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A LOW COST MEASUREMENT TECHNIQUE (DETECTION AND CONCENTRATION) OF TRITIUM IN WATER

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A DISSERTATION

SUMMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

. . .

BY

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A LOW COST MEASUREMENT TECHNIQUE (DETECTION AND CONCENTRATION) OF TRITIUM IN WATER

APPROVED BY ι DISSERTATION COMMITTEE

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## A LOW COST MEASUREMENT TECHNIQUE (DETECTION AND CONCENTRATION) OF TRITIUM IN WATER

#### CHAPTER I

#### INTRODUCTION

The potentialities of tritium, the radioactive isotope of hydrogen, as a water tracer were recognized at an early stage by workers in the low energy radiation field. It seems clear that tagging the water molecule itself is superior to introducing foreign chemicals as tracers in tracing water bodies.

Tritium measured in experiments may be divided into three catagories; i.e., "natural" tritium produced by cosmic ray interactions in the atmosphere, tritium produced by thermonuclear weapons tests, and "synthetic" tritium produced during the operation of nuclear reactors. Some areas where tracing water with tritium have been successfully employed are surface waters, ground waters, ocean water, and atmospheric water vapor. Both natural and bomb tritium have been widely used, but little use has been made of synthetic tritium as a water tag. A good discussion of tritium detection methods has been prepared by Feely, et. al. [1]. The literature survey through 1965 conducted for this research shows little recent change or improvement in detection systems or methods.

Perhaps the primary reason for the failure to use synthetic tri-

tium to any great extent is the present expensive analysis of tritium samples and the relatively lengthy and complicated procedures involved. This research was initiated in the hope of improving this situation by designing an inexpensive and simple process for tritium detection and analysis in water systems. The research was divided into three phases; the detection system development, the study of the feasibility of concentrating tritium by evaporation, and a field study using tritium as a water tracer.

Initial consideration in determining the type of detection system was based on both economics and simplicity. The decision was made to use an internal gas geiger counter as the detector since it is both inexpensive and simple to construct. Acetylene was chosen as the carrier gas since it is easy to manufacture and would also serve as the quench gas in the geiger tube.

The evaporation process was to be carried out with the sample at near-freezing temperatures under vacuum to speed the process. Kirshenbaum [2] reported the vapor pressure ratio of  $H_20$  to  $D_20$  at  $0.0^{\circ}$  C to be 1.25 and that of  $H_20$  to HD0 to be 1.12 at the same temperature. Assuming that tritium will exhibit similar vapor pressure characteristics then it should be possible to concentrate the HTO, DTO, and  $T_20$  present in an  $H_20$  sample by an evaporation process.

The field study was conducted by injecting a limited quantity of tritiated water into a small stream and measuring the downstream tritium content. Although methods and data interpretation will depend upon the individual researcher, the study demonstrated the practicality of the system for field measurements.

#### CHAPTER II

#### TRITIUM DETECTION SYSTEM

A number of methods for tritium detection have been developed, many of which are quite good. However, simplicity and cost ruled the synthesis, development, and design of this system. The system consists of an inexpensive internal gas geiger counter, a simple geiger counter scaler and high voltage supply, and a fairly hard vacuum system for the conversion of the tritium water sample into a suitable counting gas. The counting tube was shielded with two inch lead bricks.

#### Counting Tube Construction

Tube dimensions and materials were arbitrarily chosen to fit readily available materials. The cathode of all twelve counting tubes constructed during this experiment was made from two inch type K copper plumbing tubing. The center wires were #39 B and S gauge copper and 2.35 mil  $\pm$  0.07 mil tungsten. The copper wire was lacquer insulated and had to be cleaned of all insulation and polished before use. Standard copper end caps machined to fit precisely were used on three of the counting tubes but were discarded when they proved inconvenient to remove for cleaning. The copper end caps also seemed to distort the electrical field near the ends of the tubes sufficiently to cause some erratic counting. Quarter inch plexiglas end caps were used on the other

tubes. These presented some problems in sealing but otherwise proved quite satisfactory. Latronics part number 952030 metal to glass to metal seals were used in all tubes constructed as insulators and for center wire connections. Valves were either of the neoprene or teflon pressure sealing type or double seal needle valve type.



Figure 1

Basically, all tubes were similarly constructed. A typical tube construction is shown in Figure 1. The cathode tubing was cut twenty-four inches long and the ends reamed and polished. The stock tubing was deemed sufficiently smooth but needed cleaning. The tube was cleaned with a commercial copper cleaner and washed with a detergent followed by water and methanol rinses.

To construct the plexiglas end caps, a short piece of copper tubing was heated and pressed about halfway through the plexiglas and removed to provide for proper positioning of the end caps. The center of the circle thus formed was located and a hole to accomodate the metal to glass to metal seals was drilled. In one end cap of each pair a second hole was drilled near the edge just slightly smaller than the valve connection to be used. The plexiglas was then heated with a heat lamp until it was flexible. The valve connection was screwed into the hole. Care was used in order not to extend the connection completely through the plexiglas and possibly disrupt the electric field within the counting tube. This method of valve connection was chosen over more conventional methods since it seemed to give a tighter fit and strengthen the valve connection. The end caps were then fastened to the counting tube using either Hysol Epoxi-Patch or red sealing wax. The Epoxi-Patch seemed to be stronger; however, the red sealing wax was easier to rework in the event small vacuum leaks were present. The metal to glass to metal seals were positioned and sealed together with the valve using the same type sealing material. A ball joint of glass or metal was sealed to the valve for connection to the gas conversion and vacuum apparatus. The center wire was strung through the tube and soft-soldered into position

under tension. The tubes were inspected for vacuum leaks and any leaks were sealed. Cleanliness in construction was very important since even small dust particles inside the counting tubes could produce spurious or erratic counting.

Connection to the scaler and high voltage supply lead was made by means of a Fahnestock clip at the positive center wire and a ground clamp at the cathode. The end caps were rectangular so that the tube would be self-supporting within the shield.

With a gas filling of 4.0 cm Hg methanol vapor and sufficient argon to total 76.0 cm Hg those tubes using 2.35 mil tungsten center wire had a threshold voltage of 1450 volts and a plateau from 1550 volts to 1850 volts with a slope of approximately 4% per 100 volts.

In the construction of the counting tube the following parts were used: 2 ft of copper tubing 2 inches inside diameter, type K; 2 metal to glass to metal seals, Latronics part number 952030; 1 valve assembly; 1 ball joint (either glass or metal); 2 plexiglas end caps,  $\frac{1}{4}$  x 3" x 3"; 1 ground strap; 2+ feet of 2.35 mil tungsten wire; sealant.

The metal to glass to metal seals were originally secured for use with the metal end caps. They proved convenient but would not be necessary with the plexiglas end caps. Four different valve assemblies were used, all of unknown origin. Those with neoprene seals proved most satisfactory since they did not leak when opened or closed. However, the needle point valves were sealed by using some silicon lubricant around the gaskets, providing positive sealing when the valves were open. Both glass and metal ball joints were used. The metal ball joints could be threaded and screwed into the valve assembly. The glass required an adap-

tor (copper tubing plumbing fitting) and the application of a sealant. The glass ball joints, however, proved to be more easily sealed to the conversion apparatus. Small diameter copper wire was first threaded through the tube and used as a "pull string" for the fine tungsten wire, thus reducing the waste to a minimum.

Actually, only a few hours were required for the construction of a counting tube, although the time elapsed from start to completion was about three days to allow for the curing of the epoxy at each stage.

Allowing for the more expensive items that might be used in the construction as outlined, a counting tube should cost less than \$25 for parts and might be constructed for as little as \$10. This very nominal cost should mean that several tubes could be available in a laboratory.

#### Gas Conversion Apparatus and Method

In designing the gas conversion system, primary emphasis was placed on simplicity. Acetylene gas was chosen because of the simplicity of manufacture and incorporation of the tritium atom. The acetylene serves as both the tritium carrier and the quench gas. Argon was used as the counting gas.

The necessary connections for the system were vacuum, counting tube, manometer for reading pressures above 1 mm Hg, pressure gauge for pressures below 1 mm Hg (McLeod Gauge), argon, acetylene conversion apparatus, and a cold trap to prevent moisture from entering the counting tube.

Figure 2 shows schematically the completed system. The system was constructed of glass because of the relatively small cost. Size 18/7 ball joints and 2 mm bore vacuum stopcocks were used throughout. The



Figure 2

acetylene conversion apparatus was made by sealing the end of an 18/7 ball joint.

The process for filling the counting tube was direct. The counting tube was connected to the system and pumped to a relatively hard vacuum of about  $1 \ge 10^{-3}$  mm Hg to  $1 \ge 10^{-4}$  mm Hg. Argon was introduced into the system and counting tube to pressures above atmospheric and the tube and system again evacuated to help flush any entrapped vapors or gases. The stopcock to the counting tube was then closed.

The sample to be converted was prepared by placing 0.200 ml of the sample in the bottom of the acetylene conversion tube and freezing the sample in a dry ice-acetone cold bath. Before the sample was completely frozen, a plug of glass wool was inserted into the tube and sample. After the sample was frozen, about 5 cm of finely crushed calcium carbide was placed on top of the plug and a second glass wool plug inserted in the conversion tube. The conversion tube was placed in the system and kept frozen by the cold bath. The liquid level in the cold bath extended only to the top of the sample and sample plug. The conversion tube was opened to the vacuum system and pumped for about 5 minutes or until the air in the tube was removed. The stopcock to the vacuum pump was closed, and the stopcock to the counting tube opened. The cold bath was transferred to the cold trap and the water sample allowed to react with the calcium carbide. This reaction produced tritiated acetylene. When the conversion was almost completed, the conversion tube was warmed gently by a heat lamp to assure complete conversion. In the system used in this experiment the conversion process produced 6.85 cm Hg to 7.125 cm Hg acetylene.

When the conversion was completed, argon was added to give a total pressure of approximately 76 cm Hg. The counting tube valve was closed and the counting tube was placed inside a two inch thick rectangular shield made of lead bricks and connected to the scaler and high voltage supply.

With these gas mixtures. the threshold voltage was 1610 to 1625 volts for the 2.35 mil tungsten wire tubes and 2200 to 2250 volts for the #39 B and S gauge copper wire tubes, with operating voltages of 1800 volts and 2400 volts respectively. The #39 B and S gauge copper wire was eventually discarded because of its higher operating voltages, shorter plateaus, and slightly higher background counting rate.

The following items were used in the construction of the conversion apparatus: 5 high vacuum stopcocks with 2 mm bore; 1 separable type cold trap; 6 ball joints, socket section; 5 ball joints, ball section; sufficient glass tubing to make manometer (approximately 2 meters); mercury for the manometer; and a meter stick for reading the manometer. The vacuum pump used was a Welch model 1400B.

Actually, all the ball joints with the exception of the set used for the sample tube could be eliminated by using high vacuum rubber hose and connecting the pressure gauges directly to the system. The elimination of the high vacuum gauge altogether should provide no particular problem since experience shows that the sound of the vacuum pump is an excellent gauge in itself. A separable cold trap was used for its easy cleaning abilities, but a sealed unit could be used just as well and at less cost. Since only straight or "T" connections and right angle bends are necessary in the construction of the apparatus, even those relatively

inexperienced at glass blowing should have little difficulty in constructing the apparatus. Annealing the finished product is recommended, however, since it is continuously subjected to the vibration of the vacuum pump and the strain of sealing and disconnecting the counting tube. In addition, spring clamps are recommended at each ball joint connection.

The cost of the parts for the conversion apparatus as described were under \$100 and, using the suggestions made above, could be reduced to around \$50. These figures obviously do not include the cost of the vacuum pump or high vacuum gauge. Depending upon the units chosen, these would cost \$200 or more. This is still quite reasonable, particularly since commercial units are now selling for several thousand dollars.

Additional items which will be needed in the conversion process include: a tank of argon with regulator valve; silicon stopcock lubricant; 200A micropipette and pipettor (a disposable plastic syringe and a short length of tygon work well); a cold bath flask (Pyrex thermos bottle refills are suitable); calcium carbide (one pound makes approximately 100 conversions); glass wool; acetone for the cold bath; and dry ice. Approximately 9 to 12 ounces of dry ice was used per conversion and the acetone had to be replaced about twice a month. This list, with the exception of the dry ice, can be obtained for under \$100.

The cost of operation, excluding labor, overhead, etc., could probably run less than 8 cents per conversion, making this method quite inexpensive.

#### Detection System Calibration

The mechanics used in the calibration of the detection system were conventional. It was necessary to determine the background counting rate,

the dead time of the counting tube, and the counting rates of the samples to be used in the evaporation process.

In all cases, the gas filling was made by converting 0.200 ml of distilled water or counting sample into acetylene gas and adding sufficient argon to give a total system pressure of 76 cm Hg. In the system used, the acetylene produced gave a pressure of 6.90 cm Hg to 7.125 cm Hg. Breakage necessitated the replacement of the manometer three times with a result of slightly different system volumes.

A single counting tube and scaler combination was used in the evaporation process, and the following data pertains to that one tube only. However, the results obtained with the other tubes were quite similar.

#### TABLE 1

Conversion	Total Counts	Time	Count Rate
A	316,980	1100 min.	288.16 cpm.
В	298,050	1040 min.	286.59 cpm.
C	241,251	850 min.	283.83 срт.
D	471,504	1500 min.	294.69 cpm.
TOTAL	1,327,785	4590 min.	289.28 срп.

#### BACKGROUND MEASUREMENTS AT 1800 VOLTS

In the determination of the background counting rate, four comversions of distilled water to acetylene were made. A plateau of at least 200 volts in length starting at 1750 volts was obtained in each case. The plateau slope was approximately 5% per 100 volts. Table 1 shows the results obtained at 1800 volts.

A Baird Atomic model 123 scaler was used as the high voltage sup-

ply and scaler. The major source of mechanical error was probably in the resetting of the high voltage supplied to the counting tube. Experience shows that meters of the type used in this high voltage supply usually have a probable error in meter reset accuracy of  $\pm 1\%$  of full scale or, in this case,  $\pm 25$  volts. Observation shows an operator probable error of  $\pm 5$  volts. For the plateau slope of 5% per 100 volts, the adjustment of the high voltage supply resulted in a probable error of  $1.275\% = \frac{5\%}{100} \sqrt{(25 \text{ volts})^2 + (5 \text{ volts})^2}$  or a standard deviation of 1.893% in the count rate. This standard deviation combined with the observed background count rate standard deviation gives a standard deviation of 5.68 cpm. The uncertainty shown in all calculations and values herein, unless otherwise noted, is expressed as one standard deviation. The back-ground count rate is therefore expressed as 289.28 cpm  $\pm 5.68$  cpm.

The dead time measurement of the system was made using the paired source method. Two external gamma sources were used, each producing approximately 5,000 cpm. The dead time determined was approximately 30 microseconds. An oscilloscope was used to determine the resolving time (the time required between pulses for the pulses to reach their maximum size). The resolving time was approximately 7.2 milliseconds. Maximum pulse heights were approximately 70 volts.

Because of the relatively short dead time and the relatively low count rates used (less than 2,000 cpm) no correction was made for dead time.

A rough estimate of absolute efficiency was made using a calibrated tritium standard. Tracerlab lot 55-41 counting standard, H-3 in water, 69.23 µc/ml as of 6-18-65 was diluted with distilled water to

6.923 x  $10^{-3} \mu c/ml$  as of 6-18-65. Correcting this for decay gave 6.618 x  $10^{-3} \mu c/ml$  or 1.50 x  $10^4$  dpm/ml as of 5-1-66. Several conversions of this standard were made with an average count rate of 119.4 ± 4.9 cpm/cm Hg. This gave a system efficiency of approximately 28.0%. This is within reason, considering the stoichiometric reduction in the water-calcium carbide reaction and the fractionation reported by Wing and Johnston[3].

#### CHAPTER III

#### THE EVAPORATION PROCESS

The ratio of the vapor pressure of  $H_20$  to  $D_20$  of 1.25 at 0°C reported by Kirschenbaum[2] indicates that, at lower temperatures, the evaporation of water containing some tritium should produce a greater concentration of tritium in the residue.

Consider the evaporation of water containing both protium (P) and tritium (T). Assuming that the quantitative rate of evaporation of protium (P) is proportional to that of tritium (T), then

$$\frac{d(P)}{P_c} = a \frac{d(T)}{T_c}$$
(1)

Assuming also that a remains constant throughout the process and integrating over the limits from the initial amount of protium,  $P_a$ , to the amount remaining, P, and from the initial amount of tritium, T<sub>o</sub>, to the amount remaining, T<sub>o</sub> gives

$$\ln \frac{P}{P_o} = a \ln \frac{T}{T_o}$$
 (2)

or

$$\frac{P}{P_o} = \left(\frac{T}{T_o}\right)^{a}$$
(2A)

Since, in general,  $P_{o} \gg T_{o}$ , we may assume that

$$\frac{\vec{F}}{\vec{F}_{e}} = \frac{\vec{V}}{\vec{V}_{e}}$$
(3)

where V denotes the volume of water. Substituting (3) into (2A) gives

$$\frac{V}{V_{o}} = \left(\frac{T}{T_{o}}\right)^{a}$$
(4)

The value of the negative constant, a, will be dependent upon the ex-

For this experiment, the evaporation was carried out by exhausting the water vapor directly through a high vacuum pump.

A Welch model 1400B vacuum pump with a vented exhaust was used. A valve was connected between the pump and an aluminum manifold. Six needle valves were available on the manifold. Each valve was connected by a  $\frac{1}{4}$  inch copper tube to the evaporation cylinder. Rubber stoppers were used to provide vacuum seals between the tubes and the cylinders. This manifold system was used because it was available and not because it was necessary. A simple manifold made from glass "T's" and rubber tubing would have been sufficient.

The cold bath for the cylinders was a watertight plastic box sufficiently deep to cover the sample levels in the cylinders. The temperature of the water was maintained by using an old drinking fountain cooler and a water pump for recirculating the water. A thermostat was provided in the cold bath to control the operation of the cooler.

Figure 3 shows a block diagram of the evaporation system.

Ten tritiated water samples (five each of two different tritium levels) were reduced from 100 ml to less than 1 ml in two steps. Thirty data points were thus possible.

Five 100 ml samples of initial activity of 119.4 cpm  $\pm$  4.9 cpm per cm Hg and one 100 ml distilled water sample were connected to a Welch model 1400B high vacuum pump through a common manifold. The ex-



#### Figure 3

ternal temperature of the graduated cylinders used to hold the samples was held between 1°C and 5°C in a cold bath. These samples (AA, AB, AC, AD, AE) and the distilled water sample (AF) were reduced to less than 10 ml by continuous pumping for approximately  $5\frac{1}{2}$ days. 0.200 ml of each sample was converted into acetylene and its activity determined. The distilled water sample exhibited no activity above background, showing that any cross connection through the manifold was negligibly small.

The reduced samples AA, AB, AC, AD, and AE were then transferred to 10 ml graduated cylinders and, following the process outlined above, reduced to less than 1.0 ml and the activity of each determined. These samples were renumbered BA, BB, BC, BD, and BE.

The same process outlined above was followed for five samples whose initial activity was 60.25 cpm  $\pm$  2.60 cpm per cm Hg. These samples were labeled DA, DB, DC, DD, DE, and, after reduction to less than 10 mL, EA, EB, EC, ED, and EE, respectively.

Table 2 shows the actual data obtained from these samples. Table 3 shows the water volume enrichment  $(V/V_o)$ , the tritium enrichment  $(T/T_o)$ , and a, the ratio of  $\ln\left(\frac{V}{V_o}\right)$  to  $\ln\left(\frac{T}{T_o}\right)$ .

In Table 3 the value obtained for  $V/V_{o}$  is a simple ratio of the volumes.

The total volume reduction factor of each sample is the product of the two reduction factors involved. Thus, it is possible to obtain 10 more data points by multiplying  $V/V_c$  for sample AA by  $V/V_c$  for sample EA,  $V/V_c$  for sample AB by  $V/V_c$  for sample BB, and so forth. The data points for the product of the volume reduction factor for Ai and the volume reduction factor of Ei were labeled Ci. Similarly, the product of the volume reduction factors Di and Ei were labeled Fi.

The values for  $T/T_c$  given in Table 3 were determined by a similar method. It was first necessary to convert the count rate obtained to a count rate per cm Hg pressure of acetylene. This was then divided by the initial count rate per cm Hg pressure to obtain  $T/T_c$ . To illustrate, let A = initial activity per cm Hg pressure, N = total number of counts obtained, t = total counting time, B = background count rate, and p = acetylene pressure in cm Hg. Then

$$\frac{\mathbf{T}}{\mathbf{T}_{a}} = \frac{\frac{\mathbf{N}}{\mathbf{t}} - \mathbf{B}}{\mathbf{p}\mathbf{A}}$$
(5)

The values of a were determined by use of the relationship

$$a = \frac{\ln(V/V_n)}{\ln(T/T_o)}$$
(6)

The values thus determined are shown in Table 3. Figure 4 is a graph of  $\ln V/V_a$  versus  $\ln T/T_a$ . A mean (E) for a was determined and the standard

deviation for a was determined using the relation

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$$\mathbf{s} = \sqrt{\frac{1}{N-1} \sum (n-\bar{n})^2}$$
(7)

where N is the total number of samples. A value of  $a = -13.15 \pm 2.69$  was obtained.

#### TABLE 2

#### SAMPLE DATA

Sample	V <sub>.</sub> (ml)	V(ml)	Total Counts	Time (min)	Pressure (cm Hg)
AA	100_0	5.2	282187	200	6.90
AB	100_0	8.2	259032	200	6.90
AC	100,0	6.0	277013	200	7.05
AD	100_0	9.4	259070	200	7.05
AE	100,0	9.0	255234	200	7.075
BA	4.6	0.8	433550	280	7.05
BB	7.7	0.9	986769	670	7.025
BC	5.4	0,6	318311	200	7.05
BD	9.0	0,8	292953	200	6,95
BE	8,2	0.15	183175*	200	6.95
DA	100,0	8.3	166083	200	6,95
DB	100.0	10_1	155539	200	7.05
DC	100.0	9.0	163160	200	7.05
DD	100.0	10.0	159589	200	7.10
DE	100_0	6.7	164633	200	7.125
Ēà	8,2	0.8	181 381	200	7.10
EB	9.6	0.3	137303	200	6.975
ĒA	8.2	0.45	182714++	200	7.05
ED	8_8	0.5	188324	200	7.05
	6_05	0.45	184924	200	7.05
*	* sample di * sample di	iluted to iluted to	total volume total volume	e of 0.35 e of 0.5	ml ml

## TABLE 3

## CALCULATION DATA

Sample	$\frac{\underline{v}}{\underline{v}_{s}} \ge 10^2$	T T <sub>o</sub>	-8
AA	5.2	1.36	9.59
AB	8.2	1.22	12.52
<b>≜</b> C	6.0	1.30	10,66
AD	9.4	1.20	13.28
AE	9.0	1.17	15.50
BA	17.39	1.10	18,89
BB	11.68	1.16	14.81
BC	11.11	1.19	12.75
BD	8.89	1.18	14.26
BE	1.83	1.63	8,20
CA	0.904	1.49	11.74
СВ	0.958	1.41	13.50
CC	0.667	1.55	11.48
CD	0.836	1.42	13.74
CE	0.165	1.77	11.17
DA	8.3	1.29	9.72
DB	10.1	1.15	16.40
DC	9.0	1.24	11.22
DD	10,0	1.19	13.30
DE	6.7	1.24	12,35
EA	9.75	1.12	21.01
EB	3.12	1.37	11.01
EC	5.49	1.19	17.04
ED	5.68	1.29	11.21
EE	7.43	1.20	14.08
FA	0.809	1.44	13.12
FB	0.315	1.58	12.67
FC	0.494	1.47	13.79
FD	0.568	1.54	12.06
FE	0,469	1.50	13.22



Figure 4

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#### CHAPTER IV

#### FIELD TEST OF DETECTION SYSTEM

Demonstration of the field usefulness of the tritium detection system was accomplished by the injection of a small amount of tritium and a dye into a small sewage lagoon effluent stream. Downstream measurements were made of tritium content of the stream and of the dye content of the stream.

The stream and sewage lagoon chosen for this experiment were near Elanchard, Oklahoma. The lagoon effluent feeds directly into a small natural stream and, eventually, into the Canadian River. The measurements were made two days after a fairly heavy rain storm and before the stream had returned to its steady state condition. The flow rate of the stream at this time was estimated to be 0.7 cubic feet per second. The section of stream selected for this study had many bends and several poels up to twenty feet across.

Approximately 3/4 pound of potassium permanganate was mixed with about eight liters of water to make the dye. About 1.5 millicuries of tritiated water was mixed into the dye giving a concentration of less than 0.2 microcuries per ml. A fairly uniform section approximately two feet wide and fifteen feet long was chosen as the injection and first sampling point. The dye and tritium was injected at the upstream end

of this section as rapidly as possible from a wide bucket by simply dumping the contents of the bucket. Starting at the moment of injection twenty 2 cunce samples were collected within one minute at the downstream end of this short section. These samples were labeled 1 through 20. The tritium content in counts per minute and the relative transmittance of the dye samples obtained on a Bausch and Lomb Spectronic 20 are given in Table 4. Figure 5 is a graph of the results.

Two other sampling points were chosen downstream. Sampling point number two was approximately 125 feet from the point of injection and sampling point number three was about 415 feet from the injection point. These points were chosen since both were narrow and tended to focus the stream flow. Samples number 21 through 40 were obtained at sampling point number two and samples 41 through 60 were obtained at sampling point number three. The results of tritium activity and relative transmittance of the dye are, where available, listed in Table 4. Figure 6 displays graphically the results of samples 21 through 40.

Although relative transmittance measurements were made within 72 hours of injection, the dye had faded in samples 41 through 60 so that the relative transmittance measurements were indeterminate. Therefore, Figure 7 shows only the tritium activity of the samples.

The percent relative transmittance values of Table 4 are the work of Woods and Leve [4].

The same process used in conversion and counting of the samples described previously was used for all samples.

## TABLE 4

STREAM	DATA
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Sample	Time From Injection(sec)	T Activity cpm/cm Hg	& Relative (1) Transmittance
1	0	0	100
2	3	-	99
3	6	32.53	10
4	9	46,47	7
5	12	128,18	1
6	15	125.80	1
7	18	72.35	. 1
8	21	-	3
9	24		10
10	27	-	19
11	30	-	37
12	33	14,16	47
13	36	-	64
14	39	-	59
15	42	-	70
16	45	-	71
17	48	-	78
18	51	-	90
19	54	-	87
ŹÔ	57	4.77	86
21	60	<del>51</del>	100
22	120		99
23	135	1.76	99
24	150	12.97	11
25	165	15.72	2
26	180	13.05	3
27	195	-	4
28	210		9
29	225	-	25
30	240	8,29	39
31	270		80

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# TABLE 4 - Continued

STREAM	DATA

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Sample	Time From Injection(sec)	T Acticity cpm/cm Hg	\$ Relative Transmittance (1)	
32	300		97	
33	330	•	100	
34	360	1,46	100	
43	900	1,30		
44	960	1.55		
45	1020	7.21		
46	1080	3.16		
47	1140	2,95	<b>.</b>	
49	1380	2,61		
55	2160	1,93	-	
(1) Samples (1-20) diluted by a factor of 5 with distilled water.				











#### CHAPTER V

#### GENERAL DISCUSSION

The detection of tracer levels  $(3 \times 10^{-5} \,\mu c/cc)$  of tritium was not possible with the system due to the relatively large standard deviation introduced by the high voltage supply. Defining the minimum detectable activity (M.D.A.) as twice the standard deviation of the background counting rate gives an M.D.A. equal to 2(5.68) or 11.36 cpm. Considering the 28.0% efficiency of the detection system and a volume of 0.200 ml of sample gives an

$$M_{\bullet}D_{\bullet}A_{\bullet} = \frac{11.36}{(22.2 \times 10^{5})(.280)(0.200)} = 9.14 \times 10^{-5} \,\mu c/mL$$

If the minimum measurable activity (M.M.A.) is defined to be equal to ten times the standard deviation of the background counting rate, or five times the M.D.A., then the M.M.A. is equal to  $4.57 \ge 10^{-4} \mu c/ml$ . This is lower than the maximum permissable concentration of tritium in water (3 x  $10^{-3} \mu c/ml$ ) for general population continuous exposure.

A few simple changes will lower the M.D.A. and M.M.A. appreciably. Changing the high voltage system to a more reproducible one will lower these values by a factor of approximately 10. Unshielded background counting rates increased by a factor of about one third when the counting tube was changed from a vertical position to a horizontal position, Perhaps changing the shield and counting tube to a vertical position and increasing the shield thickness would be beneficial in reducing the background counting rate. Of course, an anti-coincidence counting unit would be of very great value.

Changing the counting gas filling from acetylene to hydrogen and using a transfer pump to place almost all the gas into the counting tube would increase the system efficiency to about 100%. This change in gas filling would permit the use of up to 30 cm Hg of hydrogen [5] and the amount of tritiated water converted could be increased. The inclusion of these items might reduce the M.D.A. and M.M.A. by as much as  $5 \ge 10^{-3}$ .

The gas conversion and vacuum system is adequately designed for use as a hydrogen conversion system if the calcium carbide is replaced with, for example, calcium metal. The transfer pump would be included between the vacuum system and the counting tube.

The counting tubes can be improved in several ways. Changing the center wire to a smaller size would lower the operating voltage and probably decrease the background count slightly. The use of nichrome, stainless steel, or kovar wire would have the advantages of being less fragile than tangsten and of being easier to install. The end cap would be made easily removable by the use of "0" ring seals. A spring-pressure type value assembly might also be of benefit since many of the problems encountered were caused by value leakage.

The evaporation experiment showed that the concentration of tritium per unit volume is increased by evaporation. However, the value of a determined is for these particular experimental conditions and should not be assumed as correct under other conditions. For example, higher or lower temperatures, physical form of the water (solid or liquid), the

rate of volume reduction, chemical contaminants, etc., may have an effect on a.

Obviously, much more detailed information must be obtained for complete evaluation of the evaporation process.

The proof of tritium enrichment in the evaporation process may mean that the values obtained in previous age dating work and similar processes using tritium may have to be recalculated.

The practicality of using the detection system in field studies using artificial tritium was vividly illustrated by the results of the stream study conducted in the course of this work. The peaks of activity were readily discernible and were much more obvious than those obtained with the dye used. In addition, the very rapid dissipation of the dye in these samples proved to be detrimental, since those of lower optical density were unusable soon after they were obtained. The tritium samples could have been run months or even years after collection and still have given equally satisfactory results.

Excellent discussions of both the public health and field study aspects of tritium usage have been presented by Feely, et. al. [1] and by Kaufman $\lceil 6 \rceil$ .

#### LIST OF REFERENCES

- Herbert W. Feely, Alan Walton, Charles R. Barnett, and Fernando Bazan, <u>The Potential Applications of Radioisotope Technology</u> <u>to Water Resource Investigations and Utilization</u>, Isotopes, Inc., 114-146, (1961).
- 2. Isidor Kirshenbaum, <u>Physical Properties and Analysis of Heavy</u> <u>Mater</u>, edited by Harold C. Urey and George M. Murphy, 1st edition, McGraw-Hill Book Company, Inc., 25, (1951).
- 3. J. Wing and W. H. Johnston, "Method for Counting Tritium in Tritiated Water," <u>Science</u>, <u>121</u>, 674, (1955).
- 4. C. Woods and T. Love, private correspondence with Jerrold J. Burnett.
- 5. S. Kaufman and W. F. Libby, "The Natural Distribution of Tritium," <u>Physics Review, 93</u>, 1337-1344, (1954).
- 6. W. J. Kaniman, "Tritium as a Ground Mater Tracer," <u>Journal of Sani-</u> <u>tary Engineering Division</u>, <u>Proceedings of the American Society of</u> <u>Civil Engineers</u>, <u>86 No. 346</u>, 47-57, (1960).