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Determination of Atmospheric Constituents

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The first definite idea of the composition of the atmosphere resulted from the overthrow of Stahl's "phlogistic theory", by the researches of Black, Priestley, Scheele, Cavendish and Lavoisier.

Priestley, who shares with Scheele the discovery of oxygen and who was himself a firm believer in the "phlogistic theory", noted in 1772, that combustion and respiration deteriorated tha air and diminished its volume, while plant life renewed its power of supporting combustion. Later (1775-81) Lavoisier explained the part played by oxygen in the processes of combustion, respiration and oxidation; and in 1787 established the elementary character of nitrogen.

Previous to this (1781) Cavendish had proved that at all times and in all places, the component parts of air, which he expressed in terms of the "phlogistic theory", bore an approximately constant volumetric ratio to each other. Lavoisier's "celebrated experiment" with a known volume of air confined over heated mercury, by which one-fifth of its volume disappeared to be subsequently recovered as oxygen, from the mercuric oxide formed, demonstrated that air consists approximately, of one volume of oxygen and four volumes of nitrogen.

The very constant results obtained by Cavendish led Prout and Thomson to regard air as a chemical compound of nitrogen and oxygen. Dalton of "Atomic Theory" fame insisted, however, that air was merely a mechanical mixture, and that as nitrogen is lighter than oxygen, the relative amounts of the two gases must vary at different heights above the earth's surface, the oxygen diminishing and the nitrogen increasing in amount, as we ascend. Gay-Lussac and Thenard showed this latter assumption to be incorrect by collecting air at an elevation of 7,000 metres and finding upon analysis that the proportion of nitrogen and oxygen was the same as at the surface of the earth. Later and more exact investigation by Brunner corroborated this fact.

The important question now arose, whether the composition of air undergoes variation. For this investigation more accurate methods of analysis came into use;viz., the "eudiometric" and the "gravimetric". The eudiometric method consisted of the measurement of the volumes of the component gases and depended on the well-known fact, that when oxygen and hydrogen gases are mixed and exploded by an electric spark, they unite to form water, in the exact proportion of one volume of oxygen to two volumes of hydrogen. Hence if a mixture of a given volume of air and more hydrogen than is needed to combine with the oxygen in it, is exploded, one-third of the observed contraction will be due to the oxygen. Bunsen brought this method and the attendant precautions to a remarkable degree of perfection, obtaining the figures 79.076 and 20.924 as expressive of the volumetric ratio of nitrogen and oxygen in air.

Regnault, by imperfect volumetric methods, obtained results which showed a variation in the volume of oxygen from 20.4 per cent to 21.0 per cent, and was led to the assumption, which was held for many years, that the proportion of oxygen and nitrogen varies at different times and in different places to a considerable extent. The later extended investigations of Kreusler and Hempel proved this assumption to have been based upon erroneous determinations and that the oxygen content of the atmosphere was always between 20.93 and 20.95 per cent by volume.

The gravimetric method, which was used by Dumas and Boussingault in 1841 with good results, consisted of drawing air, washed with potash solution and dried by sulphuric acid, into a weighed vacuous flask, through a combustion tube containing reduced copper heated to redness. The increase in the weight of the copper was due to the oxygen of the air drawn through, while the increase in the weight of the vacuous flask gave the weight of the residual nitrogen. The specific gravities of the two gases being known, the following composition by volume was found:

Oxygen	20.77	per cent
Nitrogen	79.23	" "
Air	100.00	" "

Owing, however, to the greater accuracy and much greater ease of manipulation, the eudiometric or volumetric methods have completely supplanted the gravimetric methods in the determination of the oxygen in the air.

In connection with these early attempts at exact air analysis, two other important facts were demonstrated. The first, that air is a mechanical mixture and not a chemical compound, was shown from the following facts: (1) All chemical compounds contain their constituents in atomic quantities, which is not the case with air. (2) In the mixing of oxygen and nitrogen there is no such thermal reaction as is always observed in chemical combination. (3) Owing to the unequal solubilities of nitrogen and oxygen, the composition of air absorbed by water or other solvents has different percentages of nitrogen and oxygen from ordinary air.

The other fact shown by the early analysts was that besides containing nitrogen and oxygen, the air constantly contains small quantities of aqueous vapor, carbon dioxide, hydrogen peroxide, ozone and ammonium salts. Very lately a number of new atmospheric constituents have been discovered, notably, "Argon", a gas associated with atmospheric nitrogen and seperated out by withdrawing the nitrogen with red-hot magnesium turnings. Its discoverers, Lord Rayleigh and Prof. Ramsay describe it as quite soluble in water, very inert and possessing a characteristic spectrum. Its density is given as 19.9, which would account for the different densities of atmospheric and chemically prepared nitrogen.

In air analysis as now carried out, the nitrogen (including Argon etc.) is still determined by difference, the other constituents being estimated volumetrically.

Of the various volumetric methods used for the determination of oxygen, the neatest, simplest, and, if proper precautions be taken, the most accurate is that of Hempel, which consists of bringing an exactly measured volume of air (confined over mercury in a measuring bulb, connected with a leveling-tube and barometer) into a absorption pipette containing a solution of potassium pyrogallate over mercury. In a short time the oxygen is absorbed by the pyrogallate and the residual nitrogen ascertained by withdrawing from the pipette into the measuring bulb and rereading volume. The whole apparatus, with exception of the pipette is kept at a uniform temperature by means of water jackets.

Carbon dioxide in the atmosphere is best determined by absorbing with a barium hydroxide solution of known strength and the determining, by titration with a standard solution of oxalic acid, the amount of barium hydroxide still unacted upon. The equation

$$CO_2 + Ba\ O_2H_2 = BaCO_3 + H_2O$$

shows the chemical reaction, by which the amount of carbon dioxide (CO_2) is calculated.

Aqueous vapor is determined gravimetrically or volumetrically in connection with carbon dioxide determinations, by absorption from a given volume of air, by means of phosphorus pentoxide showing the amount of aqueous vapor in the volume of air. Another interesting method is by means of the hair hygrometer, by which the amount of aqueous vapor is calculated from the contraction or expansion of a hair, from which the oil has been removed and which is connected with a pointer on a graduated scale. Still another method of determining aqueous vapor is by the use of August's "psychrometer", an instrument based on the fact that water exposed to the air evaporates the more rapidly. and therefore extracts more heat from its surroundings, the farther the air is removed from the condition of saturation. The tension of the aqueous vapor is calculated from the lowering of the temperature of a thermometer ($T-\grave{T}$) according to the formula,

$$\text{Aq. Ten.} = \grave{E} - K\,(T-\grave{T})\,B,$$

in which $\grave{E}$ is the tension corresponding to the temperature $\grave{T}$; B, the barometric pressure im millimetres; and K an empirical factor, which has according to the researches of Regnault the following values:

In small closed rooms -----	.00128
" large " " -----	.00100
" halls with open windows	.00077
" courts ------------------	.00074
" open air (no wind) -----	.00090

Of the other above mentioned atmospheric constituents, Ozone is of considerable interest and importance. There has been of late some discussion whether Ozone exists naturally in the air or whether the apparent detection is not due to Hydrogen Peroxide, which gives very similar reactions with the various so-called "Ozone test papers" etc. These ozone papers are prepared by dipping strips of Swedish filter paper in to a wine-red litmus solution, which contains in a cubic centimetre about .013 gram of the extracted constituents dried at 100° C. The paper is dried and then impregnated to a fourth of its length with a one per cent solution of neutral and pure potassium iodide, free from iodate. The paper is then fastened over the end of a glass tube by means of a rubber band and a measured quantity of air is drawn through by an aspirator. The ozone decomposes the potass-iodide, forming potassium-hydroxide, which colors the litmus paper blue. From the intensity of the blue coloration the amount of ozone present is determined by means of a standardized color chart. To determine large amounts of ozone, it is best to lead the gas through a solution of potassium iodide and titrate the iodine set free with a solution of sodium thiosulphate.

As evidence of the degree of perfection reached in modern air analysis, it is perhaps of interest in closing to quote Dr. Hempel's figures of a series of oxygen estimations by two of his assistants, Messrs. Oettel and Schumann. The air analyzed was kept in fused glass tubes and the two sets of analyses performed more than a year apart.

In air of April 5, 1886, Oettel found	20.93	per	cent	Oxygen.
" same (one year later) Schumann "	20.94	"	"	"
" air of April 14th, 1886, Oettel "	20.89	"	"	"
" same (one year later) Schumann"	2o.89	"	"	"

In four analyses of one sample of air Oettel found

20.936	per	cent	Oxygen
20.938	"	"	"
20.938	"	"	"
20.938	"	"	"

It is from such data as the above that we find, besides a quantitative atmospheric constituent, two prime qualitative constituents of a real chemist's character, carefulness and accuracy.