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HEALTH MONITORING OF SAMPLES FOR P-10 OXIDE

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HEALTH MONITORING OF SAMPLES FOR P-10 OXIDE

by

R. C. Thorburn
Development Division
Health Instrument Divisions

March 20, 1950

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HEALTH MONITORING OF SAMPLES FOR P-10 OXIDE

The installation of a tritium separation plant at Hanford posed numerous health monitoring problems which were somewhat foreign to past experience. Although work had been carried out with soft beta emitters such as C-14, S-35, etc., this was the first serious contact with beta rays on the order of 5-15 kev. The problem of monitoring water waste samples to be disposed of in cribs with possible transfer to the Columbia River was given to the Methods Group of the Development Division.

The chief difficulty at the start appeared to be monitoring for tritium oxide since dissolved tritium could be measured by boiling the water and collecting the evolved gases in an ion chamber or proportional counter. The presence of tritium oxide was not thought to be very probable at the time production was started but operation of the unit and subsequent personnel monitoring indicated the presence of radiological significant amounts of the oxide.

A simple, relatively rapid, procedure for the measurement of tritium oxide in waste samples has been developed and applied to biological measurements and with modifications to the determination of tritium.

I. Summary

An ion chamber of one or two liters volume is used to contain a gaseous sample produced from the suspected water. The ion current from the beta particles produced inside of the chamber is amplified by a Vibrating Reed electrometer.

Initial attempts to use hydrogen, liberated by electrolysis of the water, resulted in gross contamination of the chamber. Acceptable yields were obtained by measuring the activity in acetylene generated from the water by calcium carbide. No contamination resulted unless some molecular tritium was present.

The minimum amount detectable is about one uc/liter of liquid sample; a value 20 times below the estimated concentration in the body for the presently accepted tolerance value. One operator with one instrument can analyze about five to seven

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samples per day. Adaptations of the technique to measurement of air samples and to tritium determinations are noted.

II. Instrumentation

The ionization chambers used for all measurements were constructed from one or two liter round bottom boiling flasks with a ground glass joint. A three way stopcock was sealed to the neck for evacuation and filling. A sketch of this assembly showing the insulation, electrodes and method of mounting is given in Figure 1. A 90 volt potential is placed across the chamber while in operation. Tests with various voltages indicated that a constant ionization current was obtained above 67.5 volts.[1]

The ionization current was measured with a Vibrating Reed electrometer[2] by the rate of drift method wherein the time required to collect a given charge is noted. This rate is obtained by measuring the slope of the output line on an Esterline-Angus record (with the collecting electrode not grounded). The scale is chosen so that a full-scale deflection requires 20-30 minutes allowing the operator to prepare the next sample while the first is still being measured.

With a two liter chamber, backgrounds usually range on the order of 2-5 x 10^{-15} amperes (in a Counting Room with concrete walls one foot thick). For all of the work reported, the instrument was operated with regulated voltage in an air-conditioned room with the temperature controlled between 72 and 76°F, and the relative humidity at 50%.

Original calibrations of the equipment were calculated and these calculated values are used throughout this report. The calculations involved are given below:

Assumptions:

(1) Energy required to produce one ion pair in air is 32.5 ev.[3]

(2) Average energy of the beta particles is 5.69 kev.[4]

$$\frac{5.69 \times 10^{3}}{32.5 \text{ i.p./dis.}} \cdot \frac{3.7 \times 10^{4}}{\text{i.p./sec/uc}} \cdot 6.28 \times 10^{18} = 1.03 \times 10^{-12} \text{ amperes/uc}$$

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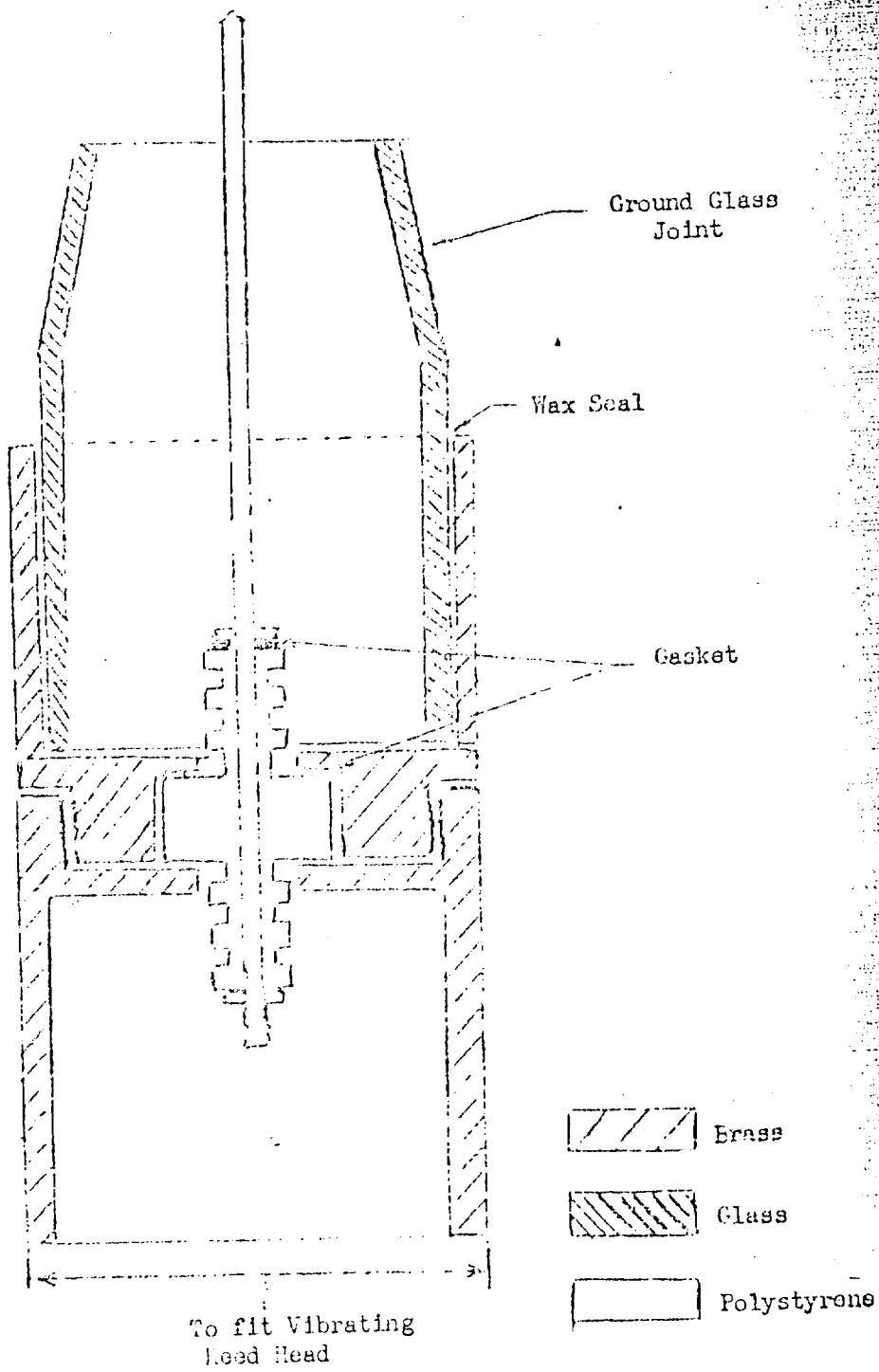

Figure 1

INSULATOR SYSTEM FOR GLASS CHAMBER

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In this calculation, the wall effect is ignored and the ionization is assumed to occur in air. If the maximum range of the beta particle is accepted as 4.12 mm[5], the wall effect will be less than 10% and has been ignored in the final result. A comparison between the energies required to produce one ion pair in air and in acetylene was made by reading the ionization current from a 104 d/m Pu-239 source mounted in the center of the chamber in an atmosphere of air and acetylene. The results of this comparison are given in Table 1.

TABLE 1
COMPARISON OF AIR AND ACETYLENE

Source Value	Observed Current		Theoretical Current
	Air	Acetylene	
d/m	amperes	amperes	amperes
103.8±3.0	$(1.4\pm0.1) \times 10^{-14}$	$(1.4\pm0.1) \times 10^{-14}$	2.1×10^{-14}

These results indicate little difference between air and acetylene in the current produced for a given amount of ionization. The 35% discrepancy between the calculated value and the measured value is probably due to inaccurate calibration of the the electrometer and unknown electrical capacity of the chamber.

A sample of active water was received from Dr. A. M. Brues of the Argonne National Laboratory as this report was about ready for issue. The label on the bottle indicated a tritium oxide content of one mc per ml. Dilutions were made to activities of 5 uc/l, 20 uc/l, 50 uc/l, and 100 uc/l and the samples analyzed by the acetylene technique. Three to five analyses were made on each solution and a summary of the results is given in Table II.

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TABLE II

ANALYSIS OF STANDARD SAMPLE

Nominal Concentration	No. Samples	Measured Concentration	Yield	Standard Deviation of Yield
uc/l		uc/l	%	%
5	3	3.4	68	10
20	5	11.4	56.9	3.2
50	4	30.3	60.5	6.1
100	5	49.8	49.8	5.5

The overall average of the 17 samples is 57.6% with a standard deviation of 8.8%. These values agree reasonably well with estimates made by measurement of the plutonium source. Further measurements are planned to eliminate pipetting errors, etc.

III. Development of Method

Tracer amounts of tritium oxide were obtained from a pellet of lithium fluoride which was submitted to this laboratory for an analysis for other activities. Oxygen, saturated with water vapor, was passed over the pellet at 700°C in the presence of a platinum catalyst and the resulting tritium oxide and water vapor collected in a trap cooled with dry ice.

Liberation of hydrogen by electrolysis and by decomposition on hot metals were utilized to obtain gas for ionization measurements. Electrolytic experiments were run in a two ml. capacity, H.-shaped electrolytic cell using platinum electrodes and a 6v storage battery. The hydrogen evolved was collected in a three liter erlenmeyer flask by water displacement. The pressure on both sides of the cell was kept constant by controlling the water displacement with a siphon. After a suitable amount of gas had been collected, the entrance tube was connected to the evacuated ionization chamber and the hydrogen forced into the chamber by water displacement. The pressure in the chamber was adjusted to 760 mm by means of a balancing column of water.

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After an active sample had been placed in the chamber, subsequent background readings gave high values even after repated evacuations and sweeping with other gases. The lining of the chamber had to be removed and a new coating of graphite applied before acceptable backgrounds could be obtained. Results of a typical run are given in Table III.

TABLE III

RESULTS OF H_2^3 MONITORING SHOWING BACKGROUND DIFFICULTY

Sample	Reading Amperes	Remarks
Initial Background	2.55×10^{-15}	Reading in air
Test Sample	100×10^{-13}	
Background	100×10^{-13}	Chamber evacuated and filled with air
Background	88×10^{-13}	Chamber evacuated and filled three times; then evacuated overnight.
Background	88×10^{-13}	Chamber disassembled and blown with H_2 in attempt to displace H_2^3
Background	2.61×10^{-15}	Chamber lining replaced.

Decomposition of water to hydrogen with a metallic oxide was accomplished by boiling the sample, passing the evolved steam over hot steel wool and collecting the hydrogen by water displacement. As would be expected background difficulties were again encountered. Both of these methods involving tritium gas were slow and not well suited to rapid work.

The method finally adopted consisted of evolving acetylene from the liquid sample with calcium carbide and noting the ionization produced. The equipment consists of a gas generator, partially filled with calcium carbide into which the sample could be forced. The generator is connected through a condenser and a glass wool filter to a large water filled flask. As the gas is evolved, the water in the flask is displaced. The condenser returns the vapor produced in the sample

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from the heat of reaction. If the presence of active dissolved gases such as $C^{14}O_2$ are suspected, the sample may be distilled or the acetylene scrubbed with appropriate solvents. The acetylene which was collected, is forced into an evacuated chamber by water displacement and the pressure adjusted to 760 mm Hg.

Reproducible results have been obtained. The chamber is easily cleaned, even with extremely hot samples, unless some dissolved tritium is present in the sample. Occasionally several evacuations of the chamber are needed if an especially active sample is measured.

One possible fault in the procedure was the assumption that the tritium reacted in the same manner as the hydrogen in the reaction.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

If this assumption is incorrect, it is possible that the acetylene could be depleted or enriched in tritium compared to the hydrogen-tritium ratio in the water. To answer this question, acetylene was generated from tritium oxide laden water and the ionization current noted. The calcium hydroxide residue from this process was heated to 600°C, and the water evolved was collected and used to produce acetylene. Three cycles were run on this process with no enrichment or depletion indicating that the reactivity of the two molecules in the reaction was the same. The data from these runs are given in Table IV.

TABLE-IV

TEST OF PARTITION OF HYDROGEN AND TRITIUM

Cycle	Calculated Concentration	
	Run 1	Run 2
	uc/liter	uc/liter
1st acetylene	62.5	44
2nd acetylene	69.9	44
3rd acetylene	69.9	40

No attempt is made to measure the volume of liquid sample placed in the genera-

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culated. In the reaction of calcium carbide and water, one mole of calcium carbide reacts with two moles of water to produce one mole of calcium hydroxide and one mole of acetylene. Although two moles of water are required, one mole is used in producing calcium hydroxide. Thus the one mole of acetylene represents one mole of water. To produce one liter of acetylene (1/22.4 = 0.0446 moles) then requires 0.0892 moles of water or 1.6 grams, and the acetylene produced represents the hydrogen in 0.8 grams.

IV. Application of Method.

This method has been used for running various types of monitoring samples obtained from the tritium area. Originally, backgrounds were measured before and after each sample in order to evaluate accurately any changes resulting from induced charges on the system or residual contamination of the walls. Any sample significantly higher than the background was rerun with new equipment to eliminate the possibility of the high result being due to induced charges. The current procedure is to evaluate the background by taking two or three measurements per day and comparing the sample to the average of all backgrounds over the preceding seven days. If one background is high, the chamber is not used until the difficulty is found and remedied.

A number of different types of samples have been analyzed. Air samples are collected by passing the air over or through calcium chloride. The samples are then flushed with nitrogen to remove entrained hydrogen, heated to 400°C and the evolved gases swept with nitrogen over palladium black to remove traces of hydrogen. These gases are then passed through calcium carbide and collected in the chamber for measurement. Stopcock grease and pump oil samples were analyzed for total tritium by burning them in a stream of air saturated with water vapor. The gases were passed over calcium carbide and then into the chamber. Other samples such as pieces of glass, cloth, etc. were analyzed by obvious modifications. Results of some of these samples are given in Table V.

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TABLE V
TRITIUM MONITORING SAMPLES

Date	Types Sample	Result
5-11-49	Air samples on $CaCl_2$ - Exhaust hood	$H_2{}^3O$ present
5-26-49	Tip of sample receiver	75 uc H^3
6-2-49	Oil from #1 line hood #1 hyvac	2.8 uc H^3/ml
6-16-49	$CaCl_2$ solution from exhaust hood	7.1 uc H^3/liter
7-1-49	4 Air samples on $CaCl_2$ - exhaust hood	$< 1 \times 10^{-2}$ uc/sample
7-13-49	Gas sample from slug cutting	125 uc H^3/sample

A sample of condensed water and mercury was removed from the liquid nitrogen trap on the process line to test for the presence of tritium oxide. A five ml. sample of the water was diluted to 30 ml., saturated with sodium chloride and distilled twice under vacuum to remove any entrained gas. After a dilution of 200 to one the sample was too active to read on the equipment then available. This indicates that the activity was greater than 50 millicuries in the ten ml. sample.

Application of the method to biological samples was first made following an implosion in the area. Personnel working in the region submitted urine samples which gave, in one case, an ionization current significantly above background. Samples were taken from other employees at P-10 and three Health Instrument Divisions' men not in the area. Four of the six men from P-10 gave values significantly higher than the background samples. Weekly samples were instituted to serve as a check on the personnel. Shortly after the weekly samples were started, the operation was stopped to allow changes in the process. The weekly samples were continued on all personnel with high values in an attempt to measure the excretion rate. The results of this test are given in Table VI.

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TABLE VI
TRITIUM EXCRETION

Date	Tritium Oxide Urine Conc.		
	Man #1 uc/l	Man #2 uc/l	Man #3 uc/l
5-4-49	5.5	-	-
5-9-49	5.5	-	-
5-13-49	5.4	2.2	1.2
5-23-49	7.0	3.3	1.5
5-27-49	Shutdown Date		-
5-31-49	6.5	4.0	-
6-6-49	-	3.7	-
6-7-49	2.0	-	-
6-14-49	-	-	4
6-23-49	-	-	3
6-27-49	1	-	-
7-7-49	1	1	-

Apparently the elimination is considerably faster than that expected theoretically from a 70 kg man excreting 2-3 liters/day since the concentration dropped with a half-life of 4-5 days. It should be noted that these results were obtained in May and June of 1949. The maximum temperature for the period June 4th to June 7th was 102°F with maximum temperatures above 90°F on the other days.

One blood sample was obtained from a man with a high urine result. This sample had the same value as the urine within the error of the measurement which would be expected if the tritium oxide is uniform in the body water. The organic residue from a dried sample of this blood was washed and redried five times, burned in oxygen, and the vapors passed over calcium carbide into the ionization chamber in an attempt to determine whether any exchange occurred between tritium oxide and C:H, N:H, etc. The sample contained no detectable activity.

V. Discussion

The sensitivity of this method is limited by the background current obtained with no tritium present and the variations in this current due to insulator leakage, strains, induced charges, etc. When frequent background measurements are made,

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such as in the original method of reading, the statistical limit of dection on a 90% confidence level is about 0.7-0.8 uc/liter on the basis of the calculated calibration. With less frequent backgrounds (current procedure) the sensitivity is about 1.2 uc/liter on the same basis. The tolerable amount of tritium oxide in the body is quoted at 1.0 mc.(4) Assuming a standard man of 70 kg with a body water content of 50 kg, the mean value would be 20 uc/liter. Again assuming that the urine is representative of the body water, the sensitivity limit is about 1/20th of tolerance.

The source of the tritium oxide in the process has not been determined. Several possibilities exist: (1) Diffusion of tritium through the hot furnace walls followed by combination with oxygen at the surface; (2) the lines are filled with air between runs, the residual air after evacuation is sufficient to produce a radiological significant amount of oxide. The second possibility is supported by the analysis of the water sample collected from the process lines.

A number of additional possibilities for the use of this monitoring method exist. Quantitative measurement of the tritium oxide in air samples is proposed by the use of a dessicant or refrigerated trap to collect the sample. Tritium may be measured by collection on palladium black followed by combustion and conversion to acetylene. A semi-continuous monitor has been proposed which would collect the tritium oxide on calcium chloride and the tritium on palladium black in alternate periods. The evolution of the gases, conversion to acetylene, and reading in a chamber would follow automatically.

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REFERENCES

1. Healy, J. W., "Urine Analysis for P-10 Oxide", HW-13949, (Letter to Dr. J. Schubert); July 27, 1949. (Secret)

2. Palensky, H., Swank, R., Grenchik, R., M-CP-2141. (1944) (Restricted)

3. Gray, L. H., Br. Jour. Rad. XXII 264, 677-697 (December, 1949).

4. Jenks, G. H., et. al. Phys. Rev. 75, 701 (1949)

5. Eyatt, W. J., et. al. Phys. Rev. 74, 699 (1948)

6. Parker, H. M., Vertal Communication on the Chalk River Conference.

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