

THE REMOVAL OF WATER FROM VOLATILE ORGANIC PRODUCTS OF OXYGEN-18 TRACER EXPERIMENTS*

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The conventional methods of drying organic compounds (e.g. Morton 1938 ; Weissberger 1955) are not always immediately applicable to the drying of small quantities of alcohols etc. isolated from tracer experiments involving the use of ^{18}O -water. Several authors have reported work recently in which the application of a better drying technique would have been advantageous.

Bunton, de la Mare, and Tillett (1959) claim that diethyl sulphite hydrolyses entirely by sulphur-oxygen bond-fission although the ethanol isolated showed an apparent oxygen-18 at. % in excess of 0.034. The authors regard this as a slight enrichment and suggest that it is probably caused by incomplete drying of the ethanol. However, it could represent up to 15% carbon-oxygen fission.

Again Bunton *et al.* (1958) fractionated the methanol obtained from the hydrolysis of monomethyl phosphate in ^{18}O -water. Several samples were collected and two middle samples were used for isotopic analysis. The remaining samples were mixed with normal water and refractionated, two middle-samples again being analysed as a check on the efficiency of distillation. Rottenberg and Thürkau (1959) investigated the oxidation of alcohols by oxygen gas in the presence of platinum using oxygen-18 as a tracer. In order to remove traces of oxygen-18 in the form of water from the products, the samples of alcohol (1 ml) were shaken in a 500 ml flask filled with "normal" carbon dioxide for 24 hr. This operation was repeated three to four times.

These reports have led us to give an account of an efficient, rapid method using anhydrous calcium sulphate for the drying of volatile substances which has been employed in this laboratory for the past 6 years. Hammond and Withrow (1933) reported the use of a similar principle in the second paper dealing with this drying agent, but for much larger quantities of material.

* Manuscript received July 7, 1960.

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Experimental

For the removal of 70–80 mg of water from a sample containing say 300 mg of methanol a vacuum system of the type illustrated by the line diagram in Figure 1 is used. Column A (0.8 cm i.d.) is packed with 7 g of calcium sulphate (40 mesh). Each of the columns I and II contains 0.6 g of calcium sulphate (40 mesh). The latter columns are constructed to the design shown in Figure 1, inset (a). All drying columns are wound with nichrome ribbon and are heated electrically to 180 °C and pumped for 15 min, or until no further water comes off, prior to use. All dryings are carried out with the columns at room temperature.

A vessel containing the alcohol to be dried is attached to the ground joint B and the alcohol is maintained at about 10 °C (so as to give a suitable vapour pressure) during the drying process. The vapour is pumped through tube A and is condensed in the U-bend C cooled in liquid air. The process is followed by means of the Pirani gauge at D.

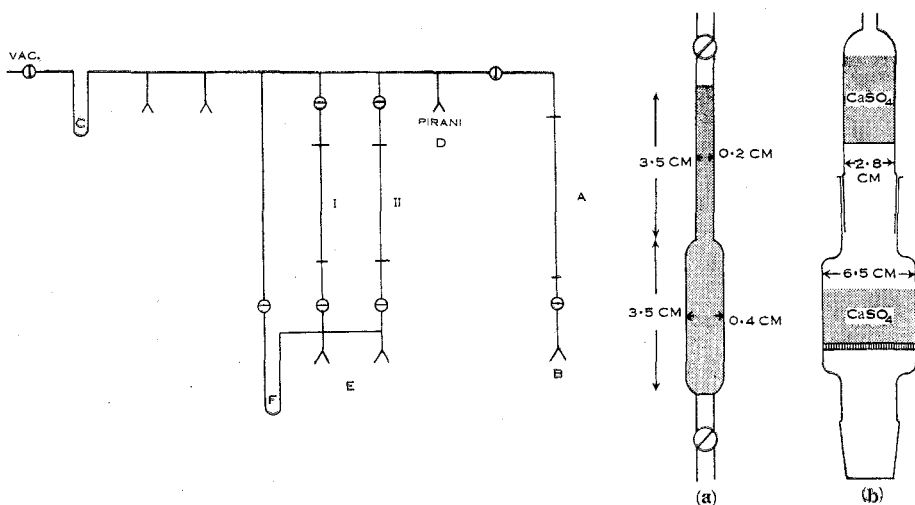


Fig. 1.—Diagram of vacuum-drying system using calcium sulphate.

Inset (a): Diagram showing design of column I.

Inset (b): Design of large column for absorbing 5 g of water.

During the drying a distinctly warm zone can be felt moving up column A. For a maximum recovery of alcohol, this warm zone should almost reach the top of the column, otherwise a small amount of alcohol remains adsorbed on the calcium sulphate. (A blank experiment is used to adjust the amount of calcium sulphate present if quantitative recovery is desired in a tracer experiment. Alternatively, more water may be pumped onto the column to make the warm zone move to the top.) If the absorptive capacity of the column is exceeded, a ring of ice forms 2–3 mm above the ring of alcohol in U-bend C. The alcohol in U-bend C is transferred to U-bend F and the process is repeated using column I and again using column II if desired. The alcohol in U-bend F is kept at about 10 °C during the drying stage.

If the water content of the alcohol is low the vessel containing the sample is attached at the ground joint *E* and columns I and II used directly.

Results

To test the efficiency of drying, two mixtures each containing 5.7 mg of water (at. % oxygen-18 in excess, 0.45) and 50 mg of methanol of normal isotopic composition were made up and then separated by passage over column I and then over column II. The pressure changes observed on the Pirani gauge are shown in Figure 2. In 3.5 min practically all the alcohol is recovered. The loss of alcohol amounted to 1.5% and experiment showed most of this occurred

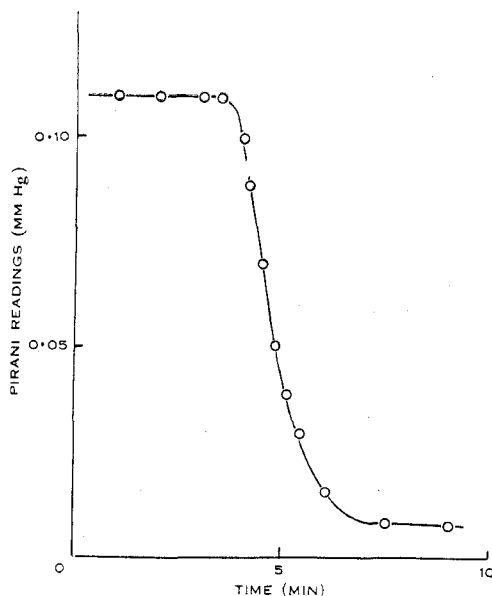


Fig. 2.—Pressure changes shown by the Pirani gauge at point *D* during the drying of methanol.

during passage through column II, when virtually no water is present to chase adsorbed alcohol off the calcium sulphate. The methanol showed a normal oxygen isotopic composition (cf. Lauder 1959; Lauder and Wilson 1959*a*, 1959*b*; Lauder and Zerner 1959).

Larger columns of the type shown in Figure 1, inset (*b*), containing a total of 225 g of calcium sulphate (40 mesh) have been used to separate 5 g of ^{18}O -water from water-dioxan-methanol mixtures resulting from tracer experiments. The calcium sulphate in the larger columns takes up about 2.5%, while in the smaller columns it takes up about 1.5% by weight, before water can be detected escaping from the top of the columns. The water adsorbed can always be recovered and weighed and in this way the progress of drying may be followed.

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