HEALTH PHYSICS AND SAFETY DIVISION

AN INTERCOMPARISON OF AIRBORNE TRITIUM VAPOR SAMPLING METHODS
AT BROOKHAVEN NATIONAL LABORATORY

George M. Marmaro

December 1973

BROOKHAVEN NATIONAL LABORATORY
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**AN INTERCOMPARISON OF AIRBORNE TRITIUM VAPOR SAMPLING METHODS
AT BROOKHAVEN NATIONAL LABORATORY**

**A Thesis
Presented to
the Graduate Council of
The University of Tennessee**

**In Partial Fulfillment
of the Requirements for the Degree
Master of Science**

**by
George Michael Marmaro**

December 1973

NOTICE

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ABSTRACT

An intercomparison study was conducted consisting of six tritium vapor samplers. Four of these were airflow samplers: a molecular sieve tube, a silica gel tube, a mixed silica gel tube (a column of clear silica gel mixed with 10% color-indicating silica gel), and two series-connected frit bubblers. The remaining two were non-airflow samplers: a thermoelectric cooler and an open petri dish containing clear silica gel mixed with 10% color-indicating silica gel.

The analytical method associated with the mixed silica gel tube and the petri dish samplers incorporated a technique for direct counting of exposed silica gel in a liquid scintillation spectrometer. The usual liquid scintillation technique was employed with all other analytes.

An experimental system was devised whereby known concentrations of tritium vapor in air could be produced and which would permit simultaneous testing of the samplers. Air concentrations ranging from 7.51×10^{-9} $\mu\text{Ci/cc}$ to 1.30×10^{-3} $\mu\text{Ci/cc}$ were generated.

The average response of most of the samplers generally indicated good accuracy, but the accompanying standard deviations demonstrated a lack of consistency and reproducibility. The mean sampled-to-generated air concentration ratios, for all samplers except the silica gel tube, ranged from 0.83 to 1.07, while the associated standard deviations ranged from ± 0.22 to ± 0.48 .

Problems encountered during this study indicate that erroneous flowmeter response can be a major source of error for airflow-type samplers. Results have shown that the direct counting technique is generally satisfactory.

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I. INTRODUCTION

Tritium (T) is a radioactive isotope of hydrogen (H) which decays by beta-particle emission and exhibits a half-life of about 12.3 years. This isotope can enter into all known chemical reactions involving those of ordinary hydrogen and can therefore exist in various molecular configurations. It is commonly found as molecular hydrogen (HT or T_2) and as an oxide (HTO or T_2O).

A major concern of the health physics profession is the accurate assessment of the radiation hazard due to airborne tritiated water vapor. Tritiated water vapor is readily taken up by the human body through the lungs and through the intact skin, and is eventually distributed throughout the body water. Once in the body, the time necessary to eliminate one-half of the total tritium uptake (biological half-life) is approximately twelve days¹. The result of such an uptake is an exposure that is essentially similar in its effects to those of whole-body irradiation. For example, a single exposure resulting in a T_2O body water concentration of one microcurie per cubic centimeter ($\mu\text{Ci/cc}_{\text{H}_2\text{O}}$) will give a total dose commitment of nine rems¹. The National Council on Radiation Protection and Measurement (NCRP) has recommended that the total dose equivalent due to whole body irradiation from occupational sources be limited to five rems in any one year². This translates to a maximum permissible concentration of tritiated water vapor in air (MPC_{air}) of $5 \times 10^{-6} \mu\text{Ci/cc}_{\text{air}}$ for a forty-hour work week³. For the general public at large the MPC_{air} is $2 \times 10^{-7} \mu\text{Ci/cc}_{\text{air}}$. While one study has estimated the natural background tritium activity at about $0.001 \text{ MPC}_{\text{air}}$ for the general public⁴, concentrations monitored at the Van de Graaff and High

Flux Beam Reactor facilities at Brookhaven National Laboratory (BNL) often indicate levels on the order of $0.20 \text{ MPC}_{\text{air}}$ for occupational personnel⁵.

Tritium is produced both naturally (cosmic ray interaction with the atmosphere) and from man-made sources (nuclear reactors, weapons tests, etc.). Naturally occurring tritium accounts for approximately 69 megacuries⁶ in the environment. Nuclear weapons tests of the 50's and 60's contributed about 1,700 megacuries⁷, but this quantity has been decaying naturally and should be reduced to about one-eighth the original by the end of the century. Meanwhile, Petersen et al.⁸ have predicted an increase of about 200 megacuries due to nuclear power production alone.

The author was first introduced to the practical aspects of tritium vapor sampling during his participation in the 1972 summer training program at BNL. Part of that program involved investigating the performance of several sampling techniques currently in use at the Lab. As an individual project, an intercomparison study was initiated to determine the relative sampling characteristics of the molecular sieve tube, the silica gel tube, and two series-connected frit bubblers. The results of that study indicated serious problems in producing accurately known concentrations of airborne tritium vapor necessary for such a study, as well as unacceptable fluctuations in sampler collection efficiencies. These problems were not entirely unexpected. Staff members at BNL had experienced such discrepancies before and have often expressed the need for a comprehensive intercomparison of the various sampling techniques.

This study was therefore undertaken as an attempt to resolve these current problems as well as to provide useful information in the field of tritium sampling.

II. SAMPLERS

All samplers in this study functioned on the principle of collecting or trapping airborne water vapor for subsequent analysis of its tritium activity.

Two novel sampling approaches not previously used or tested at BNL were included in this study. These were the mixed silica gel tube and the petri dish.

A. Airflow Samplers

1. Molecular Sieve Tube. The molecular sieve sampler (Figure 1) was a cylindrical aluminum tube containing a desiccant material. Its dimensions are: length 13 inches (33 cm), outside diameter 2 inches (5.1 cm) and inside diameter 1-3/4 inches (4.45 cm). End caps were permanently welded to the main body and were mated with Swagelok* quick-connect fittings. The tube was filled with about 300 grams of Linde** type 3-A (3 angstrom pore size) molecular sieve material in 1/16 inch (0.16 cm) pellet form. Wafer screens were positioned inside the ends of the tube to prevent blow-out of the contents during operation.

When sampling, air was directed through the tube at a known, constant rate by means of a vacuum pump and a Brooks[†] valve-controlled flow meter (0.1 to 2.5 standard cubic feet per hour). Moisture from the air flow was adsorbed by the sieve material. After sampling, the

*Crawford Fitting Co., 29500 Solon Road, Cleveland, Ohio 44139.

**Linde Molecular Sieves, Pleasant Valley Road and Route 38, Moorestown, New Jersey 08057.

[†]Brookes Instrument Co., Hatfield, Pennsylvania.

Figure 1. Silica gel tube (left), and molecular sieve tube (right).

adsorbed moisture was retrieved through a regeneration process (Appendix B), weighed, and then analyzed for tritium activity in a liquid scintillation counter (Appendix C). The airborne tritium vapor concentration was calculated by dividing the total activity collected by the total volume of air sampled.

2. Silica Gel Tube. This sampler (Figure 1) was also a cylindrical aluminum tube containing a desiccant. Its dimensions are: length 13 inches (33 cm), outside diameter 1-7/8 inches (4.76 cm), and inside diameter 1-3/4 inches (4.45 cm). One end cap was permanently affixed to the tube, while the other was threaded to permit removal. Both end caps were mated with wafer screens inside and Swagelok fittings outside. The tube was filled with about 300 grams of Davisson Chemical* silica gel material, grade 05, mesh 6-16. The sampling procedure and analyses were similar to those used with the molecular sieve tube, with the exception that, after regeneration, the silica gel was disposed of and replaced with new gel, whereas the molecular sieve material was re-used. Replacement of the silica gel was necessary because temperatures during regeneration exceed the manufacturer's recommendations and result in seriously impaired collection efficiency.

3. Frit Bubbler. This sampler (Figure 2) was a standard 250 cc. pyrex gas-wash bottle containing distilled water as the collection medium. The bottom of the inlet stem was fitted with a fritted dispersion tip positioned so as to remain submerged in the water. A known, constant

*Fisher Scientific Co., 633 Greenwich St., New York, N. Y. 10014.

Figure 2. Frit bubbler.

flow of air (measured with a Dyer* model VFB-BF valve controlled flowmeter, 0-10 liters per minute) was directed through the tip causing a bubbling action and moisture contained in the air exchanged with the water. After sampling, the water was analyzed for tritium concentration. The airborne tritium vapor concentration was calculated by dividing the total activity collected by the total volume of air sampled. In this study, two frit bubblers were series-connected during sampling. This procedure enabled determination of the relative efficiency on a comparison basis.

4. Mixed Silica Gel. This sampler was patterned after one developed by Osloond et al.⁹. It consisted of a clear lucite column, 16 inches (40.64 cm) long, outside diameter 2 inches (5.1 cm) and inside diameter 1-3/4 inches (4.46 cm). It was filled with a mixture of 90% clear silica gel and 10% color-indicating silica gel (Davison Chemical, grade 42, mesh 6-16) totaling about 300 grams. This gel changes color progressively from dark blue to white to pink, thereby indicating, qualitatively, its moisture content and saturation point. The tube ends were plugged with rubber stoppers equipped with tube connectors. Small glass wool pads positioned between the stoppers and the gel prevented blow-out of the contents.

During sampling, air was directed through the column at a known, constant rate (measured with a Dyer model VFA-23-BF valve controlled flowmeter, 0-5 liters per minute). After sampling, the exposed portion (indicated by color change) plus about 1 cm of the unexposed portion was removed from the column, mixed thoroughly and weighed. A five gram

*F. W. Dyer Mfg. Co., Michigan City, Indiana.

sample was then removed and analyzed for tritium activity using the direct counting technique (Appendix C) developed by Osmond et al.⁹. The total activity collected, divided by the total volume of air sampled, yields the airborne tritium vapor concentration.

B. Non-Airflow Samplers

1. Thermoelectric Cooler. This device, illustrated in Figure 3, was developed by the Health Physics Division at BNL. It incorporated a thermoelectric module (Cambion* #3958-1) which operates as a Peltier cooler. Current induced in the module forces the collector temperature below 0°C., thereby condensing and freezing atmospheric moisture. The ice is subsequently melted by the heat of an ordinary light bulb and collected in the sample bottle. Operation of the device is electronically cycled for the following time intervals: module current on (collecting) - 28 minutes; module current off and light bulb on (melting) - 2 minutes. (Theoretically, the current to the module may be reversed, thereby heating the collector and aiding the melting process. However, previous field experience using this mode resulted in a high incidence of module failure and was discontinued.) The water sample was weighed and then analyzed for tritium activity in a liquid scintillation counter (Appendix C). The airborne tritium vapor concentration is calculated (Appendix D) on the basis of atmospheric parameters (temperature, pressure, relative humidity).

2. Petri Dish. This sampler was simply an uncovered petri dish, 2 inches (7.62 cm) in diameter and 1/2 inch (1.27 cm) deep, containing

*Cambridge Thermionic Corp., 445 Concord Avenue, Cambridge, Massachusetts 02138.

Figure 3. Thermoelectric cooler.

about 40 grams of mixed silica gel. The dish and contents were first weighed and then exposed to the air being sampled. After sampling, they were again weighed, the contents mixed thoroughly, and a five gram sample taken for direct counting (Appendix C).

III. EXPERIMENTAL APPARATUS

The experimental apparatus incorporated four main sections (Figure 4). These were the generating section, the environmental chamber, the manifold section, and the pumping section. Overall views of the apparatus are presented schematically in Figure 5 and photographically in Figures 6, 7 and 8.

A. Generating Section

The function of the generating section was to produce known, uniform airborne tritium vapor concentrations for the rest of the experimental system. Several techniques were considered. Nelson and Griggs¹⁰ developed a system which involved a mechanically driven syringe injecting precise quantities of tritiated water into an air stream. A simpler approach used by Valentine¹¹ and others¹² consisted of evaporating tritiated water in a heated flask and introducing the vapor into an air stream.

Techniques similar to the one chosen for this study had been used previously by the author¹² and others¹⁴. It consisted of a bubbler, a primary desiccant, and a flowmeter-vacuum gauge arrangement. The bubbler was a standard 250 cc. pyrex gas-wash bottle containing a known quantity and concentration of tritiated water. It was modified slightly to reduce airflow restriction by removing the fritted dispersion tip, closing off the end, and perforating the lower portion of the stem with small holes. The primary desiccant, a lucite column, length 15 inches (38.1 cm), outside diameter 2 inches (5.1 cm), inside diameter 1-3/4 inches (4.45 cm), was filled with about 500 grams of mixed silica gel. The flowmeter was

Figure 4. Block diagram of experimental apparatus.

Figure 5. Schematic diagram of experimental apparatus.

Figure 6. View of environmental chamber (left), and generating section (right).

Figure 7. View of pumping section (left), manifold section (center), and environmental chamber (right).

Figure 8. Closer view of manifold section (center), and environmental chamber (right).

a Dwyer model VFA-24-BF valve controlled rotameter with a range of 0-10 liters per minute. A Danton* vacuum gauge, range 0-30 inches Hg, was connected between the flowmeter outlet and the primary desiccant inlet. All connecting lines were of 1/4 inch (0.635 cm) inside diameter Tygon** tubing.

The sequential operation of the generating section was as follows: room air was drawn through the flowmeter-vacuum gauge arrangement, through the primary desiccant (which removed essentially all moisture from the air), through the generator bubbler (which saturated the air with tritiated water vapor), and on into the environmental chamber.

B. Environmental Chamber

The purpose of the environmental chamber was to simulate a tritiated room atmosphere which would facilitate "external" sampling (with airflow type samplers) and also serve as a repository for both "internal" samplers (non-airflow type samplers) and atmospheric recording instruments. It consisted of an ordinary fiberglass glove box, 36 inches long by 24 inches high by 24 inches deep (91.44 cm long by 60.96 cm high by 60.96 cm deep), with a total volume of 12 cubic feet (340 liters). Several modifications were made on the glove box (Appendix E) to allow operation under slightly negative pressure and to provide adequate sealing. The chamber contained two non-airflow samplers, the petri dish and the thermoelectric cooler, as well as two meteorological instruments, a microbarograph and a hygro-thermograph, to record atmospheric parameters.

*Duro Instrument Corp., Brooklyn, New York.

**U. S. Stoneware Co., 60 East 42nd Street, New York, N. Y.

During operation, the airflow containing the tritiated water vapor from the generating section filled the chamber and was eventually exhausted to the manifold section.

C. Manifold Section

The manifold section provided the access points for simultaneous testing of the airflow type samplers. It consisted of two specially constructed five-port pyrex manifolds (one inlet and one outlet). Their dimensions were: Main body - length 19 inches (48.26 cm), outside diameter 1/2 inch (1.27 cm); Ports - length 6 inches (15.24 cm), outside diameter 1/2 inch (1.27 cm). Each port was equipped with stopcocks for airflow control. Ports #1-3 were occupied by the mixed silica gel tube, the silica gel tube, and the molecular sieve tube, respectively. Port #4 was occupied by the two series-connected frit bubbler samplers followed by the frit desiccant tube. The frit desiccant tube was a lucite column, length 7-1/4 inches (18.42 cm), outside diameter 2 inches (5.1 cm), and inside diameter 1-7/8 inches (4.76 cm). It was filled with about 200 grams of mixed silica gel and was sealed at each end with rubber stoppers equipped with tubing connectors. Port #5 served as a bypass and pressure monitoring point. All four samplers were followed by their respective flowmeters.

Airflow from the environmental chamber was directed into the inlet manifold, through the various sampling arrangements (and/or bypass), into the outlet manifold, and on to the pumping section. All connecting lines were of 1/4 inch (0.635 cm) inside diameter Tygon tubing, with the exception of the line from the chamber to the inlet manifold which was one inch (2.54 cm) inside diameter Tygon tubing.

D. Pumping Section

The purpose of the pumping section was to initiate and maintain a uniform airflow through the entire experimental system. It consisted of a Doerr* continuous duty pump, model #0522-103-G 18D, a Dwyer valve controlled flowmeter, model VFA-24-BF, range 0-10 liters per minute, an Ashcroft** vacuum gauge, range 0-30 inches Hg, and a final desiccant tube. The final desiccant tube was a clear lucite column, length 15 inches (38.1 cm), outside diameter 2 inches (5.1 cm), and inside diameter 1-3/4 inches (4.45 cm). It was filled with about 500 grams of mixed silica gel and was sealed with rubber stoppers equipped with tubing connectors. All connecting lines were of 1/4 inch (0.635 cm) inside diameter Tygon tubing, with the exception of the exhaust line which was 1/2 inch (1.27 cm) inside diameter Tygon tubing.

Air was drawn from the outlet manifold, through the final desiccant tube, through the flowmeter-vacuum gauge arrangement, and into the pump inlet. The pump outlet was exhausted to a vented hood. Air flow was regulated by either the pump control valve or the flowmeter control valve.

*Doerr Electric Corp., Cedarburg, Wisconsin.

**Ashcroft-Dresser Industrial Valve & Instrument Division, Stratford, Connecticut.

IV. EXPERIMENTAL PROCEDURE

The tritiated water source solutions used for generation purposes were prepared by diluting a portion of the primary cooling water (assayed at about 3.3 Ci/liter) from the High Flux Beam Reactor. These dilutions yielded the following concentrations: Solution #1 - 109.0 $\mu\text{Ci/cc}$; solution #2 - 1.02 $\mu\text{Ci/cc}$; solution #3 - 1.05×10^{-2} $\mu\text{Ci/cc}$, and solution #4 - 1.12×10^{-3} $\mu\text{Ci/cc}$.

In order to maintain a minimum of interference due to contamination of equipment, the majority of experimental runs were executed in groups starting with the lowest source concentration and increasing by at least one order of magnitude in consecutive groups.

All silica gel was dried in ovens at about 110°C. for at least 24 hours prior to use. The mixed silica gel was usually prepared in 2 kilogram batches.

Each experimental run involved a large amount of data collection as well as procedural redundancy. In order to assure a systematic and uniform approach, three itemized lists (Appendix A) were prepared and followed for all runs. The first list covered procedures dealing with the preparation of materials prior to a run. This included: filling the generator bubbler with a source solution and recording its total weight; filling the samplers and desiccant tubes with their respective materials and recording their weights; preparing the hygro-thermograph and micro-barograph recording instruments; placing instruments and non-airflow samplers in the environmental chamber and sealing the chamber; connecting the airflow samplers, desiccant tubes, flowmeters, etc. in their proper positions, and a final check of all locations and connections.

The next list covered procedures for operating the apparatus. It included: starting the airflow through the system; manipulation of various control valves to achieve proper flow rate, and recording all flow rate data and times.

The final list dealt with procedures for terminating operation of the apparatus. It included: stopping airflow through the generator bubbler and samplers; removing and recording the weights of the generator bubbler, samplers and desiccant tubes, and removal of samples for subsequent analyses.

V. RESULTS

The length of experimental runs ranged from 19 to 36 hours and averaged about 26 hours. This was somewhat of a compromise, since the frit bubbler is usually used as a "grab" sampler ($\sim 1/2$ hour sampling time) and airflow samplers such as the silica gel and molecular sieve tube generally sample for one week to one month, depending on flow rates and specific applications. The important point, however, is that the samplers were tested for lengths of time that did not approach saturation and still permitted sufficient collection for representative samples.

The data from several runs have been excluded for a variety of reasons. Run #1 was a full-scale test of the equipment using ordinary water as the source solution. During run #16 a flow line worked loose and caused non-uniform flow rates. An attempt to use the lowest concentration source solution (#4) during later runs (#20-22) resulted in useless data due to contamination of the apparatus from previous runs of higher concentrations. Isolated cases of missing data were due to accidental loss of samples.

A correlation based on 22 experimental runs is shown in Table I. This data express the sampled air concentrations compared to the generated air concentrations for each run. The generated concentrations covered six orders of magnitude, ranging from $7.51 \times 10^{-9} \mu\text{Ci/cc}_{\text{air}}$ to $1.30 \times 10^{-3} \mu\text{Ci/cc}_{\text{air}}$. In terms of the occupational maximum permissible concentration for a 40-hour work week, this range is $1.50 \times 10^{-3} \text{MPC}_{\text{air}}$ to $2.60 \times 10^2 \text{MPC}_{\text{air}}$. A plot of the data from Table I is shown in Figure 9 (page 24) and represents the response of each sampler in terms of the sampled air concentrations as a function of the generated air concentrations. For

TABLE I
Summary of Sampled and Generated Air Concentrations
 $\mu\text{Ci/cc}_{\text{air}}$

Run	Mixed Silica Gel Tube	Silica Gel Tube	Molecular Sieve Tube	Frit Bubbler #1	Thermo- electric Cooler	Petri Dish	Generator
2	6.54×10^{-9}	4.22×10^{-9}	6.12×10^{-9}	6.97×10^{-9}	-	2.83×10^{-9}	9.63×10^{-9}
3	13.32×10^{-9}	-	5.21×10^{-9}	-	10.60×10^{-9}	11.60×10^{-9}	10.25×10^{-9}
4	12.62×10^{-9}	3.19×10^{-9}	9.02×10^{-9}	10.73×10^{-9}	11.30×10^{-9}	14.40×10^{-9}	8.66×10^{-9}
5	11.16×10^{-9}	0.65×10^{-9}	10.28×10^{-9}	9.85×10^{-9}	11.30×10^{-9}	14.40×10^{-9}	8.66×10^{-9}
6a	16.79×10^{-9}	0.28×10^{-9}	5.90×10^{-9}	8.02×10^{-9}	-	-	7.80×10^{-9}
6b	8.66×10^{-9}	2.90×10^{-9}	6.80×10^{-9}	-	-	-	7.80×10^{-9}
7	6.32×10^{-9}	3.04×10^{-9}	6.24×10^{-9}	7.86×10^{-9}	7.64×10^{-9}	7.10×10^{-9}	7.51×10^{-9}
8	9.32×10^{-9}	1.42×10^{-9}	5.39×10^{-9}	8.31×10^{-9}	8.03×10^{-9}	7.09×10^{-9}	11.29×10^{-9}
9	76.73×10^{-9}	30.87×10^{-9}	73.23×10^{-9}	84.38×10^{-9}	86.50×10^{-9}	90.60×10^{-9}	102.50×10^{-9}
10	83.53×10^{-9}	16.08×10^{-9}	82.05×10^{-9}	57.43×10^{-9}	94.60×10^{-9}	86.10×10^{-9}	95.50×10^{-9}
11	155.30×10^{-9}	60.33×10^{-9}	112.89×10^{-9}	102.80×10^{-9}	78.30×10^{-9}	11.10×10^{-8}	127.80×10^{-9}
12	14.34×10^{-6}	2.19×10^{-6}	8.40×10^{-6}	9.17×10^{-6}	9.53×10^{-6}	11.20×10^{-6}	5.87×10^{-6}
13	13.10×10^{-6}	0.55×10^{-6}	6.08×10^{-6}	6.85×10^{-6}	7.23×10^{-6}	10.60×10^{-6}	8.72×10^{-6}
14	7.89×10^{-6}	12.55×10^{-6}	8.11×10^{-6}	8.12×10^{-6}	8.26×10^{-6}	8.54×10^{-6}	10.48×10^{-6}
15	8.95×10^{-6}	3.60×10^{-6}	9.27×10^{-6}	8.91×10^{-6}	11.84×10^{-6}	8.50×10^{-6}	12.02×10^{-6}
17	10.54×10^{-6}	9.70×10^{-6}	9.82×10^{-6}	8.61×10^{-6}	13.40×10^{-6}	11.10×10^{-6}	10.19×10^{-6}
18	9.04×10^{-6}	8.99×10^{-6}	8.41×10^{-6}	7.63×10^{-6}	11.18×10^{-6}	9.38×10^{-6}	10.39×10^{-6}
19	8.53×10^{-6}	8.99×10^{-6}	7.42×10^{-6}	7.93×10^{-6}	12.16×10^{-6}	10.20×10^{-6}	11.79×10^{-6}
23	9.68×10^{-4}	14.73×10^{-4}	12.17×10^{-4}	12.21×10^{-4}	14.60×10^{-4}	10.90×10^{-4}	11.90×10^{-4}
24	9.81×10^{-4}	11.96×10^{-4}	10.84×10^{-4}	15.16×10^{-4}	15.20×10^{-4}	10.40×10^{-4}	12.23×10^{-4}
25	9.21×10^{-4}	14.87×10^{-4}	10.98×10^{-4}	15.27×10^{-4}	15.0×10^{-4}	10.60×10^{-4}	11.78×10^{-4}
26	6.27×10^{-4}	11.24×10^{-4}	7.59×10^{-4}	13.49×10^{-4}	12.70×10^{-4}	8.72×10^{-4}	12.39×10^{-4}

Figure 9. Sampled tritium air concentration as a function of generated air concentration.

clarity, the data points for each successive sampler were off-set one order of magnitude to the right of its preceding neighbor. The dashed lines represent the ideal response curve for each sampler. Marked deviations from the ideal are apparent for the silica gel tube at the lowest and second highest concentrations. Nearly all remaining data points lie fairly close to the ideal with the possible exception of the petri dish data at low concentrations.

Another intercomparison based on the preceding data is compiled in Table II, which shows the ratio of sampled-to-generated air concentrations for each run. The data from this table are plotted semi-logarithmically in Figure 10 (page 27). Here, the silica gel tube deviations from the ideal are even more apparent, both in early runs (low concentrations) and later runs (higher concentrations). Also significant are the trends displayed by nearly all samplers in unison during runs #8 and 12.

The mean ratios of sampled-to-generated air concentrations for each sampler as a function of the number of runs is plotted linearly in Figure 11 (page 29). For example, the ratio plotted for the molecular sieve tube based on the first six runs is the mean value of the first six ratios reported in Table II for that sampler. The error bars indicate the statistical spread of the data (one standard deviation) based on all the data reported and assuming a normal distribution. The solid line represents the ideal ratio of 1.0 and is included as a point of reference. A summary of the mean ratios for each sampler and their respective standard deviations is shown in Table III.

Table IV compares the total activity collected by the final desiccant tube to the total activity generated to determine the approximate

TABLE II

Ratios of Sampled to Generated Air Concentration

Run	Mixed Silica Gel Tube	Silica Gel Tube	Molecular Sieve Tube	Frit Bubbler #1	Thermo- electric Cooler	Petri Dish
2	0.68	0.44	0.64	0.71	-	0.30
3	1.30	-	0.51	0.90	1.03	1.13
4	1.46	0.37	1.04	1.24	1.30	1.66
5	1.29	0.08	1.19	1.14	1.30	1.66
6a	2.15	0.04	0.76	1.03	-	-
6b	1.11	0.37	0.87	1.03	-	-
7	0.84	0.40	0.83	1.05	1.02	0.95
8	0.83	0.13	0.48	0.74	0.71	0.63
9	0.75	0.30	0.71	0.82	0.84	0.88
10	0.87	0.17	0.86	0.60	0.99	0.90
11	1.22	0.47	0.88	0.80	0.61	0.87
12	2.44	0.37	1.43	1.56	1.62	1.91
13	1.50	0.63	0.70	0.79	0.83	1.22
14	0.94	1.20	0.77	0.78	0.79	0.81
15	0.74	0.30	0.77	0.74	0.99	0.71
17	1.03	0.95	0.96	0.84	1.32	1.09
18	0.87	0.87	0.81	0.73	1.08	0.90
19	0.72	0.76	0.63	0.67	1.03	0.87
23	0.81	1.24	1.02	1.03	1.23	0.92
24	0.80	0.98	0.89	1.24	1.24	0.85
25	0.78	1.26	0.93	1.30	1.27	0.90
26	0.48	0.87	0.58	1.04	0.98	0.67

Figure 10. Ratio of sampled to generated tritium air concentration for each run.

Figure 11. Ratio of sampled to generated tritium air concentration versus number of runs.

TABLE III
Mean Ratio of Sampled to Generated Air Concentrations
and Standard Deviation for Each Sampler

Sampler	Mean Ratio (all runs)	Standard Deviation σ
Mixed Silica Gel Tube	1.07	± 0.48
Silica Gel Tube	0.58	± 0.39
Molecular Sieve Tube	0.83	± 0.22
Frit Bubbler #1	0.95	± 0.24
Thermoelectric Cooler	1.06	± 0.25
Petri Dish	0.99	± 0.38

TABLE IV
Final Desiccant Data

Run	Total Activity Generated μCi	Total Activity Collected by Final Desiccant μCi	Approximate Collection Efficiency of all Samplers Combined %
2	9.98×10^{-2}	4.24×10^{-3}	95.8
3	8.77×10^{-2}	19.96×10^{-3}	77.2
4	13.63×10^{-2}	14.80×10^{-3}	89.1
5	13.63×10^{-2}	14.80×10^{-3}	89.1
6a	9.63×10^{-2}	2.82×10^{-4}	99.7
6b	9.63×10^{-2}	2.82×10^{-4}	99.7
7	5.66×10^{-2}	6.02×10^{-3}	89.4
8	7.71×10^{-2}	4.47×10^{-4}	99.4
9	11.54×10^{-1}	3.55×10^{-3}	99.7
10	9.19×10^{-1}	1.53×10^{-2}	98.3
11	9.66×10^{-1}	5.39×10^{-2}	94.4
12	68.75	8.06	88.3
13	108.7	4.96	95.4
14	100.5	4.12	95.9
15	116.6	4.96	95.7
17	110.9	7.25	93.5
18	119.8	3.73	96.9
19	126.4	4.76	96.2
23	12.96×10^3	7.67×10^2	94.1
24	11.88×10^3	5.66×10^2	95.2
25	11.95×10^3	7.65×10^2	93.6
26	12.01×10^3	4.55×10^2	96.2
			Mean 94

collection efficiency of all the samplers combined. The efficiency is approximated by the relation:

$$\text{efficiency} \approx \frac{A_g}{A_g + A_f}$$

where A_g = total activity generated

A_f = total activity collected by final desiccant

Data involving the series-connected frit bubbler arrangement and based on 20 runs is presented in Table V. Here, an intercomparison of the sampled air concentrations was used to determine the approximate collection efficiencies of the two bubblers. For frit #1 the relation used was

$$\text{efficiency} = \frac{C_1}{C_1 + C_2} \times 100\%$$

and for frit #2

$$\text{efficiency} = \frac{C_2}{C_2 + C_3}$$

where C_1 = concentration sampled by frit #1

C_2 = concentration sampled by frit #2

C_3 = concentration sampled by frit desiccant.

TABLE V

Series-Connected Frit Bubbler Data

Run	Sampled Air Concentration $\mu\text{Ci/cc}_{\text{air}}$			Approximate Collection Efficiency (%)	
	Frit Bubbler #1	Frit Bubbler #2	Frit Desiccant	Frit #1	Frit #2
2	6.79×10^{-9}	7.43×10^{-10}	1.58×10^{-10}	89	79
4	10.73×10^{-9}	9.74×10^{-10}	0.59×10^{-10}	91	94
5	9.85×10^{-9}	20.10×10^{-10}	5.31×10^{-10}	80	74
6	8.02×10^{-9}	13.0×10^{-10}	0.96×10^{-10}	84	93
7	7.86×10^{-9}	9.71×10^{-10}	N.D.A.*	88	~ 100
8	8.31×10^{-9}	8.95×10^{-10}	2.22×10^{-11}	89	98
9	84.38×10^{-9}	16.70×10^{-9}	2.56×10^{-9}	80	85
10	57.43×10^{-9}	6.39×10^{-9}	7.66×10^{-10}	89	88
11	102.80×10^{-9}	17.16×10^{-6}	3.66×10^{-9}	83	79
12	9.17×10^{-6}	1.66×10^{-6}	2.99×10^{-7}	82	82
13	6.85×10^{-6}	1.72×10^{-6}	4.13×10^{-7}	75	76
14	8.12×10^{-6}	1.58×10^{-6}	1.93×10^{-7}	81	88
15	8.91×10^{-6}	1.95×10^{-6}	2.63×10^{-7}	78	87
17	8.61×10^{-6}	2.36×10^{-6}	3.60×10^{-7}	73	85
18	7.63×10^{-6}	2.60×10^{-6}	4.97×10^{-7}	66	81
19	7.93×10^{-6}	3.13×10^{-6}	3.56×10^{-7}	61	89
23	1.22×10^{-3}	2.49×10^{-4}	5.91×10^{-5}	80	76
24	1.52×10^{-3}	2.35×10^{-4}	4.03×10^{-5}	85	83
25	1.53×10^{-3}	2.02×10^{-4}	3.48×10^{-5}	87	83
26	1.35×10^{-3}	1.75×10^{-4}	2.55×10^{-5}	87	85
Mean				81	85

*No detectable activity

VI. DISCUSSION

A. Experimental Problems

A serious problem encountered during early runs (#2-10) was erroneous flowmeter readings. This problem was found to be due to two related factors: flowmeter calibration and pressure-dependence. While most of the flowmeters were new, calibrations with a dry-test meter revealed errors as high as 40%. However, a re-analysis of data using corrected flowrates still resulted in poor agreement between the sampled and the generated air concentrations. The problem was not resolved until after run #15, when additional correction factors due to pressure differentials were applied to the flowmeter data. This was made possible by the installation of vacuum gauges at strategic locations which monitored the pressure on the flowmeter floats. All previous and subsequent flowmeter data were therefore corrected, based on calibration curves as well as pressure differentials. A summary of the corrected flowrates is shown in Table VI. As a further measure in avoiding flowmeter errors, the total exhaust flow was taken to be the sum of the sampler flowrates instead of relying on the exhaust flowmeter data.

Another problem involved leaks in the threaded cap on the silica gel tube and occasional failure of the O-ring seals in the Swagelok fittings. These leaks were not discovered until run #17, at which time they were eliminated. It is not known how much effect these leaks had, but a definite improvement in the silica gel tube data is apparent after run #17.

A less serious leak problem involved the environmental chamber. Earlier tests as well as a comparison of generator and exhaust flowrates

TABLE VI
Flow Rates
(liters per minute)

	Molecular Sieve Tube	Silica Gel Tube	Mixed Silica Gel Tube	Frit Bubblers	Generator	Exhaust
Mean	0.48	0.52	1.53	2.56	4.41	5.04
Range	0.41	0.31	1.0	1.50	2.50	3.60
	to	to	to	to	to	to
	0.61	0.50	2.0	4.0	6.35	6.86

both indicated a leak rate of 10-20% of the total exhaust flowrate. Since this leak was upstream of the samplers, its only effect was to dilute slightly the air concentrations from the generating section.

B. Reliability of Generating Technique

Certain trends evident in Figure 10 (page 27) may raise questions as to the reliability of the generating section. The sharp peaks in the sampled-to-generated ratios during run #12 (for all samplers except the silica gel tube) suggest that the calculated air concentration generated is in error. This is substantiated by the data in Table IV (page 30) where the approximate collection efficiency of all samplers combined during run #12 is only 88%, compared to the average for all runs of 94%. While this discrepancy is small in number, its effect is large. If one assumes the 94% efficiency for run #12, the total activity generated would be $\sim 134 \mu\text{Ci}$. The activity balance sheet in Table VII compares the measured activity generated to the total activity collected by the system. An obvious correlation is evident during run #12, where the total activity collected is $> 67\%$ higher than that generated. If, as assumed above, the actual activity generated was $\sim 134 \mu\text{Ci}$, the resulting percent difference for run #12 in Table VII would be $\sim 15\%$, which is very close to the average percent difference for all runs. Thus it would appear the calculated activity generated is in error.

A similar argument in reverse can be applied to the data for run #8 where Figure 10 (page 27) shows a small valley for the sampled-to-generated ratios of most samplers. For this run, Table IV (page 30) shows an above average efficiency of 99%, and Table VII shows a negative percent difference of $> 27\%$.

TABLE VII
Activity Balance Sheet

Run	Total Activity (μCi)		% Difference Based on Generated Activity
	Collected	Generated	
2	7.53×10^{-2}	9.98×10^{-2}	- 24.5
3	6.27×10^{-2}	8.77×10^{-2}	- 28.5
4	14.75×10^{-2}	13.63×10^{-2}	+ 8.2
5	14.75×10^{-2}	13.63×10^{-2}	+ 8.2
6a	10.32×10^{-2}	9.36×10^{-2}	+ 10.3
6b	10.32×10^{-2}	9.36×10^{-2}	+ 10.3
7	5.87×10^{-2}	5.66×10^{-2}	+ 3.6
8	5.61×10^{-2}	7.71×10^{-2}	- 27.2
9	9.60×10^{-1}	11.54×10^{-1}	- 16.9
10	7.14×10^{-1}	9.19×10^{-1}	- 22.3
11	9.97×10^{-1}	9.66×10^{-1}	+ 3.2
12	115.11	68.75	+ 67.4
13	120.52	108.70	+ 10.9
14	99.32	100.50	- 1.2
15	102.08	116.59	- 12.4
17	118.55	110.87	+ 6.9
18	116.10	119.80	- 3.1
19	106.42	126.38	- 15.8
23	14.39×10^3	12.96×10^3	+ 11.0
24	13.34×10^3	11.88×10^3	+ 12.3
25	14.27×10^3	11.95×10^3	+ 19.4
26	11.47×10^3	12.01×10^3	- 4.5
Average			± 16

On the other hand, if one views these marked deviations as isolated cases, the remaining data indicate that the generating system is fairly reliable. Even including the questionable data it is seen that, for a large number of runs, the response of most samplers lies fairly close to the ideal. In addition, the mean sampled-to-generated ratio of all samplers combined, and based on all runs, is 0.91 ± 0.22 .

C. Comparisons With Other Studies

A previous study by the author¹³ involved intercomparisons of a molecular sieve tube, a silica gel tube, and two series-connected frit bubblers. It was based on twelve experimental runs and air concentrations of $\sim 8 \times 10^{-8}$ $\mu\text{Ci/cc}$. The mean collection efficiencies were: 78% for the molecular sieve tube, 75% for the silica gel tube, and 93% for the frit bubbler. The mean collection efficiencies for these samplers based on Table III (page 29) are 83%, 58% and 95%, respectively. Good agreement is seen in all cases except the silica gel tube.

An investigation of two series-connected frit bubblers by Valentine¹¹ based on four runs and air concentrations of $\sim 4 \times 10^{-5}$ $\mu\text{Ci/cc}$, resulted in a mean collection efficiency of $> 90\%$. This compares favorably with a mean efficiency for the frit bubbler of $\sim 95\%$ using the data from Table III (page 29), as well as the mean efficiencies from Table V (page 32), which shows $> 81\%$ for frit #1 and $> 85\%$ for frit #2.

Additional comparisons are available based on two separate studies which determined the differences in sampled air concentrations of a frit bubbler relative to a thermoelectric cooler. Cochran's study¹⁵ based on seven runs and air concentrations of $\sim 5 \times 10^{-7}$ $\mu\text{Ci/cc}$, resulted in a mean difference of 26.5% between the frit bubbler and thermoelectric cooler.

A similar study by Hilgemeier¹⁶ based on six runs and air concentrations of $\sim 1 \times 10^{-7}$ $\mu\text{Ci/cc}$, showed a mean difference of only 5.2%. A comparison of the data for the frit bubbler and thermoelectric cooler from Table III (page 29) also gives a mean difference of 5.2%.

VII. SUMMARY

A. Generating Technique

The discrepancies regarding the generating techniques in runs #8 and 12 were most likely due to human error. One explanation is that the wrong source solution may have been added to the generator bubbler prior to those runs. This could account for the large differences between the total activities generated and collected. Further errors of up to 5% may be introduced in weighing the generator before and after a run.

In view of the overall results, the generating technique was found to be generally accurate in producing known concentrations of air-borne tritium vapor. While there is need for improving its precision, its basic simplicity, ease of operation, low cost and availability of materials make it an attractive method for testing and calibrating tritium vapor samplers.

B. Mixed Silica Gel Tube

This sampler has shown a good mean sampled-to-generated ratio of 1.07. However, large fluctuations during specific runs resulted in a very poor standard deviation of ± 0.48 . This may have been due to the random process of mixing the exposed portion of the gel prior to extracting the 5 gram sample for subsequent analysis. Incomplete mixing would not yield a representative sample. Flowmeter inaccuracy during runs #2-15 may also have been a major factor. In addition, errors of up to 8% could be introduced in the weighing processes (four determinations).

In general, this sampler has several desirable characteristics. It offers a high degree of convenience in that no regeneration of moisture is necessary; the exposed gel is counted directly in a liquid scintillation counter. It is inexpensive to assemble and maintain, and could probably sample for long periods (~ one month) at low flowrates. A major disadvantage is that the associated calculations rely on flowmeter data.

C. Silica Gel Tube

The poor mean sampled-to-generated ratio of 0.58 ± 0.34 for this sampler is most likely a reflection of the leak problems and flowmeter inaccuracies during runs #2-15. While these results give little basis to judge the sampler's accuracy, they are indicative of its major faults. Since the technique employs the regeneration process, the tube is consistently subjected to high temperatures ($350^{\circ} - 400^{\circ}\text{C.}$) which eventually result in leaks around the threaded end-cap and/or O-ring seal in the Swagelok fitting. Redesign of the tube can eliminate these leaks but the inconvenience of regeneration and replenishing with new gel, as well as the dependence of calculations on flowmeter data, still make this method generally unattractive.

D. Molecular Sieve Tube

This sampler has shown a fairly good mean sampled-to-generated ratio of 0.83 and was the most consistent of all samplers tested (± 0.22 standard deviation). Here again, a leak problem may have contributed to the uniformly low response of the molecular sieve tube. While the tube itself is rugged and adequately sealed, the O-rings in the Swagelok fitting are prone to fatigue and failure due to the regeneration process.

A more reliable fitting, or periodic replacement of the O-ring can eliminate this problem. Although this sampler is more reliable and convenient than the silica gel tube, it still has the disadvantages of the regeneration process and reliance on flowmeter data for calculations.

E. Frit Bubbler

The mean sampled-to-generated ratio of 0.95 ± 0.24 shows this sampler to be both accurate and fairly consistent. The frit bubbler is simple, inexpensive, easy to use, and yields liquid samples for analysis. It can sample for up to 36 hours with satisfactory results, although it is generally used for short periods of time (1/2 to one hour). The major disadvantages of this sampling method are the diluting effect and the dependence on flowmeter data for calculation purposes.

F. Thermoelectric Cooler

This sampler's mean sampled-to-generated ratio of 1.06 ± 0.25 places it among the best tested. It is easy to operate, yields liquid samples for analysis, and the associated calculations do not depend on flowmeter data. However, the thermoelectric cooler is the costliest sampler of the group and the calculations involved are more complex than most due to the dependence on environmental parameters (temperature, pressure and relative humidity).

G. Petri Dish

This sampler had the best mean sampled-to-generated ratio of 0.99 but a rather poor standard deviation of ± 0.38 . As with the mixed silica

gel tube sampler, errors were probably due to incomplete mixing of the exposed gel and inaccurate weighing. The petri dish is the least expensive and easiest to use sampler of those tested. Calculations do not employ flowmeter data but are dependent on environmental parameters.

H. Direct Counting Technique

The reduced counting efficiency of this technique, compared to that of the standard technique, decreases overall sensitivity by a factor of 2-1/2 to 4. The resulting minimum detectable concentration was therefore about 6×10^{-6} μCi per 5 gram sample for 50 minute counts. This decreased sensitivity was considered irrelevant since the lowest sample concentrations were higher by about two orders of magnitude.

This study was not an in-depth analysis of the direct counting technique, but rather an overall comparison including two samplers which incorporated that technique. No concrete conclusions as to its accuracy are presented, other than that it is generally satisfactory. The major advantage of the direct counting technique is that it completely bypasses the time, effort and expense required by the regeneration process.

VIII. CONCLUSIONS

The generating technique, while showing a need for improved accuracy, has been demonstrated to be a fairly accurate and reliable system for testing and calibrating tritium vapor samplers.

A major problem common to all airflow-type samplers is inaccurate measurement of flowrates. Flowmeters commonly used in conjunction with these samplers are generally unreliable, need frequent recalibration, and must be corrected for pressure differentials. It is recommended that other flowrate measuring methods be investigated and employed. One approach may be the use of volumetric devices such as wet-test or dry-test meters. Another alternative may be the use of limiting orifices which restrict airflow to a specified, uniform flowrate.

The direct counting technique, employed with the mixed silica gel tube and petri dish samplers, is a satisfactory approach for direct analysis of tritium activity of moisturized silica gel.

On the average, nearly all the samplers (except the silica gel tube) demonstrated acceptable accuracy as reflected by the mean sampled-to-generated ratios which ranged from 0.83 to 1.07. However, the accompanying range of standard deviations (± 0.22 to ± 0.48) indicate a general lack of consistency and reproduceability. Improvements in flowrate measurements, weighing techniques, and other handling processes should increase the consistencies considerably. Nevertheless, the impression remains that random processes inherent in the sampling methods themselves will still result in deviations of ± 10 to 15%.

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APPENDIXES

APPENDIX A

Procedure List I

1. Record weight of molecular sieve tube.
2. Fill silica gel tube and record weight.
3. Fill mixed silica gel tube and record weight.
4. Fill primary desiccant tube with mixed silica gel and record weight.
5. Repeat step 4 for final desiccant and frit desiccant tubes.
6. Fill frit bubblers 1 and 2 about 3/4 full with distilled water.
7. Fill petri dish with mixed silica gel and record weight.
8. Record weight of thermoelectric cooler sample bottle.
9. Fill generator bubbler about 3/4 full with source solution and record weight.
10. Wind and replace charts for hygro-thermograph and microbarograph (if necessary).
11. Place hygro-thermograph, microbarograph, petri dish and thermoelectric cooler with sample bottle inside chamber.
12. Connect power line to thermoelectric cooler.
13. Grease upper seal of chamber and cover with lucite top.
14. Connect generator to chamber inlet and inlet manifold to chamber outlet.
15. Connect mixed silica gel tube to manifold port #1.
16. Connect silica gel tube to manifold port #2.
17. Connect molecular sieve tube to manifold port #3.
18. Connect frit bubblers 1 and 2 and frit desiccant tube to manifold port #4.

19. Connect primary desiccant tube between generator and flow-meter.
20. Connect final desiccant tube between outlet manifold and exhaust flowmeter.
21. Recheck all connections.

Procedure List II

1. Close inlet and outlet manifold port valves #1-4.
2. Open inlet and outlet manifold port valve #5.
3. Turn on vacuum pump.
4. Set exhaust flowmeter valve at 10 liters per minute.
5. Record generator flow rate, pressure reading and time.
6. Turn on thermoelectric cooler.
7. Start airflow to samplers
 - (a) Open inlet and outlet manifold valves simultaneously for each sampler.
 - (b) Close inlet manifold port valve #5.
 - (c) Adjust sampler flow rates.
 - (d) Readjust exhaust flow and sampler flows for proper flow rates.
8. Record all flow rates, pressure readings and times for next 1/4 to 1/2 hour.

Procedure List III

1. Record all final flow rates, pressure readings and time.
2. Disconnect generator from chamber inlet and reconnect with primary desiccant tube.

3. Open inlet manifold port valve #5.
4. Close inlet and outlet manifold port valves #1-4.
5. Turn thermoelectric cooler off.
6. Continue exhaust for time interval dependent on source solution concentration.
7. Disconnect and record weights of molecular sieve tube, silica gel tube, mixed silica gel tube, frit bubblers 1 and 2, frit desiccant tube and generator bubbler.
8. After exhaust phase, turn off pump and remove lucite chamber cover.
9. Record weights of petri dish and thermoelectric cooler sample bottle.
10. Disconnect and record weights of primary desiccant and final desiccant tubes.
11. Remove color-changed portion (plus ~ 1 cm) from mixed silica gel tube and record weight. Mix thoroughly and take 5 gram sample for analysis.
12. Repeat step 11 for frit desiccant, primary desiccant and final desiccant tubes.
13. Remove 10 cc water samples from frit bubblers 1 and 2 for analysis.
14. Remove water from thermoelectric cooler sample bottle for analysis.
15. Take molecular sieve tube and silica gel tube to Bioassay for regeneration and analyses.

APPENDIX B

Regeneration Process

Moisture adsorbed by the molecular sieve and silica gel tube samplers was retrieved by a regeneration process in the Bioassay Division at BNL. This system (Figure 12) consisted mainly of a cylindrical electric tube furnace and a water-cooled condenser. Voltage was supplied by a Variac* power supply and furnace temperature was monitored by a thermocouple-temperature indicator arrangement. Vapor was purged from the tube by a dry nitrogen gas flow of 300 cc/min., passed through the condenser, and collected as water in a vial. Voltage to the furnace was adjusted to maintain a tube temperature of 350-400°C. A typical regeneration run lasted approximately four hours.

*General Radio Company, Cambridge, Massachusetts.

Figure 12. Schematic diagram of regeneration apparatus.

APPENDIX C

Tritium Analyses

General Considerations. All samples were counted for tritium activity with a Packard* model 3214 dual-channel liquid scintillation spectrometer. Its response is arranged so that 95% of all counts occur in the red channel (low to medium energy betas), and the remaining 5% in the green channel (high energy betas). The counting compartment is continuously refrigerated to maintain a temperature of 4°C. Average background levels are on the order of four to five counts per minute. The standard scintillation solution consisted of the following components: 4 grams ppo (2,5-Diphenyloxazole); 0.045 grams dimethyl-popop (1,4-bis-2 [4-Methyl-5-phenyloxazoly]-benzene); 120 grams naphthalene; p-dioxane in sufficient amount to total one liter of solution.

Standard Counting Procedure. The normal procedure for counting liquid samples involved placing 1 cc of sample together with 15 cc of scintillation solution in a 25 cc polyethelene vial. Counting times of 50 and 100 minutes were used depending on sensitivity desired and/or machine availability. Minimum detectable concentrations (based on 90% confidence limit) were as follows: $\sim 8.45 \times 10^{-7}$ $\mu\text{Ci/cc}$ for 100 minute counts; $\sim 1.2 \times 10^{-6}$ $\mu\text{Ci/cc}$ for 50 minute counts. Two standards and two blanks were prepared and counted with each set of samples. Counting efficiency was generally about 25%.

*Packard Instrument Co., Inc., 2200 Warrenville Road, Downers Grove, Illinois 60515.

Direct Counting Technique. The technique for direct counting of exposed mixed silica gel samples was the same as that developed by Osloond, et al.⁹. This involved preparing an aliquot consisting of 5 grams of exposed gel, 2 cc of distilled water and 18 cc of scintillation solution. Two standards consisting of 2 cc tritiated water on 5 grams of dry gel plus 18 cc scintillation solution, and two blanks consisting of 2 cc distilled water on 5 grams of dry gel plus 18 cc of scintillation solution, were counted with each set of samples. Counting efficiencies ranged from 6.55% to 9.96%, and the background ranged from 4 to 38 counts per minute.

APPENDIX D CALCULATIONS

General

The standard deviations (σ) were calculated using the relation:

$$\sigma = \sqrt{\frac{N(\sum X_i^2) - (\sum X_i)^2}{N(N-1)}}$$

where X_i = experimental determination

N = number of determinations

The average temperature, pressure and relative humidity were determined by graphical analysis of the recording chart data from the hygro-thermograph and the microbarograph (Table VIII). Values for the humidity ratio (H), in Table IX, were determined graphically from a psychometric chart. The density of air (D) varied only slightly over the range of atmospheric parameters and was taken at 1.15×10^{-3} grams dry air/cc_{air}.

Samplers

The calculations used to determine sampled tritium vapor air concentrations consisted of two distinct groups. The first group involved samplers which yielded liquid samples, and the second group involved samplers which yielded exposed mixed silica gel samples.

Group #1. The measured air concentrations were determined using the following relations:

a) Molecular Sieve and Silica Gel Tube Samplers

$$C = \frac{WS}{V}$$

where W = volume (cc) of regenerated sample

TABLE VIII
Average Environmental Chamber Parameters

Run	Temperature		Relative Humidity %	Absolute Pressure	
	°F.	°C.		inches Hg	mm Hg
2	86	30	35	29.74	755
3	88	31	37	29.66	753
4	86	30	40	29.32	745
5	86	30	40	29.32	745
6a	73	23	64	29.32	745
6b	73	23	64	29.32	745
7	79	26	40	28.82	732
8	79	26	39	29.26	743
9	81	27	41	29.70	754
10	82	28	41	29.30	744
11	84	29	38	29.28	744
12	84	29	40	29.14	740
13	83	28	38	29.46	748
14	87	30.5	42	29.10	739
15	93	34	44	29.20	742
17	90	32	48	29.32	745
18	90	32	44	29.18	741
19	92	33.5	46	29.46	748
23	91	33	40	29.34	745
24	91	33	42	29.28	744
25	90	32	43	29.38	746
26	90	32	43	29.56	750

TABLE IX
Psychometric Chart Data

Run	Humidity Ratio (H) grams H ₂ O/grams dry air
2	9.2×10^{-3}
3	10.4×10^{-3}
4	10.7×10^{-3}
5	10.7×10^{-3}
6a	11.4×10^{-3}
6b	11.4×10^{-3}
7	8.4×10^{-3}
8	8.2×10^{-3}
9	9.2×10^{-3}
10	9.8×10^{-3}
11	9.4×10^{-3}
12	10.0×10^{-3}
13	9.0×10^{-3}
14	10.6×10^{-3}
15	14.4×10^{-3}
17	14.4×10^{-3}
18	13.0×10^{-3}
19	14.8×10^{-3}
23	12.5×10^{-3}
24	13.0×10^{-3}
25	12.8×10^{-3}
26	12.8×10^{-3}

S = specific activity ($\mu\text{Ci/cc H}_2\text{O}$) of sample determined by liquid scintillation counting

V = total volume of air (cc) sampled

and

$$V = Ft$$

where F = average flowrate (cc/minute)

t = total sampling time (minutes)

b) Series-Connected Frit Bubblers

$$C = \frac{WS}{V}$$

where W = volume of water remaining in bubbler after sampling

S = specific activity of bubbler water

V = total volume of air sampled

The approximate relative collection efficiency of frit bubbler #1 was determined by:

$$\text{efficiency} = \frac{C_1}{C_1 + C_2} \times 100\%$$

where C_1 = air concentration sampled by frit #1

C_2 = air concentration sampled by frit #2

c) Thermoelectric Cooler

$$C = SHD$$

where S = specific activity of water collected during sampling

H = humidity ratio $\left(\frac{\text{grams H}_2\text{O}}{\text{grams dry air}} \right)$

D = density of air $\left(\frac{\text{grams dry air}}{\text{cc}_{\text{air}}} \right)$

Group #2. The measured air concentrations were determined using the following relations:

a) Mixed Silica Gel, Primary Desiccant, Frit Desiccant and Final Desiccant Tubes

$$C = \frac{WS_0}{5V}$$

where W = total weight (g) of exposed gel

S_0 = specific activity of gel ($\mu\text{Ci}/5 \text{ g gel}$) determined by direct counting technique

V = total volume of air sampled

b) Petri Dish

$$C = SHD$$

where S = specific activity sampled ($\mu\text{Ci}/\text{cc}_{\text{H}_2\text{O}}$)

H = humidity ratio

D = density of air

and

$$S = \frac{WS_0}{5M}$$

where W = total weight of exposed gel

M = gain in weight during sampling

S_0 = specific activity of gel ($\mu\text{Ci}/5 \text{ g gel}$) determined by direct counting technique

Generator

The generated tritium vapor air concentrations were calculated using the following relation:

$$C_g = \frac{[(\Delta W)(S) - (A_1 + A_2)]}{V}$$

where ΔW = volume of source solution vaporized during generation (initial volume - final volume)

S = specific activity of source solution

A_1 = total activity collected by thermoelectric cooler

A_2 = total activity collected by petri dish

V = total volume of air passed through system during generation

APPENDIX E GLOVE BOX MODIFICATIONS

The outer surface of the glove box (excepting top and access ports) was treated with a double coating of black Glyptol* electrical sealant. The right hand port and the access ports on sides and rear were sealed with Apiezon** sealing compound and/or stopcock grease. The outlet port was fashioned by mating a large polyethelene funnel to the left hand port. A clear lucite cover, 25-1/4 inches wide by 37-1/4 inches long by 1/2 inch thick (64.14 cm by 94.62 cm by 1.27 cm) was used in place of the original top. A strip of 3/8 inch (0.95 cm) outside diameter gum-rubber tubing was glued to the upper edge of the box to provide a seal for the cover. Lead bricks were placed on the cover to assure contact with the seal. The structure was reinforced by inserting three aluminum rod supports inside.

* General Electric Company, Schenectady, New York.

** Apiezon Products Ltd., 8 York Road, London S.E. 1, England.

VITA

The author was born on March 5, 1940 in St. Albans, New York. He graduated from Hempstead High School, New York, in 1957 and was employed in various occupations before continuing his education in 1963. At that time he enrolled at Nassau Community College, Garden City, New York, and later received his Bachelor of Arts degree in Physics in 1968 from the University of South Florida, Tampa. The author attended graduate school at the University of Tennessee, Knoxville, from 1971 to 1973 as an Oak Ridge Fellow in Radiation Science and Protection.

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