Atmospheric HT and HTO

I. *Experimental procedures and tropospheric data 1968–72*

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ABSTRACT

A technique was developed for direct field sampling of atmospheric HTO and HT. Airborne, portable, and laboratory versions were implemented, and a comprehensive sampling program begun. The air is passed first through Molecular Sieve to adsorb the water, then over palladium carried on Molecular Sieve, which oxidizes atmospheric hydrogen and adsorbs the resulting water *in situ*. Both samples are subsequently extracted from the adsorbers, and the tritium content measured by internal low-level gas counting. Resolution is 4 % of present atmospheric levels. Monitoring of HT and HTO at three stations in the Northern Hemisphere shows that HT does *not* undergo seasonal fluctuations like HTO, and variations are small around the present mean of about 46 HT molecules per mg air. After the previous rise from pre-nuclear level, the tropospheric HT-inventory has reached a steady state within the past few years. Sampling transects from 40°N to 65°S in 1971 and 1972 show similar HT levels in the Northern and Southern Hemispheres indicating a long residence time of HT (and hydrogen). The HT appears to have its source at ground level, most likely from nuclear fuel element processing, underground nuclear fusion device detonations, and military and civilian handling of tritium gas. In the troposphere, there is now more tritium as gas (HT or T_2) than as HTO (water vapor).

1. Introduction

Tritium is present in the atmosphere as water (HTO), as molecular hydrogen (HT), and as hydrocarbons, primarily methane, CH_3T. Hydrogen gas produced by decaying organic matter and similar sources, and from coal mines, contains little or no tritium. Cosmic radiation and H_2–H_2O exchange reactions in the upper atmosphere produce and maintain a small atmospheric inventory of HT, but today, by far the largest part of the atmospheric HT appears to be man-made. Ehhalt (1966), Gonsior et al. (1966), and Begemann & Friedman (1968) have reported measurements on the tritium content of atmospheric hydrogen up to and including 1964. In a report by B. R. Layton (1969), data from a monitoring program at the University of Arkansas were released, which carried information from 1963 through 1966. All samples analyzed by these investigators were hydrogen extracted from the so-called 'neon fraction' obtained at liquid air plants. The specific tritium activity of the hydrogen gas of each sample was determined. Values were in the 10^6 TU range, i.e., isotope ratios around 10^{-12} of tritium in hydrogen, or a few dpm per m^3 air.

Hydrogen is produced bacterially in soil under certain conditions and also in the ocean (Schmidt, 1974). This hydrogen must have a T/H ratio of 1 to 100 TU. In addition, large quantities are released by automobile exhausts and from mining and heavy chemical industries, like ammonia synthesis and petroleum processing. The industrial hydrogen is virtually tritium-free. Since the atmosphere contains only about 0.5 ppm by volume of hydrogen gas, industrial releases are apt to affect greatly the measured specific activity of atmospheric hydrogen itself in large areas downwind from such plants. In order to normalize their data on atmospheric HT, previous investigators attempted to correct for the industrial, local additions of dead hydrogen by measuring the

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helium or deuterium contents of the neon fraction samples. The average He/He_2- and D/H ratios of unpolluted air formed the basis for this standardization. The corrected figures were all reported in tritium units (TU) of the hydrogen gas. To obtain the amount of HT per unit mass of air, one would then assume an average value of 0.5 ppm of hydrogen. However, the final data still exhibited large, short-term variations. All HT data published so far were obtained from areas with heavy chemical industry, like central Europe and Illinois, USA.

We have developed a system in which HT (and HTO) from 2 kg of air can be extracted within 10 minutes with a field sampling unit. The process is based on the catalytic combustion of the atmospheric H_2 on palladium metal. Measuring the tritium decay rate yields absolute values of number of T-atoms/kg air. Simultaneously with each HT sample, we also obtain a sample of the atmospheric water vapor, which allows the determination of the HTO content of the same air parcel. With this new device, it is thus possible to monitor the HT content of the atmosphere at almost any desired point of the globe at any time. It is possible to establish if there are synoptic, diurnal, and geographic variations.

With the new system, we have started a tropospheric monitoring program at several localities around the world, and the data for 1968–72 will be reported below.

2. Experimental procedures

2.1. *Sampling systems*

For the Hurricane Tritium Project, a system for the extraction of water vapor from the air at high flow rates was developed (Östlund, 1967), using Molecular Sieve no. 4A (Union Carbide, Linde Division). It was then established that a bed of 300 g of this sieve, exposed to an airstream of up to 300 l/min of air, adsorbs atmospheric humidity with >99.9% efficiency until at least 25 g of water are adsorbed. It is well known that hydrogen can be catalytically oxidized to water at room temperature on finely dispersed palladium. Our new system for hydrogen sampling combines these two reactions in a single unit.

The principle of the air sampling system is outlined in Fig. 1. Air at a measured flow rate, from 2 to 150 l/min, is first passed through a

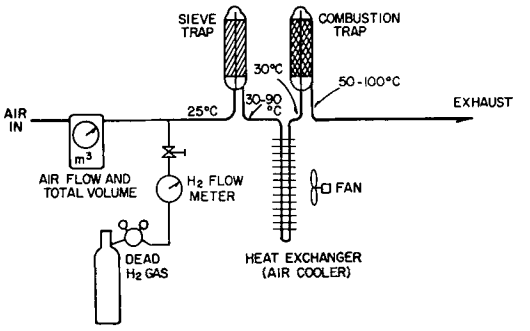


Fig. 1. System for collecting simultaneous, separate samples of atmospheric HTO and HT.

bed of Molecular Sieve, called a *sieve trap*, where all the water vapor is removed. In the moisture adsorption process, the temperature of the air increases 3°C for each g/kg of humidity mixing ratio in the intake air. Thus, in tropical air at ground level, the temperature of the dried air can increase to 90°C, and at high flow rates, the air must be cooled in a heat exchanger before combustion. At this point, or preferably before the first sieve trap, tritium-free hydrogen is added, so that the total hydrogen concentration of the air is between 0.1% and 0.5% by volume. The dry mixture of hydrogen and air is now passed through a bed of colloidal palladium, carried on Molecular Sieve no. 4A, called the *combustion trap*. By this catalyst, the hydrogen is converted to water, which is immediately adsorbed on the sieve bed supporting the catalyst. The temperature increase here is 11°C per 0.1% of hydrogen in the air. In the aircraft, the cabin air compressor fursnishes the necessary pressure drop. In other cases, an air pump is used to pull the air through. In the latter case, at high flow rates, the processed air might have to be cooled before the pump. The volume of air processed for each sample is measured by a laboratory gas meter for slow rates and by an industrial-type gas meter or an electronic, integrating mass-flowmeter, at high flow rates. The H_2 flow is also measured and integrated to give an expected amount of "manufactured" water. This quantity should agree with the amount of water actually recovered from the combustion trap.

Each run thus yields two samples of water, each adsorbed on Molecular Sieve. The sample in the first trap consists of the original H_2O,

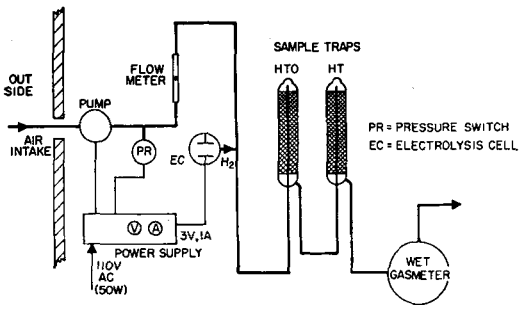


Fig. 2. Slow HT/HTO sampling system, for the collection of one sample pair in 24–48 hours.

HDO, and HTO of this particular air sample. From this one can determine the true amount of HTO per kg of air and the TU value of the moisture (if larger than 0.3 g/kg). The second trap contains all the tritium that originally occurred as HT and T_2, now in the form of HTO. From this we obtain a true measure of the quantity of tritium, as number of T-atoms, in the form of molecular hydrogen, in the air sample. Information on the specific activity and D/H ratio of the original atmospheric hydrogen gas is lost in the dilution by H_2 carrier. Variations of the atmospheric content of dead H_2 have no influence on the result. It should be noted that methane and other hydrocarbons do not burn on this catalyst at this temperature.

For obtaining daily average samples, a slow, laboratory system was built. It processes outside air at a rate of 1 to 2 lit per minute for 20 to 48 hours. The air flow is supplied by a diaphragm pump (cf. Fig. 2). A 'wet-test' gas meter is well suited to measure the air volume. Here the source of dead H_2 is electrolysis (0.2 to 0.4 amps) of tritium-free water. The addition of H_2 carrier at this slow rate is not absolutely necessary, but it is a good check on combustion efficiency to recalculate the ampere-hours to water, and compare this figure against the recovered yield of H_2O in the combustion trap. The pressure switch cuts the power to the electrolysis if the air flow should stop due to a faulty pump or a leak. The H_2/O_2 mixture could otherwise eventually reach the catalyst undiluted by air, and explode. In this machine, we usually use a smaller size (100 g) combustion trap, and 2 to 4 g of H_2O is disintegrated and recombined.

For sampling in and around nuclear industry plants, there is need for a quick, portable system, which does not have to be as elaborate and accurate as the ones described above. For that purpose, a 10 l/min variant of the above-mentioned slow system with electrolysis and a simple float-type air flow meter was assembled. Samples (HT/HTO pairs) from 10–15 minute runs, measured in a good liquid scintillation counter, will allow a sensitivity of about 3 pCi/m³ air, which is normal environmental level of HT today.

2.2. *Preparation of catalyst*

A solution is made of 7.5 g of dry $PdCl_2$ (4 g of Pd metal) in 84 ml of 1-N HCl. Distilled water is added while warming, until a clear, reddish-brown solution is obtained. The solution is cooled to room temperature, and the volume adjusted to 245 ml with distilled water. Total volume is very critical. The entire solution is quickly poured onto 600 g of Molecular Sieve no. 4A and vigorous shaking is begun immediately. The sieve should be in "virgin" condition, that is, be taken out of a factory container immediately before use. The mixture becomes hot and slushy; shaking is continued without interruption while part of the water boils off, until the whole charge cools. The grains then have a dry appearance and flow freely. If the total amount of water is just a few ml too large, the charge does not dry, but cakes. If the total quantity of water is just a few ml too small, the impregnation becomes uneven because the sieve dries too early. When this recipe is scaled up, the water/sieve ratio has to be increased to compensate for proportionately higher vapor loss and smaller radiative and conductive heat loss per g of material.

Although having a dry appearance, the freshly prepared catalyst is about saturated with water and has to be pre-dried at 300°C before loading into the glass envelopes. After filling, the combustion traps are dried according to the freeze-out procedure described below. To activate the catalyst, hydrogen gas is then passed through the combustion traps at 530°C for three hours at a rate of about 5 l/min. After the combustion trap is cooled down and filled with dry nitrogen, it is ready for use.

Table 1. *Memory in freeze-out procedure*

Procedure	Sieve type	ST size (g)	ST no.	Memory mg	Memory Avg.	Memory (mg/100 g of sieve)
A. Freeze-out 2 hr duration	4A	300	623	406		
	4A	300	621	523	430	143
	4A	300	624	365		
	4A	300	617	425		
	4A	100	J-2	97	95	95
	4A	100	39	92		
	5X	100	5X1	164	164	164
B. Freeze-out 4 hr duration (recommended)	4A	300	621	461		
			624	358		
			625	450	403	134
			626	286		
			627	463		
C. After another 8 hr bake-out	4A	300	622	397		
	4A	300	623	364		
	4A	300	628	243		
	4A	300	618	219	295	99
	4A	300	619	374		
	4A	300	620	252		
	4A	300	485	283		
	4A	300	489	232		
	4A	100	209	115	93	93
	4A	100	16	71		
	13X	100	13X1	179	186	186
	13X	100	13X2	192		

2.3. *Recovery from sieve and combustion traps*

To recover the adsorbed water, the sieve trap or combustion trap is placed in a furnace and connected to a vacuum line through a freeze trap kept at dry ice temperature. Our present vacuum system can handle 18 traps simultaneously in parallel. Pumping is started at room temperature and furnace temperature is raised in 100° to 150° increments during about two hours. Depending on the amount of water in the sieve trap, the release of it starts anywhere between 150°C and 300°C. When the oven temperature has reached 530°C, it is kept there for four hours. During that time, pumping is switched from rotary to Hg-diffusion pump. At the end of that time, the line pressure, while pumping, is usually around 5 μ. At this time, the freeze traps with the extracted samples are removed, and the sieve traps are connected directly to the vacuum line to be further pumped during bake-out for another six hours. At the end, *combustion* traps are filled with hydrogen gas and left at 530°C for 1/2 hour, and again pumped out. After cooling down, all traps are filled with nitrogen, disconnected from the system, closed and stored for future use. The yield of water in each freeze trap is weighed to ± 0.05 g.

The procedure described above is usually called the "freeze-out" procedure. It is important that the oven temperature is as high as the Pyrex glass envelopes can accept, but, this notwithstanding, an amount of water, called "memory", of the original sample composition is always left in the sieve. This memory is dependent on the *final bake-out* temperature, as was reported previously (Östlund, 1967).

We have made renewed measurements of the memory by isotope dilution technique. First "hot" water vapor was absorbed and extracted. Then "dead" vapor was absorbed and extracted. The memory manifests itself as a finite tritium activity in the second sample. The results are reported in Table 1. Two of the other kinds of Molecular Sieves, no. 5X and

no. 13X, were also tested. We again come to the conclusion that when a sample is retrieved with our standard procedure from a big (300 g) sieve trap, a quantity of 400 ± 100 mg water remains in the sieve. After further bake-out (8 hours), 300 mg of that water is still left, and carried to the next sample. Small containers (100 g) do not benefit much from additional bake-out. Memory is about 100 mg. Sieve types 5X and 13X have larger memory, which is undesirable for our purpose.

The procedure described above is suited to retrieve a water sample without affecting its *TU value* (its specific activity), and when sample quantities are large (more than 5 g H_2O/100 g of sieve), the error introduced by the memory is negligible. When working with quantities of water smaller than that (as always with the combustion trap), the size of the memory becomes significant. We therefore designed the following procedure aimed at removing the entire *tritium quantity* (HTO) from the trap, accepting that the TU value (specific activity) of the recovered sample is affected. The procedure is identical to the freeze-out until the temperature has reached 530°C. Pumping through freeze traps is now continued for two hours. Before being connected to the vacuum system, each combustion trap is outfitted with a small (10 cm^3) flask, containing 2.5 g (weighed) of tritium-free water, connected to the unused inlet tube of the glass envelope with a short piece of rubber hose and a stopcock. At the end of the two-hour period, the connection between the little flask and the combustion trap is opened, the small amount of air goes through the trap without trouble, and the tritium-free water starts to evaporate. The vapor passes through the entire sieve bed and exchanges its water molecules with the memory in the trap. When the little flask is dry and the pressure again is down around 5 μ, the memory in the sieve bed is almost free of tritium, which has been quantitatively transferred as HTO to our frozen-out sample. This procedure we usually call the "push-out". The amount of tritium left in the sieve is obviously dependent on the TU value of the original sample, so in Table 2, where we report testing the push-out procedure, we have recalculated the tritium memory to the equivalent amount of the original sample water. It is concluded that the "push-out" procedure serves its purpose very well. As an average, a memory equivalent to only 23 mg of the original sample remains in a 300-g trap.

Table 2. *Efficiency of the "push-out procedure"*
Size of trap is 300 g. The memory of HTO has been recalculated to equivalent amount of original, "hot" sample

PT no.	Added dead water (g)	T-recovery (%)	T-memory (mg H_2O)	Avg.
B13	4.94	101 ± 1	7 ± 7	
B09	4.97	—	22 ± 6	
B04	2.50	103 ± 1	16 ± 6	
B04	2.50	—	32 ± 6	
B10	2.50	99 ± 1	31 ± 6	23
B12	2.51	103 ± 1	25 ± 6	
B03	2.50	—	10 ± 5	

As an additional precaution, we keep an account of the history of each individual combustion trap and sieve trap. That account lists every sample and every treatment pertaining to the trap. Should, unexpectedly, a very tritium-rich ("hot") sample have been collected, we will know which later sample could be affected by the memory.

2.4. *Testing for combustion–adsorption efficency*

In general, our test system has been similar to the outline in Fig. 1 but with an extra combustion trap at the end. Either tritium-free or tritiated, "hot" hydrogen gas is introduced at the H_2 gas inlet. There are provisions for the introduction of dead H_2 also after the first combustion trap, and pressures and temperatures can be measured at various points along the line. In particular, the temperature distribution in the first combustion trap versus time is established by several fast-time-response thermocouple junctions pressed against the glass envelope by a styrofoam block. This arrangement has proven very useful for the early detection of impaired combustion efficiency, caused by poisoning or by too much water in the catalyst.

Of the large number of tests that we have run with our catalyst-adsorber, we can report only a few. The selection is such as to give a representative picture of the performance of the catalyst under conditions not only within, but also outside, its capacity. In most cases, tritiated hydrogen was used, and the efficiency of combustion-adsorption was determined by measuring the quantity of tritium in both the

Table 3. *Experiments with our catalyst-adsorber*
Total volume of air processed was usually about 1 m³; size of combusion trap 100 g

Exp. no. AY-	Air flow rate (l/min)[a]	Inlet temp. (°C)	Carrier (‰ H_2)	Reaction temp. (°C)	Manuf. (H_2O g)	Efficiency (%)
77	62	29	0.5	35	2.0	95.1
88	61	25	0.6	32	3.2	92.3
62	80	25	1.1	36	1.6	98.7
59	52	25	1.4	41	2.2	99.7
57	32	25	2.3	50	3.4	98.0
66	61	26	2.6	54	3.1	97
68	65	27	2.8	59	3.4	98.0
89	62	25	4.5	75	3.5	98.1
84	59	25	4.9	78	3.3	98.3
85	58	25	7.2	100	4.5[c]	93.4
79	62	25	7.4	102	2.7	94.0
76	61	25	8.9	120	1.8	95.8
82	65	−50[b]	0.42	−45[b]	0.9	45
83	75	−50[b]	0.9	−40[b]	2.4	86
73	68	65	2.5	95	4.2[c]	91.5
74	65	70	1.0	80	2.7	96.1

[a] In these experiments, 60 l/min is equivalent to a space velocity of about 25 sec^{-1}, or 0.04 sec reaction time.
[b] Approximate temperature, ±10°C.
[c] The catalytic action impaired by too much water adosrbed.

first and the second combustion trap. In this series of experiments, combustion traps of size 100 g were used and temperature, air flow rate, and carrier concentration were varied. The results are given in Table 3. The way efficiency was measured, the figure 100% cannot be reached since there is always a small 'blank' value of T in the second combustion trap.

Quite a few features appear here. The hydrogen carrier concentration should be between 2 and 4‰ by volume to give best result. If the combustion trap becomes too hot, either from too much hydrogen, or too high inlet temperature, the efficiency slips. We believe that the reason for this is that the adsorption is incomplete. Tests with preheated, moist air passed through a sieve trap indeed showed incomplete adsorption. The bad performance at very low temperature is probably due to slow reaction rates.

At this time, we cannot really explain why there should be a lower limit for the H_2 concentration, but below about 1‰ of carrier, the results become unreliable. This is even more pronounced if *no* H_2 is added, and only the 0.5 ppm in the atmosphere is processed. This way the results are very erratic, 50–99% efficiency, unless extremely low air flow rates are used.

Another series of experiments was designed to study the effects of pressure and flow rate. Higher flow rates than about 3.0 lit sec^{-1} in a 300-g combustion trap seem to result in erratic behaviour, which may be attributed to variations in trap composition or condition. A discernible trend to lower yields at lower pressures indicates either incomplete retention of water or insufficient reaction time.

A further limitation of our catalyst is the total amount of hydrogen that can be processed in a trap in one run. In the experiments, we generally processed about 3 g of water or less in a 100-g combustion trap, and we saw no strong indications of decreased catalytic action. In later experiments, however, we processed larger amounts of air, 3 to 5 m³, in each 300-g combustion trap, ending up with 10 to 15 g of manufactured water, or 3 to 5 g per 100 g of catalyst. There we ran into problems with incomplete combustion towards the end of some runs.

Poisoning of the catalyst can occur if the air ducts are not clean after soldering, or if a lubricated or graphite vane air pump is used in the

line *before* the sampling device. Such poisoning is cured by renewed five-hour H_2 treatment as in the procedure of making the trap as described above.

Summing up our experience with our own catalyst-adsorber, we are confident that better than 98% of the HT in an air sample is collected if 2 to 4‰ by volume of carrier hydrogen is added, inlet temperature is around 25°C, and air flow rates equivalent to reaction times of 0.05 sec or more (space velocity of 20 sec^{-1} or less). Thus, a 300-g combustion trap at normal pressure can handle 150 lit of air per minute, and a total air quantity of 2 kg in 10 min at 0.5 to 1 atm pressure.

We also tested two commercial catalysts under the same conditions. Engelhart's "Type D" catalyst consists of Pd supported on alumina. It had good catalytical action, but its adsorptive efficiency was grossly insufficient and the memory for water very high, ~0.5 g/100 g of material. Linde's "Sk-300" is Pd supported on type *X* sieve, but manufactured in a way different from ours. It is a hydrogenation catalyst, and did not have good enough efficiency for our purpose. Yields were between 70 and 90% under our experimental conditions.

2.5. *Tritium counting*

Our low-level tritium counting facility has been described earlier (Östlund et al., 1969), and only the most pertinent features will be described here. Of the water sample ("HT" or "HTO"), up to 4.5 g is directly reduced to hydrogen gas, which is used as filling together with a small amount of propane in our ultra-low-level counting machine. The net background is typically 0.90 ± 0.03 cpm in the tritium channel, and the filling pressure is 2.3 atm with hydrogen from 4.5 g of water plus 0.7 atm of propane from a tank. The counting efficiency is >95% calculated on the cylindrical counting volume, and 75% of the total quantity of hydrogen needed to fill the system. The "HT" samples from environmental air usually show about 5 dpm, above background, and after counting overnight, the standard deviation is about 0.06 cpm or ± 3 to ± 6 TU.

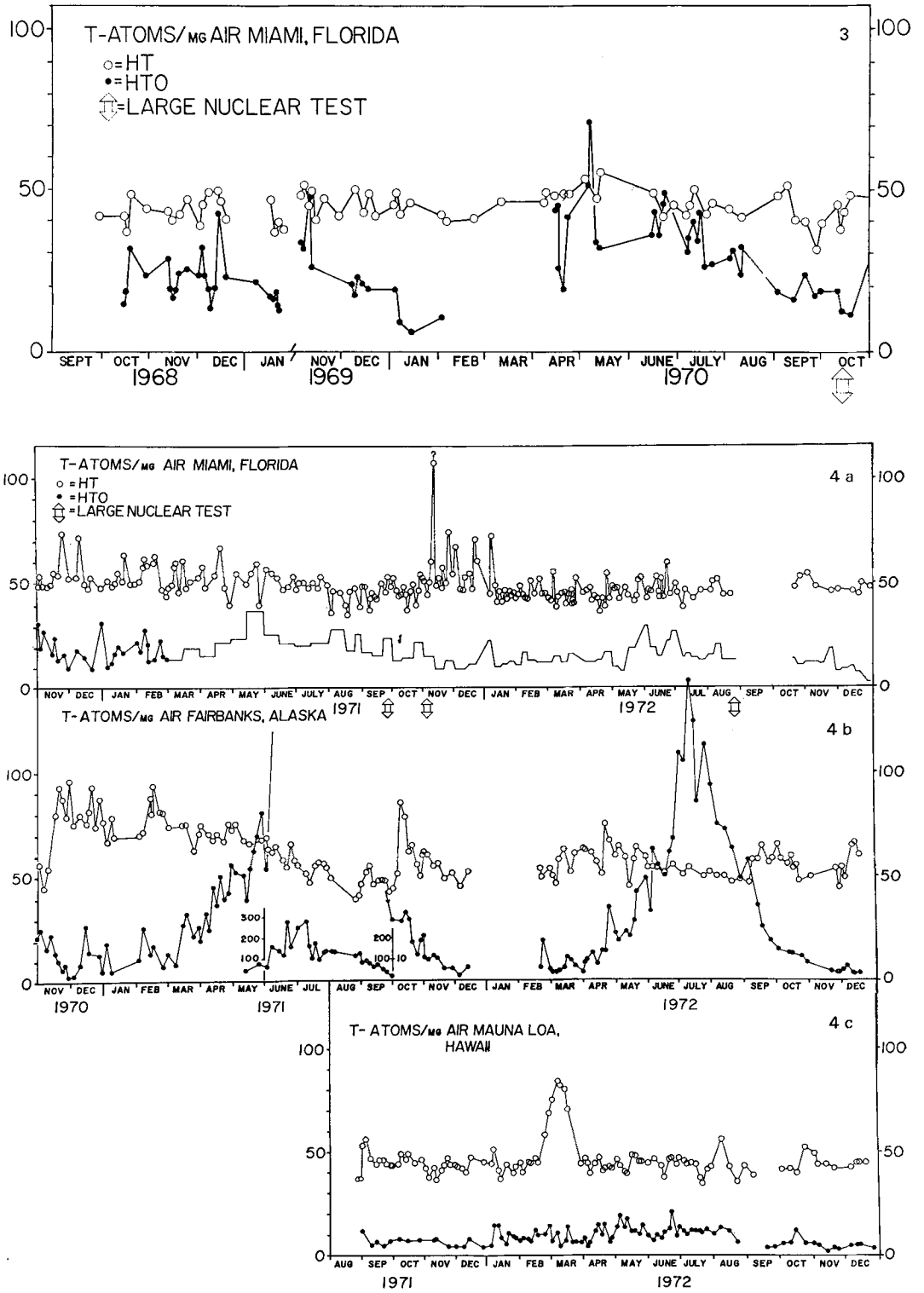
The humidity samples (the original atmospheric water) are usually larger, up to 30 g (two sieve traps), when sampling tropical marine atmosphere at ground level. In that case, we use a cold finger trap at 5°C (refrigerator) to extract most of the humidity at the beginning of the sampling train, and recombine this water with that from the sieve trap. In those samples, the specific activity is usually so low that electrolytic enrichment is necessary before counting. This procedure has been in routine operation in our laboratory for more than seven years.

3. Results on atmospheric HTO and HT inventories

The first routine sampling with the new machinery was started at our institute in Miami in 1968. With only two interruptions, we have since then regularly sampled the atmosphere for HT and HTO with the 24-hour system described above, usually twice or three times weekly. To begin with, each HTO sample was analyzed by itself, but, beginning about 1971, the water vapor samples were combined to half-monthly samples. The results of these measurements are plotted in Figs. 3 and 4A where all the points have been entered in order to give an indication of the amount of scatter in the data.

In the fall of 1970, a similar station was established at the University of Alaska in Fairbanks with the same sampling program. The Alaska HTO data in Fig. 4B exhibit the extremely high peak of the HTO data in the summer, which is the result of the well-known "spring leak" of stratospheric HTO into the high latitudes of the troposphere. Compared to previous data, which were usually expressed in TU of the water vapor (in rain), our values exaggerate the late spring maximum due to the fact that our unit of reporting is absolute amount of tritium per mg of air and the absolute humidity is very low in Fairbanks in the winter. The HT data will be discussed below.

In the fall of 1971, a third station was established at the Mauna Loa Observatory on the main island of Hawaii. It is located on the slope of the Mauna Loa volcano at an altitude of 3 399 m. The HTO values in this typical tradewind region exhibit only a very small seasonal variation, and the low absolute amounts of HTO in the atmosphere clearly reflect the intense exhcange of the atmospheric water vapor with the ocean surface (cf. Fig. 4C).



Figs. 3, 4a, 4b, 4c. Ground-level HT/HTO concentrations at Miami, Florida; Fairbanks, Alaska; Mauna Loa Observatory, Hawaii; 1968–1972, Note scale change for HTO in summer of 1971 in the Alaska plot.

If we now turn our attention to the HT values at the three stations, we find that there are several clearly exhibited peaks. In Alaska, late November 1970, the HT value jumped from about 50 to 90 T-atoms/mg air, followed by a decrease with a characteristic time constant of about a year. There could possibly have been a sub-peak in February 1971. In October 1971, another peak appears and a not-so-obvious peak in October 1972. Corresponding maxima are not so easily distinguishable in the Miami diagram, even if, however, there are indeed weak indications of peaks at about the same time as in Fairbanks, Alaska. The Hawaii HT data do not exhibit these maxima, and, except for the excursion in February–March of 1972, which we cannot explain and which must be rather local (short decay time), there are no significant variations. With the many data indicating the elevated values, and the reasonable decay times of the peaks, one will have to accept that these reflect injections of HT into the global troposphere. In recent work by Loosli et al. (1973), extremely elevated values of Ar^{37} have been detected in the air in Switzerland at approximately the same times as our HT peaks. The Ar^{37} peaks correlate nicely with underground explosions of fusion devices in US and USSR as reported regularly by the US (USEPA, 1971, 1972, 1973).

Table 4. *Yearly averages of atmospheric HT concentrations at Miami, Fairbanks, and Mauna Loa*

Station/Period (Month/Year)	Average HT conc. (T-atoms/ mg air)	Std dev of avg	Number of samples
Miami			
Oct 1968–Jan 1969	43.0	0.8	25
Nov 1969–Dec 1970	46.4	0.6	145
Jan 1971–Dec 1971	51.2	0.7	145
Jan 1972–Dec 1972	46.0	0.5	89
Fairbanks			
Nov 1970–Dec 1970	74.3	3.5	19
Jan 1971–Dec 1971	62.2	1.3	88
Jan 1972–Dec 1972	56.2	1.0	52
Mauna Loa			
Aug 1971–Dec 1971	44.7	0.8	31
Jan 1972–Dec 1972	44.6[a]	0.5	66

[a] Peak at Mauna Loa in March 1972 excluded.

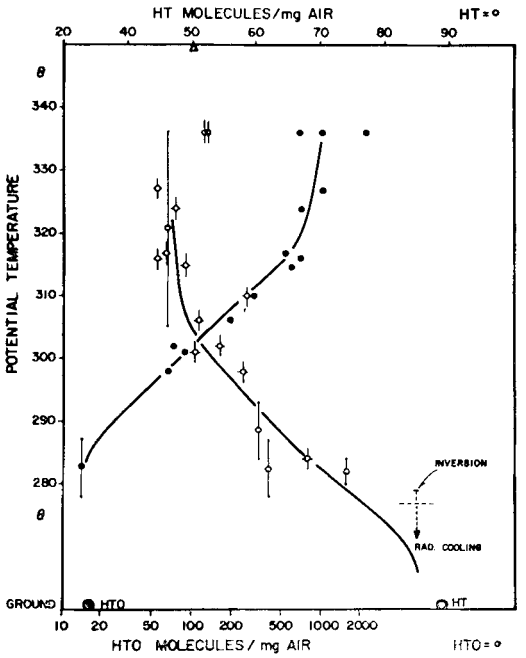


Fig. 5. Vertical distribution of HTO and HT in the lower Arctic stratosphere, north of Alaska, February 1971. (70°–75° N)

It therefore seems highly likely that our elevated values of atmospheric HT originate from the same source. The dates for large underground explosions are indicated in the graphs.

Yearly average concentrations of HT are presented in Table 4. It appears that the Miami results show an elevated value in 1971, caused by the large tests in late 1970. The local effect of these tests were seen immediately in Fairbanks, but not in Mauna Loa. Given a steady level of test activity, the "background" HT concentration will remain at about 46 T-atoms per mg air world-wide.

4. Aircraft data

In February 1971, a vertical "sounding" of HT and HTO was done between 66° and 76° N by participating in a flight on a U.S. Air Force C-135 (Boeing 707). In Fig. 5, the HTO and HT values are plotted against a vertical altitude scale expressed in potential temperature. Most of the samples were taken above the Arctic tropopause. As expected, the HTO gradient is extremely steep, indicating a flux

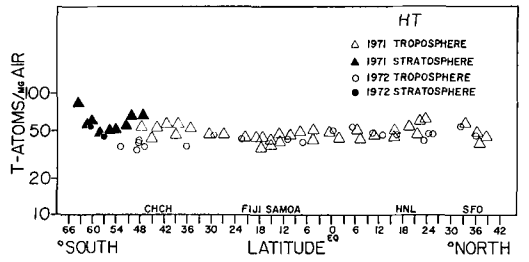


Fig. 6. Longitudinal distribution of HT in the atmosphere. Pacific and Antarctic Oceans, September 1971 and September 1972.

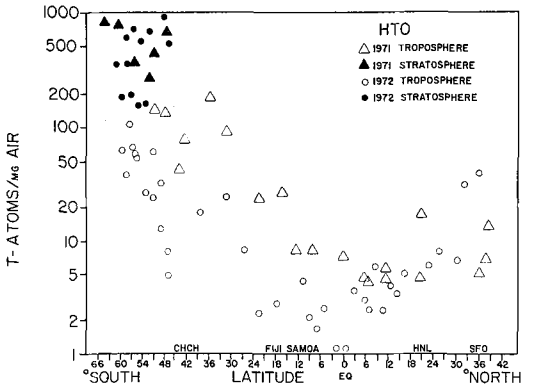


Fig. 7. Longitudinal distribution of HTO in the Pacific troposphere and lower Antarctic stratosphere in September 1971 and September 1972.

downward, with the source of HTO still in the stratosphere and the sink at ground level (the ocean). Looking at the HT gradient, we find that its slope is weak and opposite the HTO curve, thus indicating a flux upwards. However, we have to remember that, at this time, February 17, 1971, the ground-level HT data at Fairbanks, Alaska (see Fig. 4B), were anomalously high. Therefore, this HT gradient is *not* characteristic for the average situation. The curve implies, however, that the elevated HT values in Alaska during the winter of 1970–71 undoubtedly originated at ground level.

Another interesting experiment has been two flights, in September of 1971 and of 1972, from the vicinity of San Francisco all the way south almost to the Antarctic Circle, i.e., from about 40° N to about 65° S. These flights were at 10–12 km in the upper troposphere all the way, except furthest south where the tropopause was penetrated flying at about constant altitudes. The 1971 flight was undertaken five weeks after the French atmospheric fusion bomb test at about 22° S in the Pacific (Dept. of Health, New Zealand, 1972). Examining the plots for the two years as shown in Fig. 6, it appears that the latitudinal distribution of *HT* is essentially flat and that the global change between 1971 and 1972 is undetectable. This indicates that the residence time of HT in the atmosphere is long, that is, several years, so that the HT has had time to distribute itself evently between the two hemispheres. It also appears that atmospheric hydrogen bomb tests do not inject appreciable amounts of HT into the troposphere. Only close to the tropopause, south of about 50° S, the 1971 data might be slightly elevated.

Due to the French test, the general HTO level in the upper troposphere was much higher in 1971 than in 1972, the latter sampling being at a time when the hemispheric HTO pulses from the tests have subsided (cf. Fig. 7).

These flights were undertaken essentially at constant altitudes, the aircraft track penetrating into the stratosphere at high southern latitudes. This is part of the reason for the very high HTO values further south. The values indicated by filled symbols in the graph are definitely in the stratosphere.

4. Conclusions

Summarizing the obtained data of HTO for the past five years, we have established that the main reservoir of atmospheric HTO is still the stratosphere, and that its source is primarily the testing of fusion devices in the atmosphere.

For HT, the data tells us that the source is at ground level, and it is *not* the atmospheric testing of hydrogen bombs. It is probable that these sources for HT are as follows: (1) Reprocessing of nuclear fuel elements is done by first dissolving the elements in acid; thereby, hydrogen containing HT and Kr^{85} is being released. Radioactive metal isotopes are easily contained and reused. Tritiated water vapor is easily washed out in a spray tower (scrubber), but the hydrogen and the krypton are, to a great extent, released through the stack of the plant. This is probably the most important source of HT. (2) Another source is the handling of tritium gas. It is obviously impossible to find

out how much tritium gas is unintentionally released that way. (3) If we compare our ground-level station data with the Ar^{37} data of Loosli et al. (1973), it is most probable that underground explositions of fusion devices result in seepage of tritium gas to the atmosphere. This would be due to insufficient supply of oxygen to burn the remaining hydrogen isotopes. At present, the quasi-continuous source of HT to the lower troposphere about balances the radioactive and chemical decay of HT.

Today's tropospheric HT and HTO levels and their present trends are not a cause for concern of radiation exposure to mankind. With increasing use of nuclear energy, tritium is becoming only slightly more a problem than it has been so far. There is, however, a bad specter looming in the future—that is thermonuclear power generation. With the use of fusion reactors to generate power for civilian use, hundreds of kg of tritium will be handled in each power plant. Tritium gas (HT, DT, T_2), escaping through continuous leakage or accidental releases, will not be absorbed by the oceans. With the long residence times, it will stay in the atmosphere and might build up to significant radiation exposure levels to mankind. Thus if the technical problem of thermonuclear power generation is ever solved, the second greatest difficulty, maybe even the greatest, is how to contain all the tritium that will be used.

Acknowledgements

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Figs. 3–7 are based on original data available in a mimeographed report (Östlund et al., 1972), and further data reports to be released. These reports also contain sampling time and some weather information for ground-level samples and position, time and altitude for the aircraft sampling.

A slightly more detailed description of the sampling system will be avilable shortly (Mason, 1974).

Note added in proof

HT data from an air sampling program 1967 through 1969 by Dr Irving Friedman yielded an overall average of the specific activity of atmospheric hydrogen which, multiplied by an average 0.56 ppm of hydrogen, gives 46 T-atoms per mg air. (Friedman, I. & Scholz, T. G. 1074. Isotopic composition of atmospheric hydrogen, 1967–1969. *J. Geophys. Res.*, in press.)

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АТМОСФЕРНЫЕ HT И HTO: 1. ТЕХНИКА ЭКСПЕРИМЕНТА И ТРОПОСФЕРНЫЕ ДАННЫЕ ДЛЯ 1968–72 ГГ.

Разработана техника для прямых полевых определений концентраций атмосферных HTO и HT. Сделаны ее самолетная, переносная и лабораторные версии и начата обширная программа измерений. Воздух сначала пропускается через молекулярное сито для поглощения воды, затем над щитом, закрепленным на сите, который окисляет атмосферный водород и тут же поглащает получающуюся воду. Обе пробы последовательно извлекаются из поглотителей и концентрация трития измеряется внутренним счетчиком газа с низким уровнем. Разрешение составляет 4 % от содержания этих газов в атмосфере. Прослеживание HT и HTO на трех станциях в Северном полушарии показывает, что концентрация HT не подвержена сезонным флуктуациям, как HTO, и малы ее вариации вблизи современного уровня, составляющего около 50 молекул HT на *мг* воздуха. После предыдущего повышения от уровня до ядерных испытаний содержание HT в тропосфере достигло равновесного состояния в течение последних нескольких лет. Разрезы от 40° с. ш. до 65° ю. ш., проведенные в 1971 и 1972 гг., показали аналогичные уровни концентраций HT в Северном и Южном полушариях, что указывает на долгое время пребывания водорода (и HT) в тропосфере. Представляется, что источник HT находится на уровне поверхности земли, и им являются сгорание ядерного топлива, подземные взрывы термоядерных устройств и военное и гражданское использование трития. В настоящее время в тропосфере больше трития в виде газа (HT или T_2), чем в виде водяного пара (HTO).