Microdetermination of CO_2 in the Air, with Current Data for Scandinavia

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Abstract

Krogh and Brandt Rehbergs method for estimation of CO_2 in atmospheric air has been investigated and modified. The method is used for continous investigation of the CO_2 content of the air in Scandinavia. A permanent net of sampling stations has been established, 6 in Sweden, 4 in Finland, 3 in Norway and 2 in Denmark. The samples are taken three times each month. A simple method of taking air samples is described. Current data for November, December 1954 and January 1955 are published.

Preface

The problem of the carbon dioxide content of the free atmosphere and its variations has recently acquired a renewed importance. CALLENDAR (1940) published a critical survey of the entire literature relating to CO_2 determinations for the period from 1860 to the middle of the 1930's, in which he asserted that the most recent analyses show higher concentrations than the older determinations made before and at the turn of the century. The increase amounts to about 10 per cent on the average. Since, in this survey of the material, only values which were reliable from the standpoint of precision in analytical procedure were considered, and since the mean values arrived at by various investigators are in good agreement with each other, Callendar regards the increase as real. He ascribes the increase to the enormously expanded industrial consumption of fuel since the beginning of the century. He finds support for this conclusion in the observation that the total consumption of industrial fuel from 1900 to 1935 (calculated from industrial statistics) has supplied to the atmosphere a total amount of CO_2 which is in satisfactory agreement with the quantity which can be calculated from the aforementioned 10 per cent increment arrived at on the basis of the CO_2 analyses.

The principal objection which can be raised against this conclusion is that the atmosphere is involved in steady gas exchange with the sea. If one assumes that the sea and the atmosphere have achieved equilibrium with each other as a result of exchange processes operating over thousands of years, then any sudden increase in atmospheric CO_2 should be smoothed out through absorption of the excess by the sea. Callendar is also aware of this possibility, but considers that this process goes on with extreme slowness, perhaps during several thousand years, because of the sluggish vertical circulation in the sea, of whose total volume only a small fraction (about 1.3 per cent) can possibly come into immediate contact with the atmosphere at any given time.

The question of this exchange process may be regarded as a separate problem with its own intrinsic interest, but it certainly stands in an intimate connection with the question of a possible increase in the CO_2 content of the atmosphere. A settlement of this question requires a large volume of observational data distributed over an extensive region of space and time. As twenty years have now passed since the last series of observations by J. HALDANE (1936) and K. BUCH (1934, 1939 a, 1939 b) (on which Callendar in large measure based his conclusions) were published, and because the CO_2 content of the atmosphere may have been increased further since that time, it seems especially desirable to begin the collection of new series of observations, preferably over as large an area of the earth's surface as possible.

A suitable opportunity to realize this wish presented itself in connection with the plans for a world-wide investigation of "trace elements" in the atmosphere, which were drawn up on the initiative of Professor C.-G. Rossby, director of the Institute of Meteorology, Stockholm University. A resolution to begin these investigations was approved at a conference in Stockholm in May 1954 (ERIKSSON, 1954), which was attended by representatives from various parts of the world. With reference to CO_2, it was resolved to set up a regular sampling program at several stations in all these countries participating in the effort. I undertook the responsibility for organizing Finland's share of the project.

The locations of the sampling stations, the method of sampling and the analytical procedures are described in subsequent sections of this paper.

Sampling technique

The air samples are taken on open places without foliage, such as a lake- or sea-shore, or on a rock without forest. Towers, or roofs without chimneys, are also suitable places. The samples are always taken at the same place three times each month, on the 1st, the 10th and the 20th, at about 13.00 hours.

The samples are taken in gas pipettes, which have two stopcocks and a capacity of about 250 cc. A rubber bulb is connected to the pipette (figure 1) and both the stopcocks are opened. The vent of the rubber bulb is turned towards the wind direction as far as possible from the sampler (figure 2). 150—200 pumpings with the bulb are rapidly carried out, to get a complete air exchange. Then stopcock (a) is closed and two pumpings on the bulb are carried out to get an overpressure in the pipette. Then stopcock (b) is closed and the bulb removed. The samples are sent to the laboratories for analysis, with a report of the weather conditions.

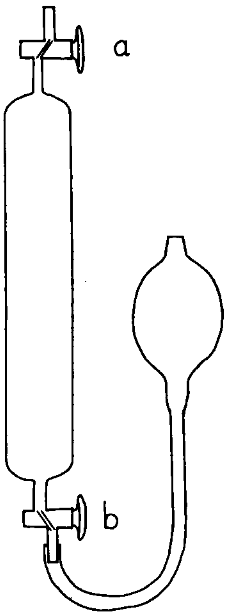

Fig. 1. Sampling Pipette with Rubber Bulb.

Fig. 2. Mr. Roland, Plönninge taking an air sample.

The samples are being taken at the following places (see fig. 3):

Sweden

Abisko Research Station of Academy of Science, by the lake Torne Träsk
(on the roof of the building)
Öjebyn Experiment Station, near Piteå
(on a gravelled plain)
Bredkälen, village, near Strömsund
(on the roof of a barn)
Ultuna Agriculture College, near Uppsala
(on a gravelled plain)
Flahult, Experiment Station, near Jönköping
(on a gravelled plain)
Plönninge Agricultural school, near Halmstad
(on a gravelled plain)

Finland

Kauhava Military Training school
(on the airfield)
Rissala aerodrome, near Kuopio
(on the airfield)
Luonetjärvi aerodrome, near Jyväskylä
(the flight control tower)
Tvärminne Zoological Station, near Hangö
(on the seashore)

Norway

Vågönäs Experiment Station, near Bodö
(on the railway embankment)
Vågåmo, Klones Agricultural School
(at the shore of the lake Vågåvatn)
Bergen, University of Bergen
(the tower of the university)

Denmark

Ödum Agricultural Experiment Station, near Vejen
(on gravelled ground)
Askov Agricultural Experiment Station, near Århus
(on gravelled ground)

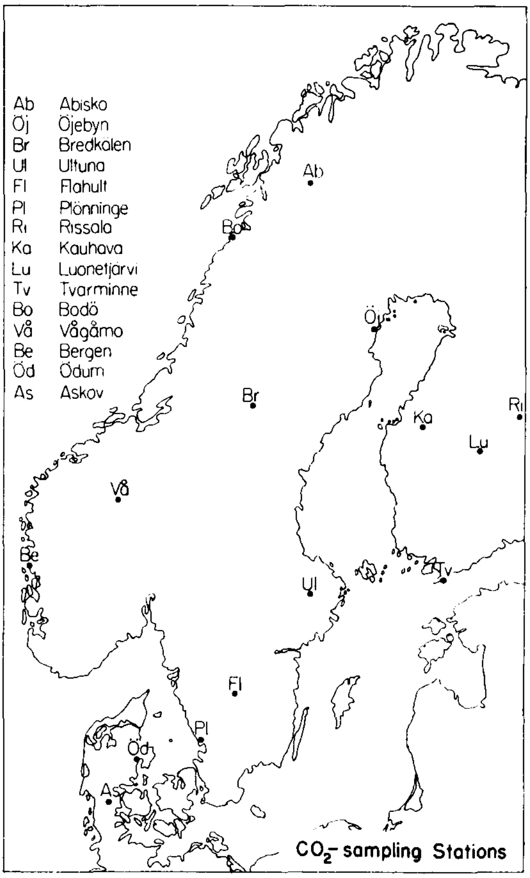

Fig. 3. Map showing the distribution of stations.

Method of analysis

The method developed by Krogh and Brandt Rehberg (1929) was used as a basis for the determination of the amount of carbon dioxide in atmospheric air. In brief, the principle of this method is to pass a definite small amount of air through a solution of barium hydroxide and then to titrate the excess of the hydroxide with hydrochloric acid.

Absorption tube. The tube has the form shown in figure 4. It is made of Pyrex glass, has an inner diameter of about 4 mm, and its lower end is drawn into a slowly tapering point (1 mm) bent upwards semicircularly. At a distance of 1.5 cm from the upper end, the tube has been blown to a bulb with 1.5 cm diameter. The total length of the tube is about 15 cm.

Apparatus. The levelling bulb A contains mercury, and G and H are three-way stopcocks. The air sample pipette B is connected between G and H. The second branch of the stopcock H is connected to an adjustable CO_2-free air stream, obtained by passing air through a sufficiently long tube E filled with Ascarite or Soda lime. The third branch is drawn out

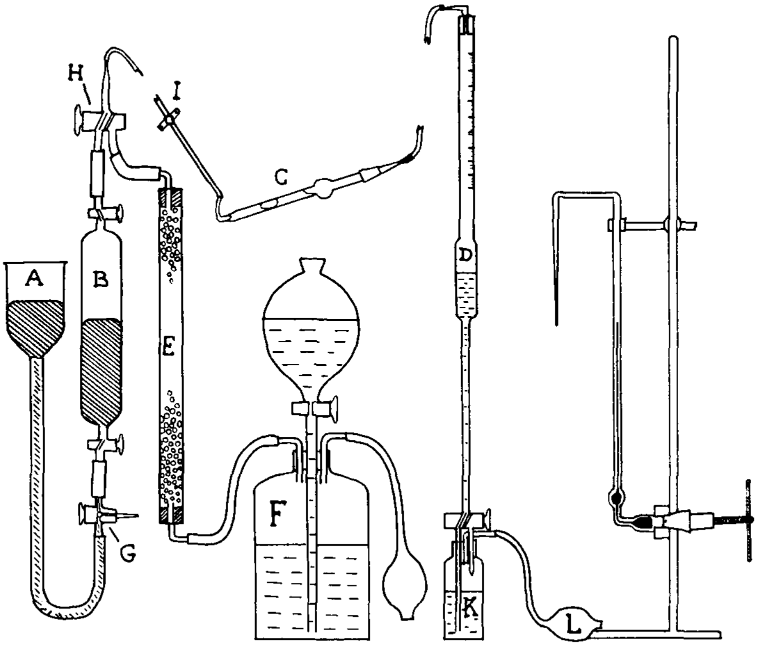

Fig. 4. CO_2-Absorption Apparatus with Microtitration Pipette.

into a capillary and connected to the capillary end of the absorption tube C with a thin pressure tube of inner diameter 1.5 mm and outer 3 mm. A pinch clamp J is placed on the tubing to regulate the rate of flow. The other end of C is connected to the measuring burette D with a similar pressure tube. The burette can have a capacity of 60 or 100 ml and is filled with water by compressing air in bottle K. (Fig. 4.)

Hydrochloric acid, 0.08956 N solution. One ml of this acid is equivalent to one ml of CO_2 at NTP. (The mol. weight of CO_2 = 44.01 and its liter weight = 1.9769 grams.)

Barium hydroxide, 0.0179 or 0.0119 N solution. If the capacity of the microburette for HCl is 0.2 ml, the stronger hydroxide is used. The other normality is used if the capacity of the burette is 0.1 ml. The solution should contain 0.5 per cent of $BaCl_2$ and be stored in bottles protected by an Ascarite tube. (Fig. 5.)

Titration of the hydroxide with the acid. The microburette for the acid, capacity 0.1 ml, is provided at the top with a U-shaped glass tip drawn into a capillary. The acid is drawn in through this capillary using a mercury and screw piston in the other end of the burette. Carbon dioxide-free air is blown through the absorption tube held in a tilted position for a few minutes, the flow being finally reduced to a very slow rate. The tube is now filled with 0.75 ml of the weaker hydroxide using an all-glass tuberculine syringe containing one ml with a scale divided into 100 units and equipped with a long glass tip ending

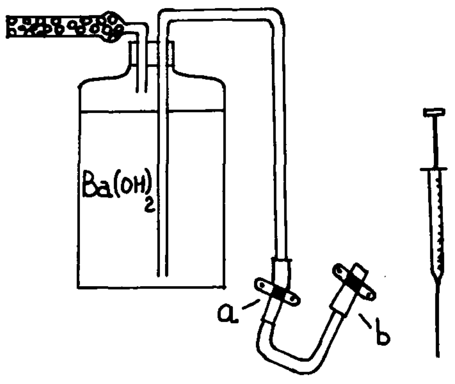

Fig. 5. Store Bottle for $Ba(OH)_2$ solution.

in a capillary. The storage bottle for the hydroxide (fig. 5) is equipped with a syphon tube and U-shaped termination. A pinch clamp is located between them. The U-tube is equipped with a rubber tube and a second pinch clamp. This second clamp is first removed and the first clamp is opened so as to allow fresh hydroxide to flow and flush out the older solution from the U-tube. The first clamp is then closed; the syringe is inserted into the open end of the U-tube, washed out once with hydroxide and then filled in the usual manner. With this technique, the aliquot taken is protected from atmospheric carbon dioxide.

When the absorption tube is filled, one drop of a 0.1 % cresol- or phenolphthalein solution is added and the titration carried out with the tip of the burette inserted into the tube below the bulb. During the titration a slow CO_2-free air stream flows through the hydroxide. Two blank titrations are not allowed to differ more than half a scale unit or 0.0005 ml from each other.

Procedure

The analysis is begun by attaching the pipette between G and H. (See fig. 4.) The cock G is first turned so as to connect the bulb A to the atmosphere. Now H is turned so that the through connection is from the pipette to the pressure tube. (The cocks of the pipette are closed.) Bulb A is raised until mercury begins to flow out of G, and this cock is then turned so as to connect the pipette to the atmosphere; the lower stopcock of the pipette is then opened so that the slight over-pressure in the pipette flushes the air out of the short length of connection tubing. At this stage G is turned so as to connect the pipette to A. The bulb is raised so as to provide an over-pressure in the pipette. The upper cock of the pipette is opened and the air is flushed out of the cock H and the rubber tubing. (At this stage the absorption tube is not yet filled with hydroxide and is not connected to the measuring burette D.) Thereafter, H is turned so that CO_2-free air can flow through the absorption tube for a few minutes. Burette D is filled to the mark with water, and hydroxide filled into C in the manner already described under titration. Next, the absorption tube is connected to burette D and cock H is turned so as to connect the pipette to the tubing leading to C. The cock of burette D is then turned so that D may drain back into Reservoir K. The rate of flow is adjusted with clamp J and also by turning the tube to a suitable tilted position. The flow is correct when the small air bubbles follow each other as pearls on a string. With this arrangement every air bubble is in contact with the hydroxide 20 to 30 seconds, and the time required to drain D (100 ml) is approximately one hour. When the main bulb of the burette is empty, the levels of mercury in A and B should be adjusted to be nearly at the same height to avoid over-pressure at the end of the absorption.

After burette D has drained completely, cock H is again connected to the CO_2-free air flow and the air is allowed to flow slowly during the subsequent titration. The absorption tube is disconnected from the measuring burette and the hydroxide titrated, as already described under titration.

To avoid appreciable changes in temperature, direct sunlight has to be avoided. During the absorption, pressure and temperature are read and the volume of the measuring burette reduced to NTP.

After an analysis the absorption tube can be used for another absorption without washing. If the tube must be washed, a blank titration is necessary.

Calculations:

1 mm^3 HCl is equal to:

$$\frac{\text{normality of HCl} \cdot 44.01/2}{1.9769}\ \mathrm{mm}^3\ CO_2 = \alpha$$

Blank titration a mm^3 of HCl
After an absorption b mm^3 of HCl
Pressure during the absorption $= p_1$
Temperature » » » $= T_1$
Volume of measuring burette $= v_1 \mathrm{mm}_3$
Volume of the air sample at

$$\mathrm{NTP} = v_0 = \frac{v_1 \cdot T_0}{P_0} \cdot \frac{p_1}{T_1}$$

$$CO_2\,\% = \frac{100\,(a-b)\,x \cdot \alpha}{v_0}$$

As mentioned above, the time of absorption for 100 ml is stated to be about one hour, and each small air bubble must be in contact with the hydroxide for 20 to 30 seconds. Krogh and Brandt Rehberg stated that 20 minutes was sufficient for absorbing the carbon dioxide from 100 ml. An investigation of the effect of the absorption time gave the results shown in Table 1.

Table 1. Effect of time on the absorption 100 cm^3 air sample, blank titration 98.0 mm^3

Time in min.	HCl mm^3 aft. absorp.	CO$_2$ cm^3/10 l
19	71.0	2.89
24	68.0	3.18
39	66.0	3.41
47	65.5	3.47
71	65.1	3.51
85	65.1	3.51

As can be seen from the table, an absorption time of about an hour is necessary. It can be mentioned also that the values given by Buch (l. c.) are based on an absorption time of this length; therefore his values can be directly compared with our own.

As the analyses have been carried out partly in Stockholm (Mr. Wärme) and partly in Helsingfors (Koroleff), systematic errors may exist in the analysis methods. To test this possibility, double samples have been taken; the first analyzed in Stockholm and the second in Helsingfors, and vice versa. However, the values in Table II show that a fully satisfactory agreement exists.

Table II

	Stockholm	Helsingfors
	CO$_2$CC/10 l	
1	3.30	3.25
2	3.48	3.51
3	3.40	3.47

In Table III, the CO$_2$ values for Nov. 1954—Jan. 1955 are given in cc per 10 l of air. As the variations of the CO$_2$ content in atmospheric air might be of interest to geophysicists and meteorologists, the CO$_2$ values will be published quarterly in this journal.

These investigations have been financed mainly by the Wallenberg Foundation in Sweden and the State Scientific Commission in Finland.

Table III. CO$_2$ values November 1954—January 1955

	November					
	Date	Hour	t °C	Wind m/sec.	Weather and Pressure	CO$_2$ cc / 10 l
Ab.	1	13	— 2	Calm		3.66
	10	—	—	—		—
	20	13	—11	SSE 5.1		3.59
Öj.	1	13	—	NE 3		(4.22)
	10	13	— 1	NE 10	Snow	3.11
	20	13	— 6	NW 5	»	3.20
Br.	1	13	+ 4	NW 3		(4.29)
	10	—	—	—		—
	20	13	— 9	N 3		3.26
Ul.	1	13	+ 8	N 3		3.23
	10	13	+ 2	N 3		3.61
	20	13	— 1	N 3		3.17
Fl.	1	—	—	—		—
	10	—	—	—		—
	20	09	— 2	N 3		3.52
Pl.	1	14	+10	SW 3		(3.95)
	10	13	+ 7	W 10		3.31
	20	—	—	—		—
Ka.	1	—	—	—		—
	10	13	0	SSW	744.9	3.41
	20	13	— 5	E	775.6	2.73
Ri.	1	—	—	—	—	—
	10	16	+ 3	SE	749.9	2.92
	20	16	— 5	NE	770.5	3.09
Lu.	1	—	—	—		—
	10	12	+ 1	SSE	735.1	3.89
	20	12	— 5	ENE	764.5	3.40
Tv.	1	—	—	—	—	—
	10	09	—	—	785.0	3.12
	20	12	— 1	NE	778.0	3.14
Bo.	1	13	+ 3	N 5		3.75
	10	13	+ 1	S 5		3.05
	20	13	+ 4	SSE 6		3.62
Vå.	1	13	—	SW 3		3.13
	10	13	— 6	NW 3		3.85
	20	13	—	NW 2		2.28
Be.	1	—	—	— 3		—
	10	13	+ 6	SSE 3	Rain	3.44
	20	—	—	— 3	»	—
Öj.	1	16	—	—		3.36
	10	14	+ 7	W 10		3.49
	20	13	+ 2	SE 15		3.39
As.	1	14	+ 9	SSW 3		3.36
	10	13	+ 8	SW 10		3.15
	20	13	+ 2	SE 1		3.46

Table III (Cont.)

December							January						
	Date	Hour	t °C	Wind m/sec.	Weather and Pressure	CO_2 $\frac{cc}{10\ l}$		Date	Hour	t °C	Wind m/sec.	Weather and Pressure	CO_2 $\frac{cc}{10\ l}$
Ab.	30	13	0	ENE 13		3.24	Ab.	30	13	—12	SSW 4		3.29
	10	13	— 5	ESE 18	Snow	3.19		10	13	—20	Calm		3.46
	20	13	— 1	WSW 5	»	3.36		20	18	—18	S 3		3.58
Öj.	1	13	— 1	SE 3		3.16	Öj.	1	14	+ 1	NW 10		3.29
	10	13	0	E 10	Snow	3.32		10	13	— 2	S 3		3.55
	20	13	— 3	Calm		3.23		20	13	— 6	NE 3		3.50
Br.	1	13	— 1	SSE 15		3.34	Br.	1	13	+ 1	W 3		3.40
	10	13	— 1	S 15	Snow	3.74		10	13	—15	NE 5	Snow	3.49
	20	—	—	—	—	—		20	13	— 8	W 3		3.63
Ul.	1	13	+ 2	SSE 3	Rain	3.60	Ul.	1	13	— 4	SSW 1		3.24
	10	—	—	—	—	—		10	14	— 3	SSW —		3.82
	20	14	+ 5	SW 3		3.68		20	13	— 9	Calm		3.63
Fl.	1	13	+ 3	S 3	Rain	3.39	Fl.	1	13	— 3	Calm		3.17
	10	13	+ 4	S 3		3.83		10	13	— 4	SW 10	Snow	3.55
	20	13	+ 5	SW 10	Rain	3.22		20	13	— 5	NE 3		3.36
Pl.	1	13	+ 6	Calm		3.39	Pl.	1	13	— 1	NE 5		3.26
	10	13	+ 5	S 10		3.33		10	13	— 3	S 5	Snow	3.27
	20	13	+ 5	W 5		3.19		20	13	— 5	Calm		3.42
Ka.	1	13	— 2	SE 9	764.9	3.18	Ka.	1	13	— 5	SSW 5	774.5	2.94
	10	13	— 1	SE 16	751.8	2.87		10	13	— 1	S 5	742.5	3.28
	20	13	0	S 9	733.9	3.24		20	—	—	—	—	—
Ri.	1	14	— 6	SE 4	764.9	3.11	Ri.	1	14	—15	SE 3	771.9	3.24
	10	—	—	—	—	—		10	15	— 1	S 5	740.5	2.98
	20	15	0	SSE 5	728.1	3.79		20	14	—15	WNW 2	739.3	2.95
Lu.	1	13	— 4	SE 6	756.5	3.06	Lu.	1	—	—	—	—	—
	10	13	— 3	ESE 8	744.9	3.36		10	12	— 1	S 5	735.6	3.65
	20	12	0	SSE 4	726.5	3.25		20	12	— 9	NW 3	731.6	3.57
Tv.	1	12	— 1	SE —	778.0	3.16	Tv.	1	12	— 3	NE —	779.0	3.02
	10	12	+ 2	S —	768.0	3.17		10	12	0	SW 12	765.0	3.17
	20	—	—	—	—	—		20	13	— 1	W 2	760.0	2.97
Bo.	1	13	+ 5	SSW 4		3.45	Bo.	1	13	+ 4	WNW 3		3.43
	10	13	+ 2	ENE 5		3.53		10	13	— 7	NE 3		3.52
	20	13	— 1	NNE 2		3.62		20	13	— 7	NE 3		3.46
Vå.	1	13	+ 2	SE 3		3.27	Vå.	1	13	— 5	Calm		3.46
	10	13	— 1	ENE 2	Snow	3.17		10	13	— 2	NE 10	Snow	3.52
	20	13	— 1	NE 5		3.22		20	13	— 3	W 10		3.50
Be.	1	13	+10	SSE 3		3.49	Be.	1	13	+ 4	Calm		3.36
	10	13	+ 6	ESE 1		3.09		10	13	+ 2	SSE 1	Snow	3.70
	20	13	+ 3	NNW 1	Snow	3.61		20	13	— 1	ESE 3		3.53
Öj.	1	13	+ 6	S 3		3.34	Öj.	1	13	— 1	NE 3		3.13
	10	—	—	— 10		—		10	13	— 1	SSW 10	Snow	3.69
	20	13	+ 7	SW 10		3.23		20	13	— 4	Calm		3.53
As.	1	13	+ 7	S 3		3.24	As.	1	13	0	NE 3		3.25
	10	—	—	—		—		1	13	0	NE 3		3.57
	20	—	—	—		—		20	13	— 2	NW 3		3.76

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