THE PURIFICATION OF ^{18}O-WATER

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Summary

A reliable method for the purification of 15 to 20 mg samples of ^{18}O-water, as a preliminary step to the measurement of isotopic composition by a density technique, is described. The method is based on the use of copper oxide as the oxidizing agent but negligible isotopic dilution is involved as the oxygen of the oxide is obtained by electrolysing a small fraction of the water requiring purification. The total purification time is about 1 hr.

I. INTRODUCTION

An essential step, prior to the determination of the isotopic composition of water by a density technique, is the purification of the water. The removal of inorganic contaminants is usually not difficult but the removal of traces of volatile organic matter presents a very serious problem. The only method found in the literature for the purification of small quantities of water (20 mg) is described by Polanyi and Szabo (1934) and Herbert and Lauder (1938). The process involves circulating the water in the vapour state over a white-hot platinum filament. Experience shows, however, that the method is not entirely satisfactory. For the purification of heavy hydrogen water, on a macro-scale, methods employing oxidizing agents such as $KMnO_4$, Na_2O_2, CuO, and CrO_3 have been adopted by Linderstrøm-Lang, Jacobsen, and Johansen (1938), by Fenger-Eriksen, Krogh, and Ussing (1936), and by Keston, Rittenberg, and Schoenheimer (1937). These methods can be used for large samples of ^{18}O-water if a dilution factor is applied. These procedures, however, are not suitable for the purification of small samples of ^{18}O-water.

A new technique has been devised which has given good results even with heavily contaminated water. The method is based on the use of copper oxide as oxidizing agent but dilution due to the exchange of oxygen between the water and the oxide is eliminated. The oxygen of the oxide is obtained by electrolysing a small fraction of the sample of water requiring purification.

II. EXPERIMENTAL

The electrolysis cell (Fig. 1) is formed from a piece of Pyrex tube (8 mm O.D.). The thickened part is about 7 mm long and has a bore of 2 mm. Unless the cell has a suitable shape considerable difficulty is experienced during electrolysis due to bubbles blocking the capillary. As an aid to the selection of suitable cells, 20 mm^3 of 0·3M Na_2SO_4 solution are added. This should just fill the capillary. With the platinum wires (0·01 in. diameter) dipping about 1 mm

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into the solution on each side, the electrolytic resistance should be of the order 1200 Ω. The volumes of the system on the two sides of the cell are adjusted during construction so that the levels of the solution on the two sides of the cell remain constant during electrolysis.

Anhydrous sodium sulphate (1 mg) is added to the cell during construction of the system and serves as electrolyte. No exchange of oxygen occurs between the water and sodium sulphate under the experimental conditions. A current of 10–50 mA is maintained between electrodes. This fluctuates considerably and so a small coulometer containing dilute sulphuric acid is placed in series with the cell in order to determine easily the quantity of electricity which has passed through the cell. Water (2 mg) is electrolysed for each purification. Electrolysis occasionally stops due to a bubble blocking the capillary, but the bubble may easily be displaced by warming one side of the system with the hand. The cell is observed by a lens during the electrolysis. The oxygen liberated reacts subsequently with copper gauze in the silica tube (see diagram) which is heated electrically. The copper gauze is wrapped in platinum foil to avoid reaction between the copper oxide and the silica. The whole procedure may be described as follows.

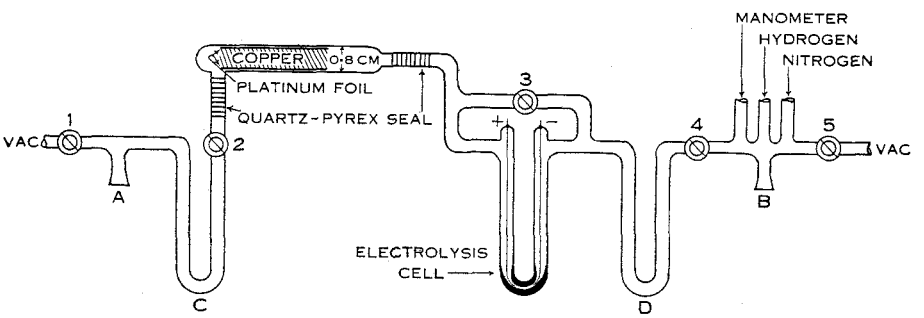

Fig. 1.—Diagrammatic representation of purification apparatus.

The vessel containing the sample to be purified is attached at *B* and the system up to tap 4 is evacuated through tap 5. The copper gauze is treated at 750 °C with hydrogen to ensure that it is free of oxide. The sample of water is pumped over the hot copper (750 °C) and is collected in U-bend *C*. During this process some organic impurities suffer thermal decomposition. The process is repeated two or three times until a Pirani gauge in the vacuum line shows no pressure rise while the vapour is passing over the copper. The latter is then cooled to room temperature and the water is condensed in the capillary of the electrolysis cell. Nitrogen is introduced to a pressure of 30 cm Hg or more. This reduces trouble due to frothing at the electrodes. With taps 4, 3, and 2 in the off position, electrolysis is started. Finally, the solution in the cell is frozen at −80 °C. The ice blocks the capillary and thus the oxygen can be held in the system while the hydrogen is pumped away. Tap 3 is then turned on to equalize the pressure on the two sides of the cell. A small heating coil is placed around the bottom of the electrolysis cell to evaporate the water to the top of the cell. If the water is simply pumped away from the cell, feathery particles of sodium

sulphate blow about the system. After allowing 15 min for the furnace to heat up to 750 °C, taps 1 and 2 are opened alternately. The oxygen is taken up by the copper and the water collects in the U-bend *C* cooled to −80 °C. The water vapour is pumped backwards and forwards over the copper oxide seven times and after the last passage it is collected in U-bend *C*. Hydrogen is introduced. The formation of water at this stage indicates sufficient copper oxide was present for the purification. All the water is transferred to a suitable vessel attached at *A*.

III. Results

The system was tested initially with the copper oxide at 400 °C, but impurities were not removed completely. At 750 °C traces of various organic compounds, methyl and ethyl alcohols, dioxane, benzhydrol, etc., were quantitatively removed as judged by the density of the sample of water purified.

At 750 °C an appreciable exchange of oxygen occurs between the quartz and the water vapour. If the quartz is initially "normal", the first sample of ^{18}O-water with an excess density of 565 p.p.m. loses 26 p.p.m. Water of normal isotopic composition passed through immediately after an ^{18}O-water sample (565 p.p.m.) turns out 26 p.p.m. heavy showing that exchange also occurs in the reverse direction. Results of this type have been obtained repeatedly. This exchange does not interfere with tracer work if three samples from any experiment are passed consecutively through the different techniques in order to eliminate memory effects.

The total purification time per sample is about 1 hr. Samples as small as 14 mg have been purified. Densities were measured with an accuracy of ±3 p.p.m. by the modified Gilfillan-Polanyi technique described in the following paper (Lauder 1959).

A larger modification of the apparatus can be used for purification of gram-quantities of ^{18}O-water.

IV. References

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