often as necessary to decolorise the indicator; he found the latter method the better. Rosolic acid was suggested as an indicator by Pettenkofer in 1876. Ballo (*Ber.*, 1884, **17**, 1097, 1101) stated that lime water was sluggish in its action, and he recommended a mixture of potassium hydroxide and barium chloride, and at least three minutes' shaking. Since then, Lunge and Zeckendorf have introduced a method which is in principle identical with Blockman's, but they use a small vessel (110 c.c.), the air being drawn in by an indiarubber hand pump, supposed to remove 70 c.c. of air from the vessel after each compression; and a $N/500$ Na_2CO_3 solution with phenolphthalein. Wolpert has patented a still smaller apparatus on nearly the same principle, and works on quantities of air varying from 10 to 50 c.c. It is obvious that such methods must be open to great error, and that the results obtained by their means have very little scientific value; but we are of opinion that Wolpert's form of apparatus is useful for making rough estimations.

To return to Pettenkofer, it is unfortunate that most of our text books describe as his a process which lacks many of the safeguards which he adopted; for example, in his later process he added a small quantity of barium chloride to the barium hydroxide to counteract the influence of small quantities of alkalis which might be present; he also used a vessel closed by caoutchouc and titrated direct through a small tube, letting down turmeric paper from time to time by means of a wire through another tube; whereas most of the text books direct the titration to be done in an open vessel, with part of the contents, either before or after filtration, and do not mention the

need of precautions against contamination from the operator, who is all the time giving out a stream of air containing at least 4 per cent. of carbon dioxide. Pettenkofer used a dry bottle, and drove the air into it by means of a pair of bellows, the bellows being furnished with a bent tube, which was pointed in the direction from which it was desired to sample the air; but as the length of the tube was not, from his illustration, apparently more than 6 inches, a turn in one direction or another could not have much influence.

Angus Smith suggested that the air should be drawn from the bottle by means of bellows, this is undoubtedly an improvement; but in either case, it is a matter of considerable labour to insure a complete exchange of air. Lebedingebbb (*J. Chem. Soc. Abstr.*, 1891, 290) found it necessary to aspirate 200 litres through a bottle holding 7—12 litres, whereas Dr. Gill, of the Laboratory of Sanitary Chemistry and Gas Analysis, Mass. Inst., U.S.A., considers it sufficient to fill the bottle four times by 15 strokes of his bellows. Dr. Louis Parkes, in his *Manual of Hygiene*, second edition, p. 260, recommends a glass stoppered vessel of 2 litres capacity to be filled with mercury and emptied in the place, the air of which is to be examined; but 27 kilograms of mercury is certainly an inconvenient quantity to deal with, and he mentions the alternative method of forcing air in by means of bellows. Dr. Notter, who contributes the article on air in Stevenson and Murphy's standard work on hygiene, says: "Perhaps the best plan is to fill a jar with clean water and empty it in that part of the air space it is desired to examine, taking care to allow it to drain." The capacity of the vessel is to be about 1 gallon; obviously no amount of draining will remove all the water, yet no allowance is made for this in the subsequent titration of half the volume of alkali used for absorption; the outflowing water, particularly the portion which slowly drains out, will absorb some carbon dioxide; and tap water, which presumably is used, always contains that gas. It is only fair to add, that he concludes his remarks with the following sentence: "Although the method for determining carbon dioxide in air does not give quite accurate results, this is the most convenient for ordinary use, and sufficiently accurate for all practical purposes." A process conducted in this way would be open to an error of about 10 per cent., and if such inaccuracy as that will satisfy, we should prefer to use some such apparatus as that suggested by Lunge and Zeckendorf, or Wolpert, rather than one which needs a cab or other vehicle for its transmission. But recent legal proceedings have shown that the estimation of carbon dioxide in air may have an important bearing as evidence of over crowding, and we have taken the liberty of quoting from some of the most prominent text books on hygiene, in order

to show the necessity for a simple accurate process such as we propose.

We use for the collection of the samples of air flasks containing only water vapour, and varying in capacity from 0.5 to 3 litres, according to the nature of the air. Vacuous flasks have been used by others, and their advantages are obvious; they will remain vacuous for months with good rubber tube and efficient clamps or stoppers; they may therefore be kept ready for use, and are extremely portable; a couple of litre flasks may be easily carried in the coat pockets, and a 3-litre flask concealed under the cape of a mackintosh or great coat. The samples of air may be taken quite unobserved; we have taken them in a police-court while sitting in the barristers' enclosure, within a few feet of the magistrate. The position from which the air is taken may be selected exactly, while the time occupied in taking the sample is only a few seconds.

We have tried various kinds of pumps for exhausting flasks, and have found it much simpler and quicker to fill the vessel with steam under pressure, and then, after closing, allow the steam to condense; the small quantity of water thus introduced does not interfere with subsequent operations. A common steam steriliser makes a good boiler, and is now found in most laboratories. Distilled water should be used, as tap water gives up its "loosely combined carbon dioxide" very slowly. The flask we use is drawn out to a neck some $\frac{3}{8}$ inch internal diameter, but it is obvious that any round-bottom flask, furnished with a caoutchouc stopper perforated by a glass tube, would answer the same purpose, and in our earlier experiments such a flask was used. The neck is continued outwards by a short caoutchouc tube in such a manner that it can be controlled by a strong screw clamp or plugged by a stopper. To remove the air, the inverted flask is placed vertically over a $\frac{1}{4}$ -inch copper tube, connected with the boiler, and sufficiently long to reach nearly up to the bottom of the flask. The steam, at about 20 lbs. pressure, is sent through, and the flask kept in position for about two minutes, until no more steam is seen to condense on its surface, when it will be quite free from air if the steam was so; it is then lifted off, and the tube at the same time closed with the fingers, protected if necessary by means of a glove. Working sometimes at 80 lbs. steam pressure, we have been able to do this without injury to the fingers. The rubber tube is then permanently closed and the flask allowed to cool. If desired, the tube can be again secured by the fingers above the water which has collected, and the water removed without allowing any air to enter, but we have not found this necessary. The flask is now ready to take a sample of air, its capacity having previously been ascertained; an allowance of 1 c.c. for each litre, is made for condensed moisture.

In preparing flasks for collecting micro-organisms, the process is slightly modified. They are wrapped in flannel and steamed in the usual way; then, when no more condensed water is blown out, the flask is removed, the nutrient medium introduced as quickly as possible, and the steaming continued for a minute with the neck of the flask uppermost and the steam pipe directed downwards to the bottom, the caoutchouc tube being closed as the steam pipe is withdrawn. We have found it convenient to use 10 c.c. of a 15 per cent. gelatin medium for each litre of capacity. The nutrient medium boils, is completely sterilised, and readily distributed over the inner surface of the flask as it cools. If not used in a few hours, it may be necessary to just liquefy the gelatin and redistribute immediately before or after collecting the sample of air.

When a sample of air is to be taken, thick-walled rubber tubing, a metre in length, may be connected with the rubber tube of the flask, and, at the time of opening, the free extremity of the smaller tube held in that place from which it is desired to collect the sample. We generally collect the sample at 1 or 2 metres from the floor, at all events well away from the line of breath of any occupant of the room; the tube is opened, and after a few seconds the narrow rubber removed and the larger tube secured. It is not necessary at this stage to note the pressure or temperature of the air. The flask is taken at leisure to the laboratory and the requisite quantity of alkali added, a small measured quantity of purified water being used to wash the last trace of alkali into the flask. The alkali may be delivered from a pipette or burette, but in any case the orifice of the measure must be in air-tight communication with the flask before the tube is opened; a small rubber plug secures this. Any ordinary pipette may be used to deliver the alkali, provided proper precautions are taken to prevent the entrance of carbon dioxide, the chief source of which is the operator. We find the following method answers well. A large size Fresenius tower is used to free the air from the carbon dioxide it contains; in the base below the aperture there is a small quantity of a solution of potassium hydroxide, and above the constriction it is filled with sticks of the same material, its lower aperture being connected with a blowball for forcing air in, and its upper with a four-cross tube, by which connection is made with the two aspirators and the pipette, as shown in the illustration, Fig. 1; one of the aspirators contains the alkali, the other pure water; from the lower orifice of each aspirator hangs a long rubber tube, closed at the end with a glass plug and having a clamp above. The pipette hangs from the cross-piece, and when not in use is closed with a rubber cap; when required for use, the rubber cap is removed, and a current of air is sent through the

pipette by pressing the blowball; it is then connected with the alkali tube, and a charge is allowed to flow in by gravitation; after this first charge has been run out, the pipette is filled a second time exactly to the fiducial mark, and the charge transferred to the flask, being blown in by pressure on the ball if necessary, but no air must be allowed to enter. In a similar manner, a charge of water is allowed to enter the flask, the tube of which is now closed.

FIG. 1.

FIG. 2.

When a large number of estimations have to be made, we prefer to use, for measuring the alkali, a special apparatus which we call a compound pipette, Fig. 2. It consists of a series of bulbs 5, 10, 10, 25 c.c. in capacity connected together by narrow tubes graduated in 0.01 c.c. divisions, it is furnished below with two glass taps after the manner of a burette; above, it terminates in a tube bent twice upon itself and furnished with bulbs; the lower bend of this tube contains the same liquid as the pipette, and serves as a final wash for the air entering the pipette through the side tube. We use this instrument to deliver, and do not wash it out, but deliver 10 c.c. of water, to wash in the alkali, from an ordinary burette protected against carbon dioxide. From our compound pipette 5, 10, 15, 20, 25, 35, 45, or 50 c.c. can be measured in one quantity with an error of about 0.02 c.c.

The flask charged with alkali is thoroughly shaken for about 10 minutes, without bringing the liquid in contact with the rubber tube. After which, if the alkali is in excess, the whole of the carbon

dioxide will be removed from the air; we have convinced ourselves of this by numerous experiments, which are detailed below. The flask is now set aside to acquire the temperature of the laboratory, or plunged into water of known temperature, and the pressure of its contents is made to correspond with that of the laboratory, by allowing a measured quantity of purified air to enter from or escape into a nitrometer or other suitable measure. The flask is not handled during this process of equalization but is supported in a wooden case containing a thermometer; the temperature should correspond with the temperature of the laboratory; the barometric pressure is also observed. The volume of air taken for analysis will then be the volume of the flask minus condensed water, alkali, wash water and air required to equalise, corrected for tension of aqueous vapour, and the temperature and pressure of the laboratory, plus the volume of carbon dioxide subsequently found. The flask is now disconnected from the nitrometer, and carried to a burette containing the acid, the rubber tube is then removed and the orifice of the flask closed by the index finger during the intervals of admission of acid—a few drops of alcoholic solution of phenolphthaleïn is added and the titration by acid carried out. We have made numerous experiments as to the best acid, indicator, and alkali to use; and after having worked with carbonic, acetic, lactic, citric, tartaric, oxalic, hydrochloric, and sulphuric acids, we prefer acetic acid. The acids have been used in alcoholic as well as aqueous solution. Alcohol certainly has advantages as a medium; the drops are much smaller; barium carbonate is less soluble in it than in water and the reaction with phenolphthaleïn is sharper; especially is this the case with those acids which form insoluble salts with barium, for the coloured phenolphthaleïn salt is carried down with the precipitate and is not then so easily acted on by acids. For the same reason, the phenolphthaleïn should be added after the precipitation of the barium carbonate. The objection to the use of alcohol as a solvent for the acid, is the necessity for frequent re-standardisation, as etherification is constantly taking place, whereas an aqueous solution of acetic acid will remain constant for weeks. We have sometimes added 20 c.c. of alcohol containing the phenolphthaleïn before titration, using the same quantity of alcohol when titrating the acid, so as to correct for the carbon dioxide it invariably contains.

The indicators experimented with were phenolphthaleïn, coral-lin and its homologue rosolic acid, cochineal, litmus, lacmoid, and logwood. In our opinion phenolphthaleïn gives the sharpest end reaction.

The alkalis we have tried are barium hydroxide, sodium hydroxide in the presence of barium chloride, calcium hydroxide, sodium

hydroxide in presence of calcium chloride, ammonia in the presence of calcium chloride, and sodium carbonate. For the rapidity of its action and for the ease with which it can be prepared, we prefer to use a mixture of sodium hydroxide and barium chloride, of such a strength that it shall correspond exactly to decinormal acid, and contain in each litre about 122 grams of crystallised barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. This mixture can be readily prepared by adding 220 c.c. normal sodium hydroxide to 1 litre of dinormal barium chloride, and diluting with recently boiled distilled water until, after thoroughly mixing, 50 c.c. of the clear supernatant liquid is exactly neutralised by 50 c.c. of decinormal hydrochloric acid, using phenolphthaleïn as an indicator. This alkaline solution is saturated with barium carbonate, as the sodium hydroxide always contains traces of carbonate. Further access of carbon dioxide is prevented in the usual way, and in order to obviate change by evaporation and condensation of moisture, the solution is covered by a layer of well-washed petroleum oil.

We find acetic acid the best acid to use, and we make it of such a strength that 20 c.c. of the alkali, coloured with phenolphthaleïn, requires 44.6 c.c. of acid to decolorise it. The acid is then equivalent to half its volume of carbon dioxide at normal temperature and pressure. We formerly used vacuous flasks in titrating, but now use vessels which have been rinsed out with pure water, and have had a current of purified air passed through them. We do not protect the acetic acid against carbon dioxide, as this gas acts precisely as acetic acid does, and is of course included in the titration, which as a matter of routine we do at the commencement and conclusion of each set of titrations, although we find the variation in most cases negligible. We are careful to make all our experiments in a room kept for the purpose well away from the general laboratory, as the number of aerated waters examined there have a disturbing influence.

In checking the various methods of estimating carbon dioxide, we have not been content to make a series of experiments to compare among themselves, the method, as far as we have been able to ascertain, hitherto invariably employed by experimenters in this country; but we have worked with carefully measured volumes of carbon dioxide of known purity, diluted with purified air.

We have contrived a special piece of apparatus, Fig. 3, by which we can measure any volume of carbon dioxide from 1 to 50 c.c. with an error of about 0.01 c.c. This apparatus is a modification of our compound pipette, and consists of a series of 1, 2, 2, 5, and 10 c.c. capacity connected by narrow tubes graduated in 0.01 c.c. The smallest bulb is uppermost, and is surmounted by a three-way tap after the manner

of a nitrometer; the larger bulb is continued downwards as a straight tube which is graduated for 10 divisions in 0.01 c.c.; below this graduation two tubes of about the same bore as the narrow part of the pipette are joined on either side and carried upwards close to and parallel with the pipette; they are open above, and serve to show the level of mercury in the reservoir; by looking across them parallax is avoided. These narrow tubes, with the pipette and a thermometer, are enclosed in a water jacket. The pipette communicates externally with a reservoir of mercury, which may be adjusted to any height, to expel or admit gas. The volume is always brought exactly to one of the graduations, the difference in level observed, and the true volume calculated by Graham's Law. When it is necessary to read at a lower pressure than the normal, the two levelling tubes must be filled with mercury and closed by caps, and the reading made directly from the reservoir.

Where possible, the flasks should be weighed before and after taking the sample. The following experiments will show to what extent flasks can be rendered vacuous by steam. All weighings were done in air, using brass weights and a closed counterpoise of approximately similar size to the flask.

The barometric pressure was 770 mm. and the temperature of the balance room 11°. The high-pressure steam was obtained from a large Galloway's boiler; the pressure was therefore fairly constant, but the steam probably contained traces of air and carbon dioxide as the boiler was continuously fed. The low-pressure steam was obtained from a sterilizer in which distilled water was boiling. As it contained only about a gallon of water the pressure varied a good deal while blowing off, it is therefore only approximately stated.

Flask E. Capacity 3119 c.c.	62 lb. steam.	15 lb. steam.
Weight after opening to admit air ..	705.47	705.32
Weight before opening to admit air..	701.52	701.52
Weight of moist air admitted	3.95	3.80
Condensed water.....	3.47	—

Flask F. Capacity 3154 c.c.	62 lb. steam.	15 lb. steam.
Weight after opening to air	640.30	640.35
Weight before opening to air	636.45	636.45
Weight of air admitted	3.85	3.9
Condensed water.....	3.05	—
Flask G. Capacity 3157 c.c.		
Weight after opening.....	684.8	684.75
Weight before opening.....	680.9	680.9
Weight of air admitted	3.9	3.85
Condensed water	3.0	—

From the above it will be seen that it is easy to check the exhaustion of the flasks by weighing at any time; 0.01 gram increase would show, correcting to N.T.P., a leakage of 0.3 per cent. or about 8 c.c., but we could detect no change of weight even on keeping flasks for months.

As serving to show the accuracy of our process and the time necessary for absorption, the following results may be quoted.

First series—3 flasks of about 3 litres capacity, which had been rendered vacuous one month previous, and since kept in the laboratory, had introduced into each of them 18.8 c.c. of carbon dioxide at N.T.P., and then the alkali (a mixture of decinormal soda and normal barium chloride).

Alkali.	Time (with frequent shaking).	CO ₂ found.
20 c.c.....	1 hour	19.1 c.c.
25 „	30 minutes	19.0 „
25 „	15 „	19.1 „

Another series, recently rendered vacuous, had the same quantity of 18.8 c.c. of carbon dioxide at N.T.P. introduced, and gave, with decinormal barium hydroxide, the following.

N/10 Ba(OH) ₂ .	Time.	CO ₂ found.
25 c.c.....	1 hour	19.0 c.c.
25 „	50 minutes	19.0 „
25 „	30 „	19.0 „
25 „	30 „	19.0 „
25 „	20 „	19.1 „

A flask into which no carbon dioxide had been intentionally introduced gave after one hour 0.2 c.c. of carbon dioxide.

In a third series, one of us added the amount of carbon dioxide, and it was then estimated by the other, who was not aware of the quantities added until his results had been calculated (in all cases due

correction was made for pressure temperature and tension of aqueous vapour).

	CO ₂ added.	CO ₂ found.
1	7.6 c.c.	7.6 c.c.
2	5.9 "	5.7 "
3	22.9 "	22.8 "
4	20.0 "	19.9 "
5	20.8 "	20.8 "

The following are some examples of the process applied.

Sample of air taken in the yard of a factory in Camden Town 15 feet away from the building on a bridge 30 feet from the ground. Barometer 760 mm.; temperature 11.0°; damp morning.

Capacity of flask.	N/10 alkali.	CO ₂ per 10,000.
845 c.c.	5 c.c.	3.8
2994 "	5 "	4.7
2796 "	20 "	4.5
3157 "	10 "	4.2

This is really an example of irregular results due to proximity of buildings, one of which was a soda-water factory.

Samples of air taken in a soda-water factory, 15 ft. away from any source of carbon dioxide, 3 feet from the floor.

Capacity of flask.	N/10 alkali.	CO ₂ per 10,000.
3197 c.c.	20 c.c.	12.4
3119 "	20 "	12.7
3154 "	20 "	12.9

Samples taken from the same place on a cold evening, 6 P.M., when all the doors were shut. (23.10.95.)

Capacity.	N/10 alkali.	CO ₂ per 10,000.
5350 c.c.	30 c.c.	47.1
7500 "	30 "	48.5

It is to be noted that the employes in the factory do not appear to suffer in any way from the large amount of carbon dioxide which they must inhale.

The following are some miscellaneous examples.

I. Air taken in Southwark Police Court during the hearing of the Salvation Army Shelter case, 4 P.M. (24.10.95.) Barristers' enclosure, centre of Court. II. Air taken in the 4d. gallery, Standard Theatre. III. At Brewery Exhibition among the crowd in the gallery. IV. At Brewery Exhibition away from the crowd. V. Crowded gallery, Drury Lane Theatre, Saturday night, 10 P.M., before fireworks. VI. Another sample same time and place. VII. Bedroom, 1,047 cubic ft., at St. George's Buildings, Southwark,

occupied by two adults, four children, fire in room, but door had been occasionally opened; two samples taken with a few minutes interval.

	Capacity of flask.	N/10 alkali.	CO ₂ per 10,000.
I	2280 c.c.	20 c.c.	11·7
II	2322 "	10 "	29·2
III	1815 "	10 "	29·1
IV	1680 "	10 "	7·8
V	2337 "	10 "	20·6
VI	1630 "	10 "	19·0
VII	{ 1718 "	10 "	17·8
	{ 2337 "	10 "	19·3

With regard to the amount of carbon dioxide produced by burning gas, most of the text-books state erroneously that 1 cubic foot of gas produces 2 cubic feet of carbon dioxide. That this is an error may be seen on calculating the theoretical amount producible from the figures given of the composition of ordinary gas, or by reference to the result of its explosion with oxygen. It will be then found that 1 cubic foot of gas produces from 0·6 to 0·65 of carbon dioxide, so that an ordinary burner, consuming 5 feet per hour, would introduce nearer 3 feet than 10 feet—that is, it is equal to about 5, not 16, men at rest.

For the purpose of further experiment, a disused, slate tank, having a capacity of 100·6 cubic feet, was covered with enamelled iron and glass, the joints being made air-tight by pasting over with paper and subsequently varnishing, all bung-holes being stopped.

In this tank the authors of the paper made a series of experiments, the air being kept constantly in motion by moving a fan, a piece of wood 4 feet square, up and down in the centre of tank. Making due allowance for the bulk of the occupants and apparatus, there would be less than 50 cubic feet per person, but rather more than obtains in a railway carriage full of passengers. Samples of air were then taken in Lunge and Zeckendorf's and Wolpert's air testers, by Pettenkofer's open bottle, by the water vessel of Notter, at stated intervals, and, simultaneously, into our vacuous flasks. All the samples were drawn from very nearly the same position, and the operators took care to direct their breath away from the vessels in the direction of the fan.

The following is an example: Two operators in tank with fan; after being 10 minutes in the tank, three flasks were started, the interval between the first and third being 40 seconds. The results were 53·7, 54·8, 56·5 CO₂ per 10,000. After 20 minutes, three other flasks were taken; they gave 67·2, 67·3, 69·9, and after 27 minutes three others; they gave 88·2, 88·2, 84·2.

We have made a few experiments in this tank with the object of comparing our process with those commonly in vogue, and also with the intention of estimating in the same sample of air as that we used subsequently for the estimation of carbon dioxide, and the number of micro-organisms, or the albumenoid ammonia, and the matter capable of absorbing oxygen from permanganate; at present we do not feel justified in publishing our work in this direction. It is obvious that such small volumes of air must be very foul indeed to yield measurable quantities, except as regards micro-organisms, and these bear no relation to respiratory impurity, although they may afford other valuable information.

We desire to place on record our thanks to Messrs. Idris & Co., Aërated Water Manufacturers, Camden Town, for placing their laboratories at our disposal, and for kindly providing all appliances.