[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COPENHAGEN]

A BURET FOR MICRO GAS ANALYSIS[1]

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During work with gases at very low pressures (0.1–0.01 mm.) it is often necessary to analyze quantities of gas of the order of magnitude 10^{-6} moles, or 20 cu. mm. or less. The problem has been solved by different authors[2] in several ways but as the apparatus described below presents some new details and seems to have certain advantages, it will perhaps be of interest to workers in similar lines.

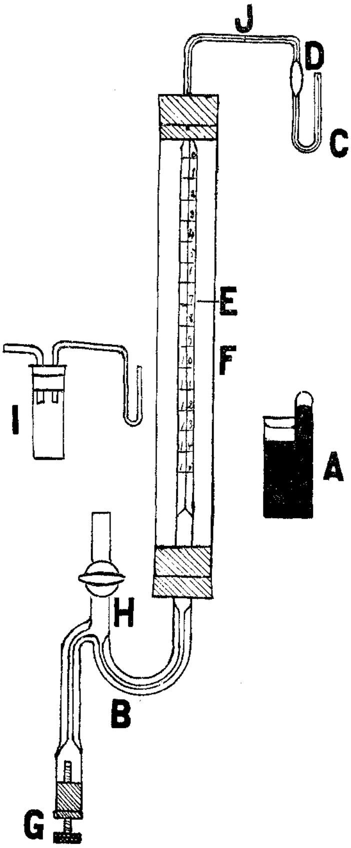

Fig. 1.

In order to avoid very complicated apparatus, I have adopted the plan of pumping off the gas with a Toepler pump, collecting it over mercury and analyzing it at atmospheric pressure.

The gas was collected in gas holders of the type A shown in Fig. 1. They were made from sampling tubes of suitable dimensions, the smaller one (8 by 27 mm.) being cemented to the inner side of the greater one (25 by 50 mm.) by means of de Khotinsky cement in such a way that the tip C of the gas buret B could be introduced into it from beneath. The gasholders were filled with mercury, the small tube by suction with the Apparatus I.

The construction of the gas buret B appears from the figure. The main parts of it are the intake tip C, the absorption bulb D, the graduated tube E surrounded by the water-filled tube F, the mercury-tight screw G and the tap H. The capillary E and the screw are of the type recommended by Professor A. Krogh,[2c] the tube being divided in millimeters on a length of 15 cm. and having a volume of about 10 cu. mm. for a length of 15 cm.,

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[1] Read at "Det 17 'de skandinaviske Naturforskermøde," Gøteborg, **1923.**

[2] (a) Langmuir, THIS JOURNAL, **34,** 1313 (1912). (b) L. Hamburger and W. Koopman, *Z. analyt. Chem.*, **57,** 121 (1918). (c) A. Krogh, Abderhalden's "Handbuch der biochemischen Arbeitsmethoden," Urban and Schwarzenberg, Berlin, **1915,** VIII, p. 495. (d) Silvan Ott, *Z. physik. Chem.*, **109,** 1 (1924).

the bore being about 0.3 mm. The screw is made from hard rubber and fits tightly in a steel nut, cemented into the glass tube by means of de Khotinsky cement or sealing wax. The tip C, and the capillary connecting the tube E and the absorption bulb have a bore somewhat smaller than that of the capillary E, about 0.1 mm., but it is essential for good operation of the apparatus not to make it too small. The volume of the absorption bulb must be somewhat greater than that of the measuring tube, a proportion of 1.5:1 to 2:1 being suitable. It must be so narrow that a mercury column entering through the upper capillary will not break; about 1.5 mm. is suitable. The tip C is broken sharply as shown, and to get a regular intake and delivery of gas it is filed as plane as possible by means of a very fine file, moistened with camphor in turpentine. The tap H is only used for filling the apparatus with mercury and is not absolutely necessary. The arrangement of the lower part of the apparatus serves to prevent air bubbles or grease from reaching the capillary E. The apparatus is filled with mercury and calibrated by pressing out small drops of mercury and weighing them one by one. A small air bubble in E serves as index during this procedure.

The absorption liquids are conveniently stored over mercury in gas holders of the type described above. The ordinary reagents are used, a 20% solution of potassium hydroxide for carbon dioxide, an alkaline solution of sodium hydrosulfite for oxygen and an ammoniacal solution of cuprous chloride for carbon monoxide. As confining liquid both water and mercury can be used but water is the more convenient. The mercury in the gas holder and the containers for the absorption liquids are covered with water, which must be removed after use (else the cement will very frequently leave the glass).

The analyses are carried out as follows. By means of the screw G the whole apparatus is filled with mercury. The gas to be analyzed is drawn from a gas holder into the bulb by means of the screw, and the tip is then transferred to the water covering the outer surface of the mercury. By further unscrewing, water is drawn in and the gas bubble thereby transferred to Capillary E where its length is measured, the tip C being covered with water.

Now the gas bubble is forced into Bulb D, so that only the tip remains filled with water, and the tip next transferred to the absorption liquid. This is drawn back into the bulb, where the absorption is effected by operating the screw back and forth several times. If necessary, the rate of the absorption can be controlled by further unscrewing until the boundary reaches the mark J, and reading the position of the lower surface of the gas bubble. When the absorption is complete the liquid is pressed back into its reservoir as completely as possible, the tip placed in the water layer and the solution washed out by repeatedly filling the bulb with water and pressing out again. Finally, the length of the gas bubble is again measured. All the absorptions are carried out in this manner.

Combustible gases (hydrogen and methane) can be determined in a very simple way in the same apparatus by exploding them with oxygen. To accomplish this the sample from which carbon dioxide, oxygen and carbon monoxide have been removed is mixed with a suitable volume of oxygen from a micro gas holder (Type A) and the volume of the mixture measured as described above except that the water covering the mercury is acidulated with a few drops of dil. sulfuric acid, and the liquid is thus used for confining the gas. After measurement, the mixture is pressed into the bulb D. It is then confined between mercury covered with a small column of water (this layer always forms during the absorptions) on the one side and a column of acidulated water, which is electrically connected to the water on the surface of the oxygen container, on the other. When now the poles of a small induction coil are connected, respectively, to the mercury (or the water) of the oxygen container and the steel nut G, a spark can be passed through D and explosion will occur. After explosion the volume is measured again, and if methane is present the carbon dioxide formed by the combustion is determined by absorption as described above. The content of hydrogen and methane can then be determined by means of the well-known equations. Sparking between uncovered surfaces of mercury must be avoided, as oxidation in this case invariably occurs.

Of course the danger of oxidizing nitrogen exists, just as in an ordinary (macro) explosion pipet, although the cooling effect in the present case must be much more pronounced. However, I have never noted any serious error arising from this cause. Only one precaution must be taken. The contraction occurring must be distinctly observable and accompany the first spark, as prolonged sparking will tend to oxidize nitrogen and thus give rise to errors. If the mixture is very poor in combustible gases, it may thus be necessary to add detonating gas, just as in the ordinary explosion analysis.

The use of mercury as confining liquid is only necessary, when the carbon dioxide content is great and must be accurately determined. On trial it will be found very easy to modify the above procedure so as to apply also in this case, and consequently a detailed and rather tedious description of the method is not necessary. It must be noted, however, that to secure a well defined pressure at the moment of measurement of the length of the gas bubble, the confining column of mercury must have the shape ∩, so that one of its surfaces is at the zero (upper) point of the scale on the capillary E, while the other is in the bulb D and always at the same height. It is thus necessary always to use the same volume of mercury for confining the gas, which can of course easily be arranged. For the purpose of using mercury it is especially necessary not to make the intake tip too narrow. To secure a regular movement of the mercury it must be pure and the column must not be broken by small drops of water.

The advantage of this apparatus over the original apparatus described by Krogh is that an analysis can never be lost on account of a gas bubble parting from the rest in the measuring tube, as bubbles can always be collected again, either in the bulb beneath the measuring tube or in the absorption bulb, but of course one must be very careful not to drive the gas too near the tip, and thus incur losses. Another advantage is that the absorption liquids are protected against the influence of the air, and also that the operation is cleaner. A disadvantage is, that it works somewhat more slowly than Krogh's apparatus, a complete analysis being performed in one-half to three-quarters of an hour. The accuracy in the determinations by absorption is the same as with Krogh's apparatus, namely, about 0.1% absolute, when 10 cu. mm. can be disposed of. When the precautions mentioned above are taken the analyses by combustion also have about the same degree of accuracy.

Summary

A simple form of apparatus is described for the convenient micro analysis of quantities of mixed gases up to 20 cu. mm.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. VIII. THE PHYSICAL PROPERTIES OF MONOGERMANE[1]

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Introduction

In 1923 Dennis, Corey and Moore[2] prepared and isolated digermane, Ge_2H_6 and trigermane, Ge_3H_8. In the course of that investigation, about two liters of monogermane, GeH_4, was obtained, which was identified and stored in gas holders. This compound has already been studied by Voegelen,[3] Müller and Smith,[4] Paneth and Schmidt-Hebbel,[5] and Schenck.[6] Schenck obtained the gas in considerable amount and showed by analysis and vapor-density determinations that its composition was represented by

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Dennis, Corey and Moore, THIS JOURNAL, **46**, 657 (1924).

[3] Voegelen, *Z. anorg. Chem.*, **30**, 325 (1902).

[4] Müller and Smith, THIS JOURNAL, **44**, 1909 (1922).

[5] Paneth and Schmidt-Hebbel, *Ber.*, **55**, 2615 (1922).

[6] Schenck, *Rec. trav. chim.*, **41**, 569 (1922).