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THE USE OF WATER AS A SAMPLING
MEDIUM FOR TRITIUM OXIDE

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I. INTRODUCTION

The radiation protection program at a heavy water reactor such as the Plutonium Recycle Test Reactor (PRTR) is complicated by the presence of tritium, primarily in the form of tritium oxide. Neutron activation of the deuterium in reactor systems produces tritium which escapes to the working environment through system leaks and accidental heavy water spills. The human body readily assimilates tritium in the oxide form from the environment by inhalation and direct absorption through the intact skin.

The presence of tritium in the air and on exposed surfaces is difficult to detect with ordinary sampling techniques and monitoring instrumentation because of the low energy of the beta particle emitted during the disintegration of the tritium atom (0.018 Mev, maximum energy). This paper describes rapid, reliable, and simple methods of sampling for airborne and surface tritium contamination with a high collection efficiency.

II. SUMMARY

A sampling technique for airborne tritium oxide was developed and tested. Under the experimental conditions considered, the efficiency of this method averaged 98%. The technique employs a gas wash bottle filled with ordinary distilled water through which air is bubbled at a constant flow rate. The method is rapid, reliable, and sensitive and has been proven under a variety of field conditions. The minimum detectable tritium oxide air concentration that can reliably be measured is 1×10^{-7} $\mu\text{Ci/cc}$. Additionally, a technique is described for determining the amount of tritium oxide surface contamination. Because of difficulties in measuring the collection efficiency of the technique, it is presently used for qualitative measurements as a trend indicator only.

III. SAMPLING AND MONITORING TECHNIQUES FOR TRITIUM

Among the methods employed to monitor for airborne tritium is an ion chamber device through which air is continuously drawn after passing through an ion trap. The chamber may be gamma-ray compensated if it is used in a high gamma-ray background area, or the sample may be drawn from the work area to a low background location where the instrument is situated. This method does not provide any discrimination against interfering airborne radio-activity such as that emitted by noble gases produced during reactor operation and serious errors in estimates of the air contamination status may result.

An alternative method for tritium monitoring is to sample the moisture contained in the working atmosphere. A popular medium for moisture collection is a silica gel trap which collects water by adsorption and has a low efficiency for interfering gases. The water is driven off the silica gel by heating, collected, and analyzed for tritium content by liquid scintillation counting or internal gas counting. Certain problems exist with the silica gel sampling technique for tritium. The procedure is cumbersome and time consuming, requiring additional equipment such as a furnace and water condenser. The collection efficiency of silica gel for water varies with use both in successive sampling periods and during a single sampling period. Finally, all the water collected during a sampling period is not distilled out of the silica gel which leads to dilutions or concentrations of subsequent samples.

Another method sometimes used to sample air for tritium oxide employs a freeze trap apparatus. Moisture is frozen out of the air which is drawn through a chamber cooled by dry ice or liquid nitrogen. The sample is then

analyzed for tritium content by liquid scintillation or internal gas counting. This method requires a long sampling time to obtain a sample of adequate volume, particularly in atmospheres of low relative humidity. In addition, the method does not have a very high collection efficiency because ice crystals formed in the chamber may behave as small particles and pass right on through the chamber.

Because of the above problems with each of the monitoring or sampling methods for tritium, a different technique was developed in which air is bubbled through distilled water. The water is then analyzed for tritium by liquid scintillation counting and the quantity related to airborne tritium concentration. A series of tests were devised to investigate the collection efficiency of the method under various environmental conditions.

IV. AIR SAMPLING - TEST PROCEDURE

A series of experiments was devised to test the effectiveness of the sampling technique for tritium oxide collection. The collection efficiency of the technique was measured for various combinations of sampling time, tritium concentration, and relative humidity. The experimental arrangement is shown in Figure 1. Dried room air was drawn through a gas wash bottle containing approximately 100 mls. of dilute tritium oxide of known concentration. The air carried moisture from the solution in the gas wash bottle to the sampler. Provisions were included to route the air through another gas wash bottle while samples were being changed. The air was exhausted through silica gel to remove most of the water leaving the experimental set-up. Air flow rate as measured with a rotameter was maintained at 3 liters per minute. The relative humidity of the resulting atmospheres was approximately 80%. In order to measure collection efficiency at lower

relative humidities, the apparatus was changed slightly as shown in Figure 2 by the inclusion of a silica gel column. The line was branched downstream of the gas wash bottle containing the tritium solution to permit measurements of the wet and dry bulb temperatures. Calculations of the moisture weight per unit volume of air and relative humidity of the air passing through the sampler were made based on wet and dry bulb temperatures. Temperature measurements were made with a 0-50° C precision thermometer. It was assumed that the moisture in the air entering the sampler had the same tritium concentration as that in the spike solution. Measurements of the tritium concentrations in the water solutions were done by liquid scintillation counting. A total of 9 trials were completed, each trial lasting approximately 3 hours.

All gas wash bottles and silica gel columns were weighed before and after a trial run to measure the water balance of the system. In addition, the amount of tritium lost from the spike solution was measured and compared to the total amount of tritium collected. Results of the water balance and tritium recovery measurements are given in Table 1.

V. TEST RESULTS

The results of the efficiency measurements are given in Table 2. Sampling time had little effect on the collection efficiency of the system. As sampling time increased, the measured efficiency decreased slightly due to water losses from the sampler, which amounted to 0.1 ml during a 5 minute sampling period or less than 1% for a sample collected for 30 minutes. There was no evidence that the collection efficiency depended upon the relative humidity nor on tritium concentration in the range 7×10^{-7} to 1×10^{-3} $\mu\text{Ci/cc}$. From the data in Table 2, a five minute sampling time is

TABLE 1

Water Balance and Tritium Recovery
of the Experimental Arrangement

Run Number	Water Balance - gms		Tritium Recovery		
	Total Weight before Run	Total Weight after Run	$\mu\text{Ci H-3}$ Lost from Spike	$\mu\text{Ci H-3}$ Gained in Equipment	Percent Recovery
1	Not Determined		5.9	5.0	86
2	3041.5	3040.0	9.9	9.0	91
3	3054.1	3057.9	44.2	40.7	92
4	3054.2	3054.0	89.8	84.0	94
5	3049.7	3050.4	0.41	0.44	107
6	3041.7	3039.5	377	342	91
7	3033.7	3030.9	936	863	92
8	3415.6	3415.9	18.4	16.8	92
9	3380.9	3380.8	51.0	44.6	87

TABLE 2

Percent Collection Efficiency of the Bubbler
Technique in Sampling for Airborne Tritium Oxide

Calculated Tritium Air Concentrations $\mu\text{Ci/cc}$	Relative Humidity	Sampling Times			
		5 Minutes	10 Minutes	20 Minutes	30 Minutes
7×10^{-7}	78	106	92	95	96
7×10^{-6}	81	94	94	91	94
1×10^{-5}	77	96	91	91	96
6×10^{-5}	79	96	100	95	96
1×10^{-4}	80	96	94	93	96
7×10^{-4}	76	100	96	97	92
1×10^{-3}	73	98	96	91	100
3×10^{-5}	42	100	99	-	-
7×10^{-5}	29	95	97	-	-

adequate to achieve an average collection efficiency of 98% in the range of air concentrations studied.

VI. DISCUSSION AND FIELD EXPERIENCE

The largest error in the test procedure involved measurement of the temperature. The thermometers used had an indicated precision of $\pm 10\%$. Calculations of the water volume per unit weight of dry air were completed rather than determinations of the water volume per unit weight of moist air. This error is estimated to be less than 1%.⁽¹⁾ The maximum error in the collection efficiency measurements is estimated to be 10%.

The minimum tritium concentration in a water solution detectable by liquid scintillation counting is $1.3 \times 10^{-5} \mu\text{Ci/cc.}$ ^{*(2)} For a five-minute sampling period, this yields a tritium air concentration of $\sim 1 \times 10^{-7} \mu\text{Ci/cc.}$ The normal levels encountered at the PRTR range from 10^{-7} to $10^{-5} \mu\text{Ci/cc.}$

The bubbler sampler developed for field use is shown in Figure 3. The vacuum source is a small diaphragm pump which draws an air sample through 100 mls. of distilled water at the rate of 3 liters/minute. The gas wash bottle has a 125 ml. capacity. The system has been used routinely at the PRTR under a variety of operating and outage conditions. The main virtue of the system is the simplicity and ease with which a sample may be collected. Experience has shown that results of a sample analysis can be available in as little as 30 minutes after the sample is collected. The typical air concentrations measured with this system through an operation-outage cycle at the PRTR are shown in Figure 4. A plot of the particulate beta-gamma airborne radioactivity collected at a location near the tritium

*For a sample volume of 1 ml. and a 30 minute counting period, the accuracy is $\pm 25\%$ and the counting precision is $\pm 20\%$ at the 95% confidence level.

sampling station is given for comparison. Airborne tritium contamination levels remain relatively constant during operation, then increase at the beginning of an outage and gradually decrease to pre-operational levels. The average tritium air contamination level during operation has been 3×10^{-6} $\mu\text{Ci/cc}$, while during shutdowns it increases to an average value of 1×10^{-5} $\mu\text{Ci/cc}$. The airborne beta-gamma contamination (composed primarily of fission gases and their daughter products⁽³⁾) is somewhat higher during operation but falls off rapidly at the start of an outage. The highest airborne tritium levels normally occur in the vicinity of an irradiated heavy water spill. The maximum concentration measured to date in this situation is 3×10^{-3} $\mu\text{Ci/cc}$.

VII. SURFACE CONTAMINATION SAMPLING

A different technique for determining semi-quantitatively the amount of smearable tritium surface contamination was also developed. The technique involves taking a wet smear of a known surface area with a dampened 2" x 2" gauze pad, adding a known amount of distilled water to the gauze pad in a container, and allowing equilibration of the tritium in the pad and the water to take place over a pre-determined period of time. The distilled water is then drawn off and analyzed for tritium content by liquid scintillation counting.

Studies were completed to define the parameters involved in the smear technique. The first study was designed to determine the quantity of tritium that would be recovered in the added distilled water. Four gauze pads were moistened with 0.5 ml. of solutions containing known amounts of tritium. Approximately 80% of the tritium added to the gauze pads was detected in the distilled water in this and subsequent studies. The results of the test are given in Table 3.

TABLE 3

Percent Recovery Measured for the
Wet Pad Tritium Smear Technique

Equilibration Solution - 10 ml.
Equilibration Time - 10 min.

<u>Spike Concentration μCi/cc</u>	<u>Tritium Added to Pad - μCi</u>	<u>Tritium Detected in Equilibration Solution - μCi</u>	<u>Percent Recovery</u>
307	154	126	82
64	32	26	81
17	9	6	67
1.5	0.8	0.9	110

Another study was designed to determine the variation in results with various quantities of distilled water equilibration solutions. The results are given in Table 4. The data does not indicate any appreciable variation in results with the various amounts of equilibration solution used. However, there is not sufficient data to indicate this with certainty.

TABLE 4

Variation of Percent Recovery with
Different Amounts of Equilibration Solution

Equilibration Time - 10 minutes
Spike - 0.5 ml. of 64 μCi/cc tritium solution

<u>Equilibration Solution - ml.</u>	<u>Tritium Detected in Equilibration Solution - μCi</u>	<u>Percent Recovery</u>
5	19	60
10	19	60
20	28	88
30	21	66

A final study was done to estimate the time necessary for equilibrium. The results given in Table 5 indicate that the equilibration time is short and that 10 minutes is adequate for equilibrium to be established.

TABLE 5

Variation of Percent Recovery
with Different Equilibration Times

Equilibration Solution - 10 ml.

Spike - 0.5 ml. of 64 $\mu\text{Ci/cc}$ tritium solution

<u>Equilibration Time - Min.</u>	<u>Tritium Detected in Equilibration Solution - μCi</u>	<u>Percent Recovery</u>
5	21	66
10	22	69
20	21	66
30	24	75

Because of difficulties in preparing a surface with a known quantity of tritium oxide contamination and because the collection efficiency depends on the characteristics of the surface being smeared, collection efficiency measurements were not completed. The technique has some value qualitatively as a trend indicator. The sampling technique presently used involves a smear of a 4 sq. ft. area, an equilibration solution of 10 ml. of distilled water, and an equilibration time of 10 minutes. It is estimated that the minimum smearable tritium surface contamination detectable by this method is $5 \times 10^{-5} \mu\text{Ci/sq. ft.}$ for a 4 sq. ft. area. Normal smearable tritium oxide surface contamination at the PRTR has been approximately $0.03 \mu\text{Ci/sq. ft.}$

REFERENCES

1. Unpublished work of R. J. Engelman.
2. Unpublished work of L. S. Kellogg.
3. D. McConnon, A Review of the Air Monitoring Program at the PRTR, HW-82705, May 15, 1964.

FIGURE 1

Experimental Arrangement for Determining Tritium Oxide Collection Efficiency

FIGURE 2

Modifications of Experimental Arrangement for Determining Tritium Oxide Collection Efficiency

FIGURE 3

Tritium Oxide Air Sampler

FIGURE 4

Typical Air Contamination Levels at the PRTR