Det Kgl. Danske Videnskabernes Selskab.
Mathematisk-fysiske Meddelelser. **I,** 12.

THE COMPOSITION OF THE ATMOSPHERE

AN ACCOUNT OF PRELIMINARY INVESTIGATIONS AND A PROGRAMME

BY

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1742

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BIANCO LUNOS BOGTRYKKERI
1919

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CONSIDERING the importance of the problem from several points of view it is rather surprising to see how little is definitely known about the composition of our earth's atmosphere. Taking into account only quite recent summaries of our knowledge the average percentages of the different gases are stated to be as follows:

Nitrogen	78.13—78.03 %	79.07—78.97 %
Argon	0.94 %	
Neon	0.0015 %	
Helium	0.0005 %	
Oxygen		20.90—21.00 %
Carbon dioxide		0.03 %
Hydrogen		0.0001—0.02 % (Generally 0.003 %).

This table shows that the uncertainty is especially large with regard to the hydrogen and the relation between oxygen and nitrogen. I shall mention a few literary data concerning these two points.

Hydrogen. GAUTIER[1], who was the first to proclaim the presence of hydrogen in atmospheric air, found that water was formed when perfectly dry air was treated with copper at a red heat. He determined the water by absorption with phosphor pentoxide and found that it corresponded on an

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[1] Ann. de Chimie 22, 1901.

average to 0.02 % hydrogen by volume of the air treated. His results have been adversely criticised by several writers.

Lord Rayleigh[1] found that there is a very faint hydrogen line in the spectrum of pure atmospheric air, but the line becomes quite distinct when 0.01 % hydrogen is added. The hydrogen added can be removed again by treatment with chlorine in bright sunlight, but the faint trace of the hydrogen lines remains.

By combustion experiments according to Gautier Rayleigh found at first high values similar to those of Gautier himself, but these could be obtained repeatedly from the same sample of air and turned out to be due to impurities in the phosphor pentoxide employed. Substituting a pure sample of the reagent, Rayleigh found on an average 0.003 % hydrogen, and this result has been very commonly accepted, though Rayleigh himself says that he does not wish to draw any conclusions from his own experiments, beyond the one that he does not think that the hydrogen percentage in air is likely to be greater than 0.003 %.

Later Claude[2] has studied the problem by fractional condensation of very large volumes of air. By this method he determined the quantities of Neon and Helium given above, and found that hydrogen was present in extremely minute quantities — about 0.00005 %, or 1 part in 2 millions. When, however, he added 1 part in 1 million, he was able only to recover 1/2 the quantity added, and he therefore thinks that the actual percentage may be about 0.0001. His result has not inspired complete confidence, and generally Rayleigh's value has been accepted by meteorologists.

Certain rather far-reaching conclusions have been based upon the hydrogen percentage found in the air at the surface of the earth. Since, namely, each separate gas in the

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[1] Philosophical Magazine Ser. VI, vol. **3**, 1902.

[2] Comptes rendus **144**, 1909, p. 1454.

atmosphere behaves as if it were alone present, the percentage composition of the gasmixture must become altered with increasing height above the ground, the partial pressures of the lighter gases decreasing more slowly than those of the heavier. In accordance with this proposition, the validity of which for those strata in which vertical currents are absent, cannot be doubted, the percentage of hydrogen must increase with increasing height, and assuming RAYLEIGH's value for the hydrogen percentage at the surface, WEGENER[1] has calculated that at a height of 70 km. hydrogen will be the chief constituent of our earth's atmosphere, and this has been correlated by WEGENER with a number of phenomena regarding spectra of meteorites, northern lights etc. It is obvious that if the actual hydrogen percentage at the surface is, say, 10 times lower than assumed by WEGENER, the boundary line of the hydrogen sphere must be displaced accordingly.

Oxygen and „nitrogen"[2]. Until recently all investigators who have analysed a fairly large number of samples of atmospheric air have observed variations of 0.1 °/o or more in the oxygen and „nitrogen" percentages, and have ascribed these either to the influence of combustion processes (or assimilation), or to the mixing of different strata of the atmosphere, since at high altitudes the oxygen percentage must be lower than at the surface, because oxygen is a heavier gas than nitrogen. The first cause can be ruled out, however, since the combustion of fuel and the respiratory exchange of organisms must cause a production of carbon dioxide which is similar in amount, though on the whole slightly smaller than the quantity of oxygen used up, while the assimilation of plants must diminish the carbon dioxide

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[1] A. WEGENER, Thermodynamik der Atmosphäre. Leipzig 1911.

[2] Here as elsewhere in the present paper "nitrogen" is used to denote the mixture of inert gases comprising nitrogen, argon, neon etc.

to an extent equal to the increase in oxygen. Variations in the carbon dioxide corresponding to those of the oxygen have never been observed, however, in reliable determinations. The carbon dioxide in pure atmospheric air shows variations which are always below 0,01 %[1] and generally only 1—3 thousands of 1 %. All variations in oxygen and carbon dioxide percentage due to combustion, respiratory exchange or assimilation should leave the "nitrogen" percentage practically unaltered.

The possibility that mixing of different atmospheric strata, and especially the descent of air from high altitudes, may account for the observed variations in the relative amounts of „nitrogen" and oxygen cannot be excluded a priori, but it must be remarked that a definite correlation between atmospheric conditions and the observed variations in "nitrogen" percentage has never been established.

When the series of analyses of different observers are averaged, the averages are found to differ considerably, which shows that the various analytical processes employed cannot claim to give absolute results, but must have various systematic errors. I mention as examples that Bunsen[2] found an average of 20.92 % oxygen, Regnault[3] 20.96 %, Kreusler[4] 20.91 % and Hempel[5] 20.93 %.

I 1912 a paper vas published by F. G. Benedict[6] from the Carnegie Nutrition Laboratory in Boston, which marks an epoch in the history of the subject, since it was shown by a very extended series of analyses that the composition

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[1] My own determinations in Greenland (Medd. om Grønland vol. **26**, 1904, show larger variations, which are independent, however, of the variations in oxygen. I fear that they must be erroneous.

[2] Bunsen: Gasometrische Methoden. Braunschweig 1857.

[3] Ann. d. Chim. et de Phys. Sér. 3. **36**. 1852.

[4] Landwirthschaftl. Jahrbücher. 14. 1885.

[5] Ber. d. deutsch. chem. Ges. **18**. 1885.

[6] F. G. Benedict: The composition of the atmosphere. Carnegie Publication No. 166. Washington 1912.

of the atmosphere varies — if it varies at all — within much narrower limits than formerly supposed. From April 1911 to January 1912 over 200 analyses were made of the air outside the laboratory with the result that the oxygen percentage practically never varied more than ± 0.01 % from the average, and the CO_2 never more than ± 0.005 %. The variations observed in the oxygen percentage are very slightly larger than the corresponding variations when air of constant composition from a steel cylinder was analysed, and it is therefore possible, nay probable, that the composition of the atmosphere is even more constant than directly shown by the analyses. The variations in the carbon dioxide are obviously due to the influence of the large town, though no correlation has been found between the O_2 percentages and the oxygen percentages.

The absolute oxygen percentages found are — as pointed out by BENEDICT himself — not to be relied upon, since it was shown that different concentrations of the potash pyrogallate employed as absorbing reagent for oxygen gave different results, showing a higher oxygen percentage the more concentrated the solution. Researches by TACKE, HEMPEL and HALDANE[1] have shown that this is due to the formation of carbon monoxide by the absorption of oxygen, and there is no guarantee that even the strongest solution employed does not produce a slight amount of carbon monoxide. There are also other possible sources of systematic error which make the general average somewhat doubtful. Assuming that the strongest solution of pyrogallate employed does not give rise to any formation of carbon monoxide, and disregarding the other sources of systematic error, the general average is 20.952 % oxygen, 0.030[2] % carbon dioxide and consequently 79.018 % "nitrogen".

[1] I. S. HALDANE: Methods of air analysis. London 1912.

[2] BENEDICT himself gives the average carbon dioxide percentage as 0.031, but a recalculation shows 0.030 to be the correct figure.

A new gas analysis apparatus. For purposes of accurate gas exchange determinations on man and animals I have worked out during the last few years a new gas analysis apparatus which should allow the determination of carbon dioxide, oxygen, "nitrogen" and combustible gases to within 0.001 %. The details of this apparatus will be described elsewhere, and here I shall only briefly mention the chief points which distinguish the apparatus from earlier types and insure the increase in accuracy claimed.

The most essential novelty is the introduction of three separate gas burettes (1, 2 and 3, fig. 1) instead of one. The first of these serves only for moving the air sample to and from the absorption pipettes, and for saturating the air with moisture, while the second (2) is of a size convenient for measuring the air before and after the absorption of carbon dioxide. The narrow stem of this burette is divided into 100 parts, each of which corresponds to 0.01 % of the total volume which is 50 cm^3. The graduations of the third burette are of the same size, but its total volume is only about 79 % of that of the second, so that it will hold the residual gas after the absorption of oxygen. The first burette contains a relatively large amount of water which will saturate the air and reestablish the vapour tension lost to the concentrated solutions in the absorption pipettes. The two measuring burettes contain each a very small and measured quantity of water, just enough to insure complete saturation of the air. With proper precautions the quantity of water can be maintained constant over long periods[1], and as the water does not at all enter the narrow graduated part of the burettes, absolute volumes can be determined.

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[1] The chief point is that the temperature of the waterbath must never be higher than that of the room. Otherwise water will distill off from the burettes and become condensed in the tubing above.

The accumulation of dirt in the burettes, which militates so strongly against accurate determinations, is minimized by

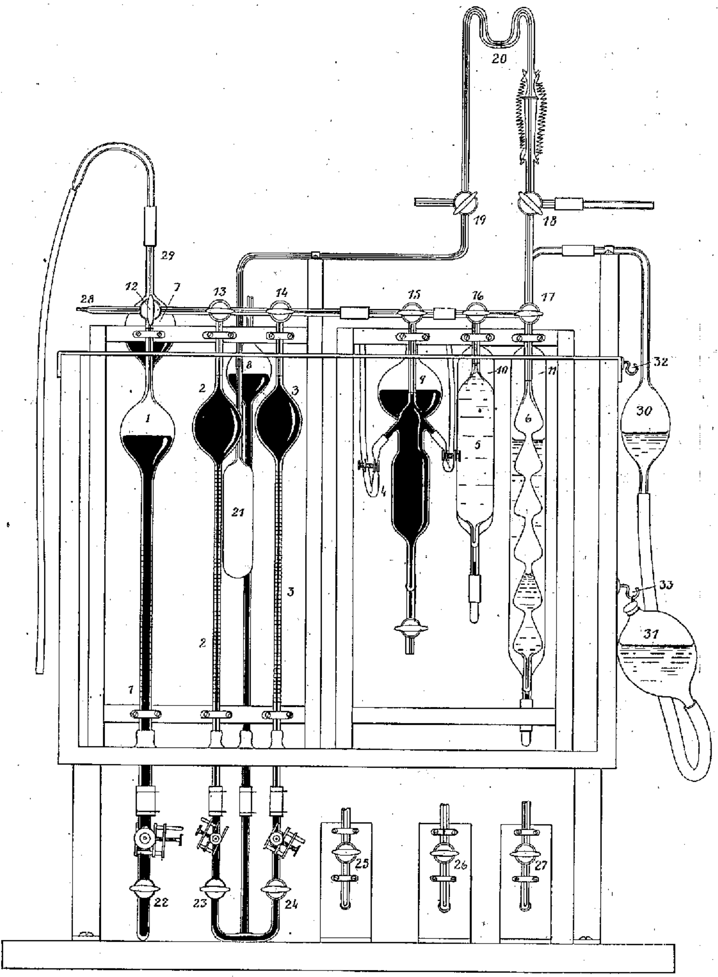

Fig. 1. Frontal view of the gas analysis apparatus.

the avoidance of long rubber connections. The mercury is moved in the burettes and in the combustion pipette by means of air pressure applied in the reservoirs (7, 8 and 9) placed in the same waterbath which can be kept at a constant temperature.

There are certain further improvements in the construction of the pipettes (4, 5 and 6) etc., but these are probably not of the first importance.

Numerous control analyses and double determinations of the same air have shown that the dispersion (standard deviation) of single determinations from their average is 0.00025 % for the carbon dioxide and 0.0005 % for the oxygen determinations in atmospheric air.

When analyses made over a prolonged period are to be compared, and especially when the condition mentioned in the note on p. 8 cannot be fulfilled, a control is established by alternating analyses of a supply of pure and dry air of absolutely constant composition kept in stock under a pressure of a few atmospheres in a 2 l. glass bulb.

This apparatus has been in constant use during a couple of years for gas exchange work, and incidentally and by way of testing the instrument we have made some determinations of the composition of atmospheric air which are, I think, of sufficient interest to warrant their publication in the present paper and to serve as a basis for a more thorough study by the methods described of the composition of the atmosphere and its variations.

1. Combustible gases in the atmosphere.

When pure, dust free atmospheric air is introduced into the combustion pipette (4, fig. 1) of the gas analysis apparatus, and the platinum wire is kept at a bright red heat for about 1 minute, the volume becomes diminished on an average about 0.001 %, and a product is formed which can be absorbed in potassium hydroxide. By the absorption there is a contraction in volume of about 0.002 %. These figures would correspond to the presence in the air of 0.002 % carbon monoxide. I have satisfied myself, however, by the extremely delicate blood test that carbon monoxide is not to be found in the atmosphere in any quantity approaching 0.001 %, and moreover the reaction described can be repeated again and again on the same sample of air. I suppose that it is due to combination of oxygen with nitrogen, but the matter will require further investigation.

When the platinum wire is heated just enough to make it visibly glowing, the contraction on combustion for 1 minute is absent or at least very doubtful. Experiments on 6 separate samples of atmospheric air have given the following contractions:

— 0.0005 %
\+ 0.0005 %
\+ 0.0005 %
\+ 0.0005 %
0.000
0.000

Average 0.0002 %

In two experiments air was analysed to which 0.010 ± 0.001 % hydrogen had been added, and here I found a contraction, after 1 minute's heating to the same temperature as in the six experiments just mentioned, of 0.152 % and 0.1505 % respectively, corresponding to a hydrogen percentage of 0.1008 % which shows that the heat applied was sufficient to insure the complete combustion of hydrogen. It can therefore safely be concluded from the analyses that atmospheric air contains less than 0.0005 % hydrogen (or other combustible gas) and probably less than 0.0002 %, which agrees, as far as it goes, with the result obtained by Claude (0.0001 %), and shows the figures found by Gautier and Rayleigh to be altogether too high.

2. The relative quantities of carbon dioxide, oxygen and nitrogen.

A series of analyses of street air in Copenhagen, made before the final calibration of the apparatus, and with undetermined quantities of water in the burettes, show occasional variations in the carbon dioxide percentage and corresponding variations in the oxygen. When the carbon dioxide percentage of the uncontaminated atmosphere is taken as 0.030 %, the air in a large town will occassionally show this percentage in spite of the very large production of carbon dioxide going on. This means of course that the air is so rapidly renewed by the atmospheric currents that the carbon dioxide produced is less than 0.001 % of the ventilation. Usually, however, the carbon dioxide percentage is increased from 1—7 ‱ (between 0.031 and 0.037) above that of the free atmosphere, and I have found that the oxygen varies inversely with the carbon dioxide: there is usually an oxygen deficit corresponding to the increase in carbon dioxide.

I reproduce the series of determinations, giving only the increases in carbon dioxide above 30 ‱, the oxygen deficits (occasional increases in oxygen percentage being denoted by a —) and the variations in "nitrogen" percentage about their average.

Date 1917—1918	CO_2 increase ‱	O_2 deficit ‱	"N_2" variation ‱	Respiratory quotient $CO_2 : O_2$
Oct. 4	4	2.5	— 1.5	1.6
5	2.5	3.5	+ 1	0.7
8	2.5	3.1	+ 1	0.6
Novb. 6	7	8	+ 1	**0.9**
10	6.5	6.5	0	**1.0**
23	0	— 1	— 1	
Decb. 7	1	— 2	— 3	
12	1	— 2	— 3	
15	2	— 2.5	— 4.5	
18	5	5	0	**1.0**
19	3	5.5	+ 2.5	0.5
21	4	5.5	+ 1.5	0.7
22	5	5.5	+ 0.5	**0.9**
Jan. 25	2	4.5	+ 2.5	0.4

When oxygen is used up and carbon dioxide produced by the respiration of organisms or by combustion of fuel, the proportion of the volume of carbon dioxide produced to the volume of oxygen consumed is called the respiratory quotient of the combustion process, and this quotient depends exclusively (provided the combustion is complete) upon the nature of the substance burned — its content of carbon, hydrogen and oxygen. For pure carbon (coke) and for carbohydrates the quotient is 1.00 since we have

$$C + O_2 = CO_2$$

or

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O,$$

but for other fuel substances and foodstuffs the quotient is below unity being for instance for

wood and peat	0.95
coal	0·9
protein foods	0.8
fats	0.7
ordinary gas	0.5

The average respiratory quotient for the combustion and respiratory processes going on in a large town is probably about 0.9, and the average quotient observed on those days when the increase in carbon dioxide was sufficient to allow a fairly reliable computation of the quotient (increases of 0.005 % or over) is 0.95.

When the respiratory quotient differs from unity the percentage of nitrogen in the air becomes altered by the process, though the quantity of nitrogen is not affected unless free nitrogen is formed, which is the case only by the combustion of explosives. If therefore we could accept the quotients given in the fifth column of the table (p. 12) as real, the corresponding changes in "nitrogen" percentage would not indicate any formation (or consumption) of nitrogen nor any admixture of air from strata having a different nitrogen percentage. It is obvious, however, that some of the quotients observed cannot be real and most of the variations found in the "nitrogen" percentages must be due either to errors in the analyses or to real variations in the composition of the uncontaminated atmosphere. As mentioned above the only possible source of such variations is the admixture of air belonging to higher strata, since the production of gaseous nitrogen is much too small to account for them — even when explosives are used as freely as in 1917.

I do not venture to affirm that the variations in "nitrogen" percentage so far observed are real, since the analyses were not made with the utmost care and were not duplicated, but the analyses do show unmistakably that the constancy of the atmospheric "nitrogen" percentage at the surface is remarkable, since the variations — if any — do not exceed ± 0.003 %.

3. The absolute composition of the atmosphere at the surface.

When the variations in the "nitrogen" percentage of pure atmospheric air taken near the surface are of the magnitude indicated, or smaller, the average "nitrogen" percentage can be determined from a comparatively small number of analyses to at least three decimal places, and must be regarded as one of the geophysical constants. As such it ought, I think, to be determined with every possible precaution and care, for future reference, if not for any other reason.

Such a determination will require primarily the detection and elimination of the systematic errors which may be involved in the gasanalytical processes.

As mentioned above, one of the most serious systematic errors involved in gas analysis by means of a single burette, viz. the distillation of water from the measuring burette to the absorption pipettes, has been eliminated in my apparatus, and the accuracy of the volume determinations depends exclusively upon the calibrations of the burettes. Such calibrations have been carried out repeatedly with the utmost care, and while it was found that the volumes became appreciably altered during the first year after the mounting of the apparatus, they have now become constant, and the relation determined between the two burettes is reliable to within 0.0005 %. The remaining sources of systematic error are — so far as I am able to see — only two in number, viz. 1) incomplete absorption of oxygen by potassium pyrogallate and 2) the formation of carbon monoxide during the process of absorption. These two possibilities can be investigated in the apparatus itself by means of combustion analysis of the residual gas after the absorption of oxygen. I have not so far tested the completeness of the oxygen absorption, because I have good reason to consider it as complete beyond the 0.0005 % which can be read off, but I have made a special search for combustible gases in the nitrogen after the absorption of oxygen.

This is done in the manner described above (p. 10) under the heading: combustible gases in the atmosphere, after adding such an amount of pure carbon dioxide free air that the first measuring burette can be filled with the mixture.

In a preliminary series of determinations I heated the platinum wire to a bright red heat for several minutes and observed an average contraction on combustion of 0.0029 ± 0.00065 % and a further contraction after absorption by potassium hydroxide of 0.0055 ± 0.0004 %. When pure atmospheric air was treated in the same way the contraction on combustion was 0.0012 ± 0.0008, and after absorption 0.0032 ± 0.0004. The combustible gas formed by the absorption can consequently be taken to be carbon monoxide, since the volume of carbon dioxide produced is double the volume of the contraction by combustion, and its amount in ‱ is $\frac{2}{3}(2.9 + 5.5 - 1.2 - 3.2) = 2.7$ ‱. A second series of determinations made after the introduction of fresh pyrogallate solution, and at the lowest possible temperature of the platinum wire, gave a carbon monoxide formation of 2.3 ± 0.2 ‱. The quantity of carbon monoxide formed by the absorption of oxygen in an analysis of atmospheric air is therefore taken to be 0.0025 %, and a corresponding correction must be subtracted from the "nitrogen" percentages directly observed.

I have made two very careful analyses of atmospheric air just after the final calibration of the apparatus, and with a carefully determined quantity of water in both burettes, and found

Carbon dioxide	0.0305 %	0.030 %
"Nitrogen" (corrected)...	79.0215 %	79.0215 %
Oxygen	20.948 %	20.9485 %

When the average of BENEDICT's 200 analyses is corrected for the formation of 0.002 % Carbon monoxide it becomes

Carbon dioxide	0.030
"Nitrogen"	79.016
Oxygen	20.954

A further correction for the amount of water removed from the measuring burette by distillation during the analysis would diminish BENEDICT's oxygen percentage and increase the "nitrogen" percentage by a few thousandths of 1 %, but the exact value of this correction cannot be made out. The agreement between my two analyses and BENEDICT's average is at all events remarkable.

It would, in the opinion of the writer, be desirable to institute a more thorough research, based upon the analytical methods here given, to establish the absolute average composition of pure atmospheric air, and to study its possible variations, especially in higher strata of the atmosphere.

It is generally assumed that the lower atmospheric strata — the troposphere — up to a height of about 11—12 km. are the seat of extensive vertical movements, by which the air of these strata is so thoroughly mixed that the increase in nitrogen percentage with increasing height is counteracted and completely obscured. If no mixing took place the "nitrogen" percentage at a height of 10 km. should be 81.6 °/o against the 79.0 °/o found at the surface. There can be no doubt from the determinations made — few though they be — that up to a height of about 6 km. the variations in nitrogen percentage do not exceed a few hundreths of 1 °/o, but they may be much smaller, since the analyses so far made are reliable only within a few hundreths. Accurate analyses of series of simultaneous samples from various heights up to the 5 or 6 km., which could be reached by means of drakes or aëroplanes, would probably give valuable information about the completeness or otherwise of the gas mixture, and by a certain number of such series suitably distributed over the year, it would be possible to determine the average composition of the air of the troposphere with that degree of accuracy which its constancy will admit.

It appears to the writer to be a natural assumption that the limit between the troposphere and the stratosphere is not absolute, but that occasionally more or less considerable quantities of air, which normally belong to the stratosphere and possess the high nitrogen percentage corresponding to a height of 12 km. or more above the surface, may be involved in a vertical downward movement and become mixed with the ordinary tropospheric air. Such an admixture would give rise to a local and temporary increase in nitrogen percentage, and it might very well be possible to detect such increases by analyses, especially of air from comparatively high strata in the troposphere.

It is obvious that the greater the height from which samples could be obtained for analysis the greater would be the chance of detecting such variations, but of course the difficulty of getting samples will be much increased with increasing height. For an analysis accurate to 0.001 %, 60 cm^3 air at 760 mm pressure will be necessary, and 110 cm^3 if duplicate analyses are to be made. The volume of air required from a height of 5 km will be doubled, and 210 cm^3 from 10 km height will correspond to 60 cm^3 at normal pressure.

It would not, I think, be impossible to send up by sounding balloons evacuated glass vessels of say 250 cm^3 capacity, provided with reliable taps, and have them automatically opened and closed again at any desired height.

Samples from the stratosphere itself would probably differ so much from the tropospheric air that they would not require to be analysed with the greatest possible accuracy, and for an analysis, which can be made absolutely reliable within about 0.01 %, a sample of 15 cm^3 would be amply sufficient. 250 cm^3 air from a height of 20 km would give 17 cm^3 at ordinary pressure.

It would not be necessary in taking the samples to provide any instruments for recording the height, since the reduced volume of the air sample itself would provide an accurate index of the height at which it was collected.

Summary.

1. A gas analysis apparatus is briefly described which allows the determination of CO_2, O_2, "N_2" and combustible gases with an accuracy of 0.001 %. By suitable arrangements and precautions the systematic errors which are usually

involved in gas analysis can be eliminated and absolute determinations secured.

2. The hydrogen percentage of the atmosphere is not 0.003, as commonly assumed, but much lower. The percentage of combustible gases, which may or may not be hydrogen, is certainly below 0.0005 % and probably below 0.0002 %.

3. In the streets of Copenhagen the CO_2 percentage is usually, but by no means always, increased by 0.001—0.007 % above the normal 0.030. There is a corresponding deficit in the oxygen percentage. The respiratory quotient of the processes responsible for these variations is a little below unity (probably 0.9).

4. The "nitrogen" percentage shows a remarkable constancy, the variations observed being within $\pm$ 0.003 % from the average. The real variations are possibly even smaller.

5. The absolute composition of the atmospheric air at the surface has been found by two analyses to be 0.030 % CO_2, 79.022 % "N_2" and 20.948 % O_2.

6. The average "nitrogen" (nitrogen + the inert gases) percentage of the air of the troposphere is claimed to be a geophysical constant which it would now be possible to ascertain to within 0.001 %.

7. It is suggested that the analytical methods developed should be utilized for a thorough study of the composition of atmospheric air, including the analysis of samples from great heights obtained by means of aëroplanes, drakes and possibly sounding balloons.

Forelagt paa Mødet d. 13. Decbr. 1918.
Færdig fra Trykkeriet d. 7. Marts 1919.