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Abstract

Hydrogen uranyl phosphate (HUP), a solid proton electrolyte, getters tritium gas and water vapor from air by DC electrical action. We have reduced the formation of residual tritiated water to less than 2%, and demonstrated that HUP can clean a 5.5 m^3 working glove box. Data are presented to illustrate the parameters of the gettering and a model is derived. Two other tritium gettering electrolytes have been discovered.

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The managers of many tritium facilities now worry about their emissions into the atmosphere. The only method presently used for cleaning tritium out of air is to catalyze the formation of tritiated water which is adsorbed, along with the overwhelming bulk of naturally occurring water vapor, on a zeolite molecular sieve. This method generally costs several million dollars for a small system, because of the necessary steel ducting, compressors and holding tanks.

We have long had the dream of finding another getter that might be cheaper to use and would, hopefully, not make tritiated water (HTO). In a previous paper, we reported that hydrogen uranyl phosphate (HUP, with the formula $HUO_2PO_4 \cdot 4H_2O$) getters 1 ppm of tritium gas out of moist air.[1] This makes HUP the first known "direct" tritium getter to work in air. However, the tritium enters a network of waters of hydration within the HUP, so that it is effectively still in "water" form within the HUP. Because of this, we found up to 10% tritiated water formed during the previous gettering experiments.

The HUP is a canary yellow ionic conductor, which passes electric current as protons instead of electrons. Tritium gas enters the HUP through the porous anode and hydrogen from the HUP comes off at the cathode. Tritiated water also can supply tritons, with molecular oxygen being left behind at the anode. Palladium black must be smeared on the anode inner surface to provide dissociation of the incoming tritium gas or water vapor. HUP is unusual in possessing the exceptionally low vapor pressure of 0.6 torr water vapor at 298 K.[2] This allows HUP to be used in fairly dry environments.

I. LOW RESIDUAL WATER RUNS

The formation of 10% tritiated water in the first experiments[1] was distressing. We first rebuilt our 1.2 liter bulb system, which is a gold-plated ionization chamber, to make minimum water on its walls. A -117°C cold trap was added to the inlet line to trap out impurities. The zeolite molecular sieve was operated at room temperature to catch the HTO produced in the gettering. We then baked out the system at 200°C for 16 to 24 hours before each run. The zeolite was taken to 500°C to recover and evaluate the HTO after the run. Finally, the zeolite itself was found to be a maker of HTO at 500°C and we replaced it with a liquid nitrogen cold trap. The resulting HTO was counted as before.

The new system is dynamic, and a diaphragm pump circulates the air at 0.2 ft^3/min. The runs on the old system were static, and the gas moved only by diffusion.

We have already described the making of HUP discs pressed to almost the theoretical density of 3.43 g/cc.[1,3] We also developed a 2.1 g/cc variation more suited to large-scale fabrication. This is made by a 24-hour compression of HUP-withelectrodes at 6000 psi rather than the 30,000 psi used for the dense form.

There is some question as to whether HUP or the phosphoric acid residue on its surface is the better conductor.[4,*] We, therefore, tried to standardize our HUP washing after precipitation. The liquid is decanted, and a pH4 solution of phosphoric acid is added in quantity and the material reslurried. After stirring for five minutes, the precipitate is allowed to settle again over 2-3 hours. After 3 such washings, the crystals are dried in air with periodic mixing for about 5 days. In the last stages of dryness, the crystals are pulverized with a grinding pestle to complete dryness in room air.

We emphasize the catalytic nature of water vapor in forming tritiated water. Earlier work with our "uncleaned" system showed HUP with 1 ppm T_2 in one atmosphere gas making 3.9% HTO in dry air and 3.5% in dry argon. However, it made 14.0% HTO in moist air (5000-7000 ppm water vapor) and 11.2% in moist argon. In our "clean" system, we now reduce the (no-HUP) backgrounds to 0.2% HTO in dry air and 0.8 to 2.6% in HTO in moist air, after 24 hours in both cases.

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[*] The mystique of the solid electrolyte may be dispelled by considering concentrated phosphoric acid, which also has a low vapor pressure of water. There is no reason why tritium cannot be gettered electrically into phosphoric acid.

We next ran 1-inch diameter, 1/2-mm thick HUP samples for 20 hours at 4 V DC. The procedures of counting the gas and HUP remained the same.[1] Table 1 lists the results. In the moist air runs, we averaged 98.0% gettering into the HUP and averaged 1.7% HTO; this is close to that formed inherently by the gold walls. We believe that it should be possible to lower the HUP-formed-HTO to levels below what we report here.

II. CLEANING A 5.5 m^3 SPACE

We next turned to demonstrating the clean-up of an actual tritium handling box of 5.5 m^3. We scaled up our getter to 1-square foot HUP plates. A square foot of stainless steel porous electrode was lightly smeared with palladium black, and the powdered HUP was uniformly spread on top. The other electrode was put on top and the sandwich was placed inside a metal "picture frame", which is bolted together with plastic screws, so that no short circuit will occur between the anode and cathode. Pressure plates were put on either side of the assembly, and it was pressed at 465 tons (6,500 psi) for 24 hours. The thickness of the resulting HUP layer was 0.5 to 1 mm, and the HUP density was about 2.5 g/cc.

The volume to be cleaned is an air-tight, one-atmosphere glove box made of lucite with a steel skeleton. It contains a hoist and other metal fixtures capable of catalyzing water formation. It is cleaned by a conventional precious metal catalyst/zeolite system. The tritium level was monitored with an ionization chamber, and a helium-driven injector put in a measured amount of T_2 gas. A Panametrics hygrometer measured the moisture content by electrical capacitance. An aliquot of air was removed when needed and analyzed for HTO as before. The HUP was dissolved in nitric acid and counted.

A blank run, with no HUP, was conducted. A fan of about 100 ft^3/min was used to gently move the air. A sample of 15.1 Ci (1 ppm) T_2 gas was injected. It showed 0.25% HTO formation after 20 hours and 0.32% after 20 days. The box is not as efficient in making HTO as was the gold-plated bulb. The leakage of T_2 out of the box was also measured over 7 hours and was found to be 0.02 Ci/hr.

We made two box runs with 1 ppm T_2 in one atmosphere air. The first run used a one-square foot panel, and air with 6500 ppm moisture. A high speed fan of 200 ft^3/min moved the air. The HUP potential was varied from 4 to 6 V DC and temperature spikes up to 40°C occurred when the potential changed. The gettering, as seen by the ionization chamber, is shown in Fig. 1. In 168 hours, we gettered 81% of the tritium but formed 15% HTO. The HUP panel then sat 10 days with no potential. At the end of this time, only 0.3% of the tritium was found in the HUP. We cannot explain this loss of tritium, and we were not able to reproduce it in the bulb runs. We believe that the air flow over the HUP face may have been too high and that damaging potential and heat spikes might have occurred. In bulb runs, 6 V is allowable, although no more gettering is obtained than at 4 V. However, at 10 V, the HUP begins to disintegrate, releasing quantities of HTO. Heat is possibly also a factor, especially in the large plates.

The second box run employed three HUP panels in air of 3700 ppm moisture. The fan speed was lowered to 100 ft^3/min. The potential was kept at 4 V DC. This box run is also shown in Fig. 1. The 1/e-time (to 0.368 of T_2 gas) was about 9 hours, and we gettered 83% in 23 hours. At this point, 5.3% of unreacted T_2 was found and 10.6% of HTO. The moisture content during the run dipped to 3200 ppm at 5 hours and rose to 3500 ppm by the 10th hour. Each plate carried about 0.5 A current. The plates gettered 3.4, 3.4 and 2.6 Ci of tritium.

One plate was placed in a container with Drierite for three weeks to see if HTO would come out of the HUP. Only 0.03% of the gettered tritium came loose. To summarize, the three-panel system gettered quickly but made too much tritiated water.

For comparison, a newly-activated, conventional palladium/zeolite system was used to getter 1 ppm T_2 from the box air. The 1/e-time was 2 hours with a 1.5% residual tritium background at the end.

III. GETTERING PARAMETERS

Our bulb runs allow us to generalize much of the HUP behavior. Figure 2 illustrates two important features. The first is that the *residual tritium* (I_∞ *on the ionization chamber*) is a true equilibrium value. We have already seen that this is caused almost exclusively by HTO vapor by the time true equilibrium is reached. The second point concerns the HUP surface area. The 1/e-gettering time τ is inversely proportional to the HUP surface area A. We postulate that A/V, the area to volume-of-gas-gettered ratio, is the true variable. The HTO equilibrium concentration measured at the end of the experiment is also found to be inversely proportional to A. We got our best bulb gettering runs when we went from 1/2 to 1-inch diameter HUP discs.

Figure 3 illustrates that *first-order kinetics are called for*. The ionization chamber function Y is defined as

$$Y = \frac{I - I_\infty}{I_o - I_\infty} \qquad (1)$$

The ionization chamber readings are at time t (I), time zero (I_o) and at equilibrium at long times (I_∞). The decay curves are exponential, although some show an incubation effect at short times (see the 1 ppm dynamic curve in Fig. 3). Also, the 1 and 15 ppm lines in Fig. 3 show the same time constant - another feature of first-order kinetics.

The last important point is shown in Fig. 4. Here, we use the same HUP disc to getter successive fresh batches of air with 1.1 to 1.4 ppm T_2 and 5000 to 7000 ppm water vapor. The gettered tritium, therefore, builds up in the HUP. The equilibrium HTO level rises with the amount of tritium in the HUP. This means that exchange out of the HUP is the likely process, rather than direct HTO formation on the anode. The time constants for gettering are similar once the HUP has "warmed up" in the first run.

IV. Model of the HUP

We now define x as being the mols of T_2 in the gas phase, y the mols of tritium in the HUP, and z the mols of HTO in the gas phase. The increase in gettered tritium goes according to:

$$\frac{dy}{dt} = \lambda_1 x - \lambda_2 y + \lambda_3 z \qquad (2)$$

where λ_1, λ_2 and λ_3 are rate constants. The first term describes the exchange back out as water vapor. The third term describes the gettering of tritium as HTO. This must be present or no equilibrium of z would be possible. In our 1.2 liter bulb, 6000 ppm of water vapor amounts to 2×10^{20} molecules. The average HUP current is 1 mA or 6×10^{15} carriers/s. All the water vapor theoretically passes into the HUP in 9 hours. The HUP can certainly getter the HTO.

We might expect that $\lambda_1 >> \lambda_3$ because hydrogen gas is ionized on an electrode at over a volt less than is required for water. However, we have found that the HTO is mostly present at the end of the gettering, so that we would guess that $\lambda_1 = \lambda_3$. This means that the T_2 is "dissolved" in the more abundant H_2O vapor and is carried in with it to the HUP at the same rate. Then, we have

$$\frac{dy}{dt} = \lambda_1(x + z) - \lambda_2 y \tag{3}$$

$$\frac{dx}{dt} = - \lambda_1 x \tag{4}$$

$$\frac{dz}{dt} = \lambda_2 y - \lambda_1 z \tag{5}$$

where

$$x = x_o - y - z \tag{6}$$

The amount of T_2 at the start is x_o. The solutions to these equations are:

$$x = x_o \exp(-\lambda_1 t) \tag{7}$$

$$y = \frac{\lambda_1 x_o}{\lambda_1 + \lambda_2} \left\{ 1 - \exp[-(\lambda_1 + \lambda_2)t] \right\} \tag{8}$$

$$z = x_o - x - y =$$

$$\frac{\lambda_2 x_o}{\lambda_1+\lambda_2} - x_o \exp(-\lambda_1 t) \left\{ 1 - \frac{\lambda_1}{\lambda_1+\lambda_2} \exp(-\lambda_2 t) \right\} \tag{9}$$

At long times; $x \to 0$ and

$$y \to y_\infty = \frac{\lambda_1 x_o}{\lambda_1+\lambda_2} \tag{10}$$

$$z \to z_\infty = \frac{\lambda_2 x_o}{\lambda_1+\lambda_2} \tag{11}$$

The ionization chamber current I is

$$I = z_\infty + y_\infty \exp[-(\lambda_1+\lambda_2)t] \tag{12}$$

so that the measured gettering time constant τ is

$$\tau = \frac{1}{\lambda_1+\lambda_2} \sim \frac{1}{\lambda_1} \tag{13}$$

because $\lambda_1 >> \lambda_2$ in most of our runs.

Now we consider the relation of our rates to A/V. The true gettering rate λ_1 should be proportional to A/V but λ_2 is not. This is because λ_2 is the product of the tritium concentration in the HUP (i.e., y/Ad, where d is the HUP thickness) times the area available for exchange back into the gas ($\sim$A). The HUP areas cancel and λ_2 becomes a constant.

Equation 13 becomes

$$\tau = \alpha\left(\frac{A}{V}\right)^{-1} \tag{14}$$

where Table 2 lists our measured values of α, which are fairly constant.

The fraction of HTO formed at long times in a single run is

$$\frac{z_\infty}{x_o} = \frac{\lambda_2}{\lambda_1+\lambda_2} = \frac{1}{\beta\left(\frac{A}{V}\right)+ 1} \tag{15}$$

where β is a constant to be determined. We go to Table 2, which shows β for various runs of considerably different dimensions. We expect the static runs to have a lower β, simply because the gas cannot reach the anode as easily. Why box #1 is so high (i.e., low HTO) is unknown. We believe that the model is reasonably well validated by these numbers. For HUP with dynamic flow, β ∿ 150 m^{-1}. This model allows us to calculate the HTO to be formed, and we find that, indeed, we do not have sufficient HUP surface area for our 5.5 m^3 box even though the gettering time constant τ is short.

Let us turn to the multiple-run experiment shown in Fig. 4. In each run, clean gas with initial T_2 of x_o was introduced. The final gettered tritium of the (i-1)st run is the initial value for the ith run. We find that

$$y_\infty(i) = \frac{\lambda_1}{\lambda_1+\lambda_2}\,[x_o+y_\infty(i-1)] \tag{16}$$

which leads to

$$\frac{y_\infty(i)}{x_o} = \frac{\lambda_1}{\lambda_1+\lambda_2}\left[1 + \frac{\lambda_1}{\lambda_1 + \lambda_2} + \left(\frac{\lambda_1}{\lambda_1 + \lambda_2}\right)^2 + \dots + \left(\frac{\lambda_1}{\lambda_1 + \lambda_2}\right)^{i-1}\right] \quad (17)$$

At equilibrium, we find that a similar relationship holds for the HTO vapor. From Eq. 5, we get:

$$\frac{z_\infty(i)}{x_o} = \frac{\lambda_2}{\lambda_1+\lambda_2}\left[1 + \frac{\lambda_1}{\lambda_1 + \lambda_2} + \left(\frac{\lambda_1}{\lambda_1 + \lambda_2}\right)^2 + \dots + \left(\frac{\lambda_1}{\lambda_1 + \lambda_2}\right)^{i-1}\right] \quad (18)$$

In our multiple run sample, we made 2% HTO on the first run. With $\lambda_2/(\lambda_1+\lambda_2) = 0.02$, $\lambda_1/(\lambda_1+\lambda_2) = 0.98$. On the twentieth run, the 2% HTO has increased by 16.6 times to 33.2% in this model. Figure 5 shows the measured $z_\infty(i)/x_o$ data, and the straight line is the model's results. The dashed line shows a linear extrapolation from the first run.

IV. DISCUSSION

We have demonstrated a material that can pull tritium from moist air. The further development of this type of getter depends on lowering somehow the water exchange rate λ_2. This might be done by cooling the HUP and reducing its vapor pressure and proton mobility. Other, better materials may have to be discovered. We have found two others that show the same activity HUP does, and the data from several static gas runs are shown in Table 3. One of these materials is sodium-exchanged HUP, $NaUO_2PO_4 \cdot 3H_2O$, which is the next best conductor in the HUP family.[5] The other material is the pyrochlore form of antimonic acid, $HSbO_3 \cdot xH_2O$.[6] This is shown as the best of its family and only a cut below HUP in electrical conductivity. Both appear to have a similar mechanism to that of HUP, and both warrant further study. We tried various other compounds but failed to obtain more than 3% gettering. These materials include: lithium and potassium-exchanged HUP,[5,7] $KH_2Sb_2O_7$,[6] KH_2PO_4,[8] and KHF_2.[9] The last pair are low mobility proton electrolytes with a mechanism different from the HUP.

The presence of palladium black on the anode face of the HUP is necessary for gettering but is a possible source of HTO formation. As seen in Table 3, platinum black is equally good. However, iridium, powdered nickel and gold, and Raney nickel and cobalt all failed, with no more than 2% gettering. Clearly, only the best catalysts for dissociating tritium can be used.

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References

1. P. C. Souers, R. T. Tsugawa and C. G. Stevens, J. Vac. Sci. Technol. A2, 717 (1984).

2. A. T. Howe and M. G. Shilton, J. Solid State Chem. 31, 393 (1980).

3. A. T. Howe and M. G. Shilton, J. Solid State Chem. 28, 345 (1979).

4. E. Skou, I. G. Krogh Andersen, K. E. Simonsen and E. Krogh Anderson, Solid State Ionics 9 & 10, 1041 (1983).

5. C. M. Johnson, M. G. Shilton and A. T. Howe, J. Solid State Chem. 37, 37 (1981).

6. U. Chowdhry, J. R. Barkley, A. D. English and A. W. Sleight, Mat. Res. Bull. 17, 917 (1982).

7. F. Weigel and G. Hoffmann, J. Less Common Metals 44, 99 (1976).

8. M. O'Keeffe and C. T. Perrino, J. Phys. Chem. Solids 28, 211 (1967).

9. J. Bruinink and G. H. J. Broers, J. Phys. Chem. Solids 33, 1713 (1972).

Figure Captions

Fig. 1. Gettering of 1 ppm T_2 in moist, one-atmosphere air in a 5.5 m^3 glove box. The HUP area is shown.

Fig. 2. Two HUP runs that illustrate the long-time equilibrium and the effect of surface area. We are using 1 ppm T_2 in static moist air.

Fig. 3. Exponential gettering behavior of HUP discs in moist air. Note the same time constants occur for the 1 and 15 ppm T_2 runs.

Fig. 4. Multiple runs of the same HUP disc with fresh batches of moist air containing 1 ppm T_2. The run number is shown.

Fig. 5. HTO formed in a multiple run with the same 1-inch diameter HUP disc. Fresh moist air with 1.1-1.4 ppm T_2 is introduced for each run. Run times were 90 to 850 minutes. The theoretical curve is fixed at 2.0% HTO formed in the first run.

No.	Initial T_2 Conc. (ppm)	Ioniz. Chamber	Moisture, HUP density	% of Tritium In HUP	% of Tritium HTO	% of Tritium Unaccounted for
101	1	off	dry, 3.4 g/cc	96.4	1.4	2.2
102	1	on	dry, 2.1	98.4	1.6	-
98	1	off	moist, 3.4	97.0	2.4	0.6
99	1	off	moist, 3.4	97.5	2.2	0.3
104	1	on	moist, 2.1	98.2	1.6	0.2
105	20	on	moist, 2.1	99.2	0.3	0.5
106	20	on	moist, 2.1	97.9	2.1	-

Table 1. Low HTO HUP runs in the "clean" 1.2 liter bulb with one atmosphere air. All runs have 1-inch diameter HUP, 4 V DC, were dynamic and were run for 24 hours. "Moist" means 6000 ppm water vapor.

Type HUP	Area (m^2)	Volume (m^3)	Gettering Time Constant τ (hours)	α (m)	HTO fraction z_∞/x_o	β (m)
dynamic 1-inch diameter	5.1×10^{-4}	1.2×10^{-3}	0.5-1.7	0.2-0.7	0.017	130
static 1-inch	"	"	0.7-2.3	0.3-1.0	0.04	55
static 1/2-inch	1.1×10^{-4}	"	5-6	0.6-0.7	0.16	50
box #1	0.090	5.5	45-50	0.8	0.15	340
box #2	0.27	5.5	9	0.4	0.106	170

Table 2. Model parameters α and β as derived for 1/2-mm thick HUP discs at 4 V but with widely varying surface areas.

	Pd black catalyst			Pt black
	HUP	Na-exchanged HUP	$HSbO_3 \cdot xH_2O$ pyrochlore	Na-exchanged HUP
T_2 in gas	1.5%	1.4%	0.3%	1.5%
HTO in gas	14.0	5.0	12.0	7.9
T in getter	83.0	90.9	85.2	89.0
	98.5%	97.3%	97.5%	98.4%

Table 3. Tritium gettering activity of two other compounds as compared with HUP in static runs with the "unclean" system. Again, 4 V DC was used.

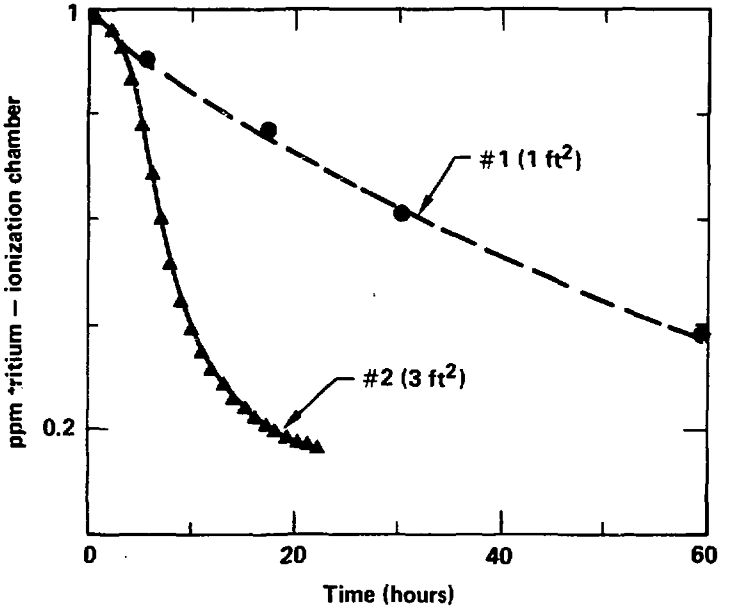

Fig. 1. Gettering of 1 ppm T_2 in moist, one-atmosphere air in a 5.5 m^3 glove box. The HUP area is shown.

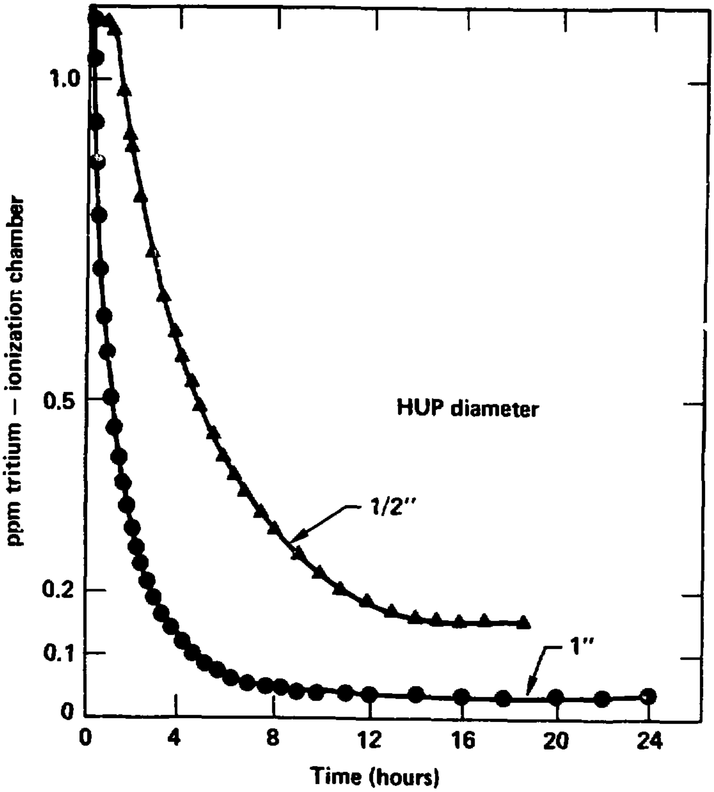

Fig. 2. Two HUP runs that illustrate the long-time equilibrium and the effect of surface area. We are using 1 ppm T_2 in static moist air.

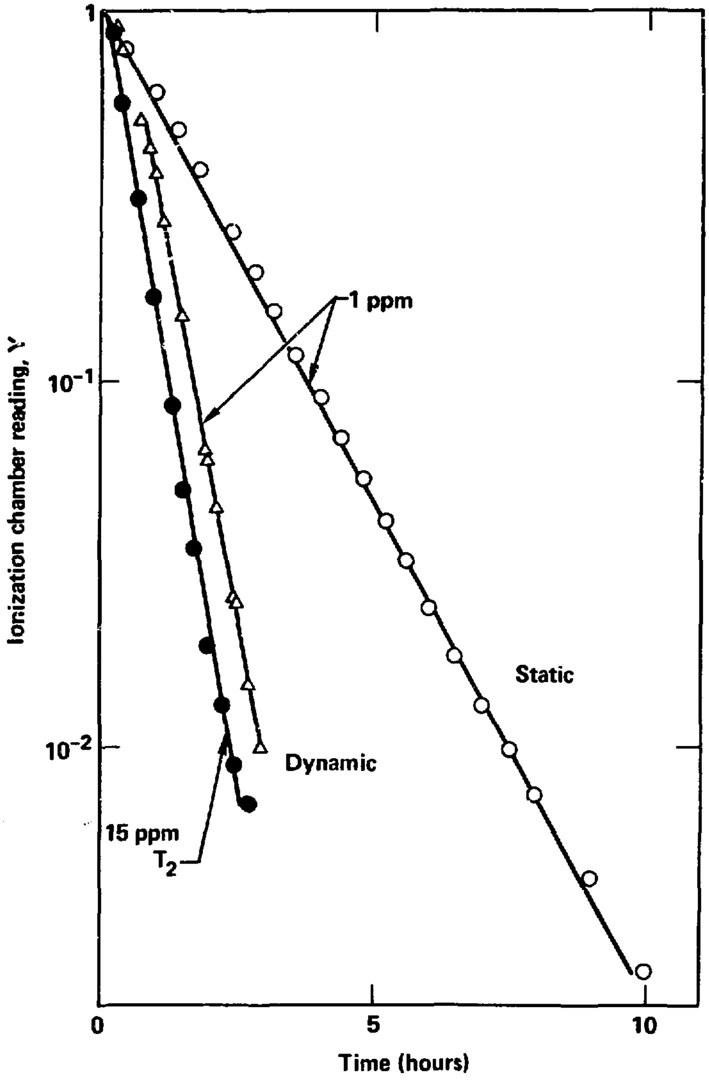

Fig. 3. Exponential gettering behavior of HUP discs in moist air. Note the same time constants occur for the 1 and 15 ppm T_2 runs.

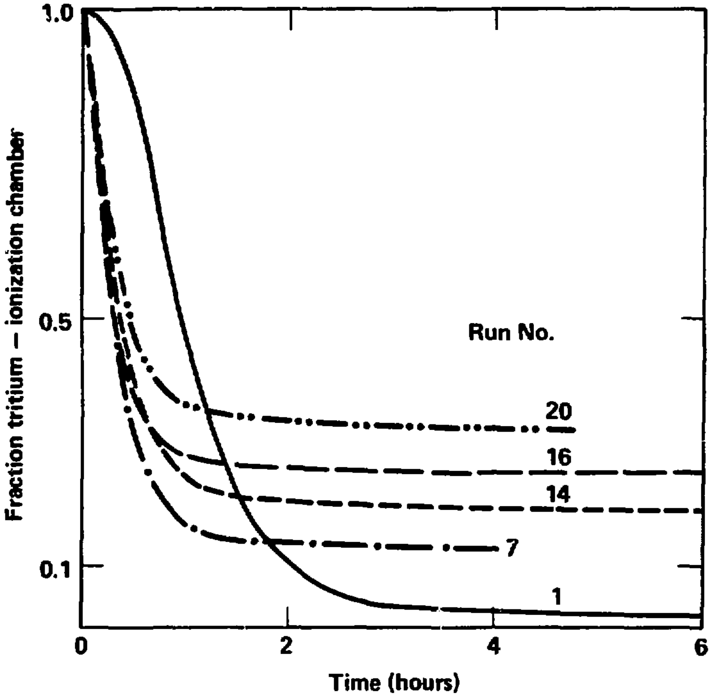

Fig. 4. Multiple runs of the same HUP disc with fresh batches of moist air containing 1 ppm T_2. The run number is shown.