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Preparation of Tritiated Water, Sulfuric Acid and Trifluoroacetic Acid

H. A. DUGGER and H. J. SCHWARZ
Sandoz Pharmaceuticals, Inc., Route 10, Hanover, New Jersey, U. S. A.
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SUMMARY

A safe, efficient and inexpensive method for preparing small quantities of tritiated water, sulfuric acid and trifluoroacetic acid is described. The preparation involves introducing the preassayed tritium sample into a carrier gas, 0.5% hydrogen in air, passing over a palladium catalyst heated to 800° C. The resulting tritiated water is gradually eluted from the catalyst and collected in suitable traps.

INTRODUCTION

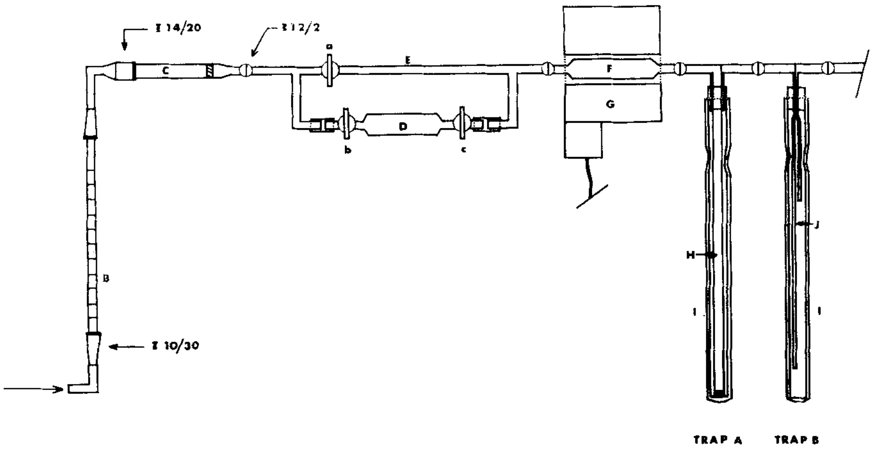
The apparatus in common use for preparing tritiated water and substances derived from it, for example, H_2SO_4-^3H, CF_3CO_2H-^3H, are usually only a small part of an extensive manifold designed for general purpose work with tritium gas and tritium labelled materials (1).

Since tritiated water is needed for both acid-base catalyzed and transition metal catalyzed exchange reactions, a simpler, less versatile method to prepare water-^3H is needed. This paper reports on an apparatus designed to oxidize preassayed quantities of tritium (obtainable in the U.S.A. for a small handling charge) in a standardized gas-buret and to collect the resulting water in a form suitable for exchange reactions. In subsequent sections, the materials and apparatus required are described in detail as are the techniques for preparing H_2O-^3H, H_2SO_4-^3H, CF_3CO_2H-^3H.

EXPERIMENTAL

Materials.

The tritium gas was purchased from New England Nuclear Corporation in specially made gas burets (see Fig. 1) supplied by us. In each case, the amount



A. Gas cylinder containing 0.5 % hydrogen-air mixture. (Not Shown).
B. R. G. I. Flowmeter available from Kontes Glass Co.
C. Drying tube filled with aluminium oxide. The drying agent is held in place with a fritted disk.
D. Gas sampling tube filled with tritium. The size (2-6 cc) varies depending on the amount of tritium to be oxidized.
E. By-pass Bridge.
F. Quartz catalyst tube made by Thermal American Fused Quartz Co. The catalyst is 0.5 % palladium on 1/8" Alumina pellets from Engelhard Industries; chemical catalyst division. The catalyst is held in place with quartz wool.
G. Hoesli micro combustion furnace.
H. Standard delivery tube designed to fit I.
I. Carius combustion tube available from Corning Glass Co.
J. Standard delivery tube designed to fit I.
TRAP A. Consists of H. and I. used as the initial trap to prepare H_2SO_4-^3H, CF_3CO_2H-^3H and to collect water in dimethyl acetamide.
TRAP. B. Consisting of I. and J. used as the initial trap to prepare H_2O-^3H.

FIG. 1. Apparatus for preparing small quantities of tritiated solvents by oxidation of tritium.

of tritium was as stated ±10%. Other chemicals used were reagent grade as supplied by the manufacturers without additional purification. The carrier gas, 0.5% hydrogen in air, was purchased from Matheson Co. The catalyst was 0.5% palladium on 1/8" alumina pellets prepared by Chemical Catalyst Division, Engelhard Industries. In the construction of the apparatus, all ball and socket joints were TS 12/2, all stopcocks were TS # 2 and where possible, all glass tubing was 2 mm I.D. The catalyst chamber was made of quartz and the catalyst was held in place by quartz wool.

The system was developed and checked using portions of a mixture of 1 curie of tritium in 22 liters of hydrogen also obtained from the Matheson Co.

Method.

The apparatus as shown in Figure 1 is initially set up with the carrier gas from the gas cylinder (A) (not shown) passing through flowmeter (B) through a drying tube (C) and then into the upper arm of the bypass (E). That is, stopcock (*a*) is open while stopcoks (*b*) and (*c*) are closed. The gas buret (D) containing the tritium to be burned is designed to be attached by sleeves of Tygon tubing to complete the lower arm of the bypass. From the bypass the gas stream enters the quartz catalyst chamber (G) maintained at about 800° C by a Hoesli micro combustion furnace (F). The gas exiting from the catalyst chamber passes through a series of traps. Two types of traps are depicted in Figure 1. The type used and the order in which they are arranged depends on the ultimate use of the water-^{3}H collected. To insure that no exchangeable radioactivity leaks into the atmosphere, the last trap in the line should be of type A and should contain 95% sulfuric acid. Once the system is in order and working properly, stopcock (*a*) is closed and the tritium is introduced by opening stopcocks (*b*) and (*c*). A carrier gas flow of 45 ml std. air/min is maintained for 6 hours to insure removal of all the water-^{3}H from the catalyst.

Flow rate.

The effect of flow rate on the rate of elution of the water-^{3}H is shown in two experiments (see Fig. 2). The slower flow rate (5 ml std. air/min) was

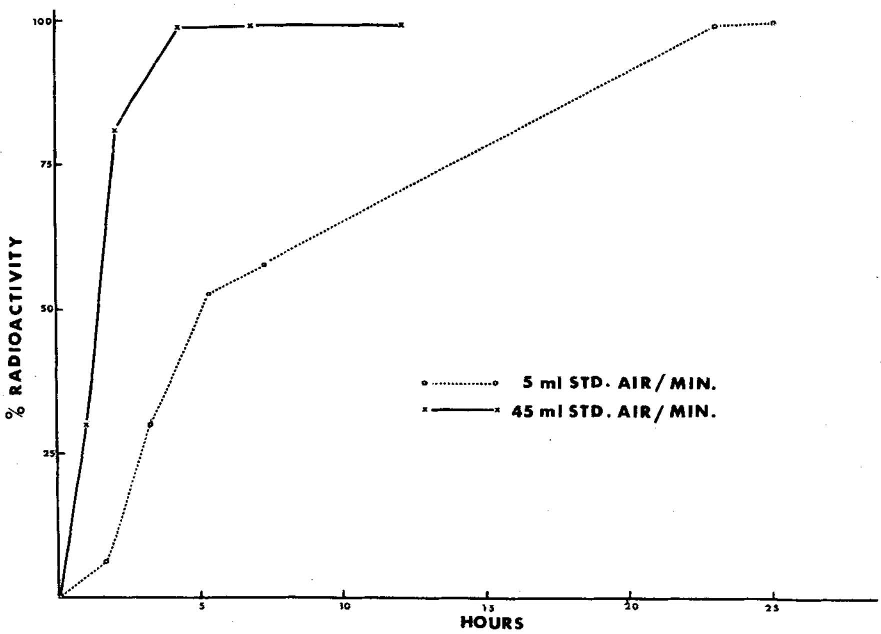


FIG. 2. Rate of elution of tritiated water from the catalyst as a function of flow-rate.

used in the earlier work where narrower tubes were used for the traps and the faster rate (45 ml std. air/min) is used currently with traps of a larger diameter. In both cases, these rates are the maximum velocity before foaming becomes a problem. In these experiments after a small sample of tritium- hydrogen mixture (90 μc) was introduced into the system, the rate of elution was followed by periodically changing the traps containing 95% H_2SO_4, and assaying the contents. The elution was followed until the amount of radioactivity in the trap was less than 1% of the total.

Preparation of sulfuric acid-^{3}*H.*

95% or 98% sulfuric acid (1-3 grams) in a trap as shown in Figure 1, trap A, is used to collect the water-^{3}H, produced as described above. The tube containing the sulfuric acid is a commercially available Carrius tube, eliminating the need to transfer the highly radioactive product. One removes the fritted bubbler, washes it into the Carrius tube with a little sulfuric acid held back for this purpose, adds the compound to be labeled and the tube is ready to be sealed. The first three entries in Table I show the results of this method.

Preparation of trifluoroacetic acid-^{3}*H.*

Trifluoroacetic anhydride, 2.0 cc, is placed in the initial trap, type A, Figure 1, and cooled to −78° C with a Dry ice-isopropanol bath so arranged that only the liquid is cooled to any extent and the general method followed. At intervals of 1½-2½ hours, the gas flow is stopped and the ice crystals which form in the bubbler tube are allowed to melt by removing the cooling bath for a few minutes. After six hours the gas flow is stopped, the bubbler removed and washed with a small amount of trifluoroacetic acid and the calculated amount of water necessary to complete the conversion of trifluoroacetic anhydride to the acid is added. The result of one such experiment is at the bottom of Table I.

Preparation of water-^{3}*H.*

Tritiated water is prepared by the general method and collected in one of two ways. If tritiated water is needed as such, a special trap is used (see Fig. 1, trap B). Here the inlet tube is shorter than the outlet tube. The trap is emmersed in a Dry-ice-isopropanol bath so that 1 cm of the inlet tube is below the level of the cooling bath. This design allows one to collect only 70-90% of the eluent radioactivity. The remaining radioactivity is found in subsequent traps. If the water is intended for use in a transition-metal catalyzed exchange reaction where dimethylacetamide can be used as solvent, this solvent cooled to −78° C can be used in the first trap (Fig. 1, trap A) to improve the efficiency. The results of such an experiment are shown in Table I on the fourth line.

Table I.

Starting tritium curies [c]	Flow rate ml st. air/min	Time (hr)	Trap No.	Type of Trap [d]	Contents	Temperature	Amount of Radioactivity (mc)
15	5	24	1	A	95% H_2SO_4	R.T.	15,700
			2	A	95% H_2SO_4	R.T.	7
			3	A	95% H_2SO_4	R.T.	0
5	5	24	1	A	95% H_2SO_4	R.T.	5,190
			2	B	Air	−78° C [a]	0.6
			3	A	95% H_2SO_4	R.T.	0
10	45	6	1	A	95% H_2SO_4	R.T.	10,400
				A	95% H_2SO_4	R.T.	0.5
10	45	6	1	A	D.M.A. [b]	−78° C [a]	11,800
			2	B	Air	−78° C [a]	21
			3	A	95% H_2SO_4	R.T.	0
5	45	6	1	A	$(CF_3CO)_2O$	−78° C [a]	4,390
			2	A	95% H_2SO_4	R.T.	845

[a] Dry-ice-isopropanol bath.
[b] Dimethyl acetamide.
[c] As supplied by New England Nuclear Corp.
[d] See Figure 1 for depiction of the two types used.

As in the previous case, trifluoroacetic anhydride, where a low temperature bath was used, the ice which forms in the delivery tube is removed at intervals.

Discussion

The catalyst which is marketed for the removal of traces of hydrogen from industrial air streams seemed ideal for our purpose but in practice, it proved to be very hygroscopic. Even at 800° C, using air as a carrier gas, very little of the radioactivity introduced was to be found in the traps when a mixture of hydrogen and tritium (2 cc) was oxidized. This difficulty was overcome by incorporating a small amount of hydrogen, 0.5%, into the carrier gas. In effect, this dilutes the tritium, a factor which is more important when samples of carrier free tritium are oxidized (2), and elutes the tritiated water from the catalyst surface. The time required for elution of the radioactive product depends on flow rate which in turn depends on the size of traps used and the contents. Each time the flow rate is changed due to a change in traps or trap contents, the optimum time must be redetermined. The time required for removal of 90-100% of the radioactivity at a flow rate of 45 ml std. air/min is 4-6 hours.

The preparation of H_2SO_4-^3H is straightforward but the preparation of tritiated water and trifluoroacetic acid are in some ways inconvenient. Both involve low temperature traps in which ice forms at least partially blocking the flow of air. If the ice is not removed every 1½-2½ hours, the flow can be completely stopped. There is so little pressure built up that there is no danger of a leak of radioactive materials into the atmosphere. The rate of flow simply drops to zero until the ice is removed.

The preparation of tritiated water collected as such has the additional disadvantage in that only 70-90% of the radioactivity is found in the first trap. With proper planning this may be turned to advantage — material for two exchange reactions could be prepared simultaneously. In practice, to prepare 10 curies of tritiated water, one begins with 15 curies of tritium. The added expense is negligible.

The inconveniences are more than offset by the advantages. 1) The method is easy, only three stopcocks to turn. 2) The use of a palladium catalyst gives a cleaner product than oxidation of tritium over CuO. 3) The apparatus is easily assembled, disassembled and stored when not in use. The only parts requiring special storage are the delivery tubes used in the traps and the catalyst chamber. 4) A great advantage is that since the Carrius tube is part of the trap in which the radioactive exchange medium is prepared, no transfer of highly radioactive and in some cases hygroscopic material is necessary. 5) Since a gas buret can be sent to most suppliers of tritium and returned within about 7 days, the need to store large quantities of tritium in the laboratory is eliminated. And finally, 6) this preparation reduces by 80-85% *, depending on the number of curies prepared, the price of tritiated sulfuric acid, trifluoroacetic acid and water.

In summary, this apparatus offers an easy, safe, efficient and inexpensive method of preparing small quantities of tritiated solvents suitable for exchange reactions.

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* This is calculated based on prices in the United States as of February 1, 1967.