Quantitative Determination of Tritium In Natural Waters

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By C. M. HOFFMAN *and* G. L. STEWART

RADIOCHEMICAL ANALYSIS OF WATER

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ABSTRACT

This report describes the methods and procedures used by the U.S. Geological Survey Tritium Laboratory to analyze natural waters for tritium activity.

Samples having low activity are electrolytically enriched in cells with nickel and steel electrodes, and their tritium concentration is subsequently determined by liquid scintillation and gas phase counting techniques. Samples having high tritium concentrations can be counted directly, and no enrichment is required.

Theory, calculations, equipment, and procedures are described in some detail.

INTRODUCTION

In recent years, as the Nation's water supply problem has caused more concern, the hydrologist has turned to radioisotopes to aid him in his studies of water residence times and movement patterns. Tritium is superior to other water tracers in some kinds of hydrologic studies because it is incorporated directly into the water molecule.

Tritium, a naturally occurring radioactive isotope of hydrogen, has a mass number of 3. It is a soft beta emitter and has a maximum energy of 0.018 Mev (million electron volts) and a half life of 12.26 years.

The discovery of tritium is attributed to Sir Ernest Rutherford and his coworkers at the Cavendish Laboratory in England; they produced tritium by deuteron-deuteron interaction:

$$_1H^2(d, p)_1H^3. \tag{1}$$

In this reaction, He^3 is also produced, and Rutherford was unable to ascertain which isobar was radioactive. Later, Alvarez and Cornog (1939) at Berkeley, Calif., determined tritium to be the radioactive component and He^3 to be stable and naturally occurring.

Rutherford also attempted to detect tritium in natural waters. He attempted to concentrate tritium by electrolyzing large quantities of natural water but was unable to detect tritium in the enriched water by mass spectrometry.

In 1951, Dr. Willard F. Libby, at the University of Chicago, measured the enriched water produced by Rutherford with a Geiger-Mueller detector instead of the less sensitive mass spectrometer and found the sample contained radioactive tritium.

Tritium is produced naturally in the atmosphere by cosmic radiation, and the following mechanism is believed to be mainly responsible for its production:

$$_7N^{14} \ (n,t) \ _6C^{12}. \tag{2}$$

It is also produced naturally in geologic formations by the following reaction:

$$_3Li^6 \ (n,\alpha) \ _1H^3. \tag{3}$$

In addition, tritium is produced synthetically in thermonuclear explosions, and large concentrations are trapped in rain and snow.

The usefulness of tritium in dating or tracer studies depends on the accuracy of its analysis. Tritium levels for some natural waters are extremely low, and the analysis may require special enrichment techniques and other critical steps, all of which must be performed with great care to produce accurate and meaningful results. The following discussion presents methods employed by the U.S. Geological Survey Tritium Laboratory to determine quantitatively the tritium concentrations in natural waters.

Acknowledgments.—The authors are grateful to Mr. T. A. Wyerman and Mr. R. K. Reaves for the assistance they rendered in the Laboratory while the authors were working out the analytical procedures reported here.

ELECTROLYTIC ENRICHMENT

Pre-hydrogen bomb tritium concentrations in water are low, and it was calculated by Faltings and Harteck (1950) that there is only one mole of natural tritium in the entire atmosphere, or one tritium atom for every 10 cc (cubic centimeters) of air. As a convenience, tritium concentrations are normally expressed in tritium units, 1 TU being defined as one tritium atom for every 10^{18} hydrogen atoms. This ratio is approximately equal to 3.2 picocuries per liter.

Low tritium concentrations in natural waters are not directly measurable and therefore the water samples must be enriched. Four methods of enrichment are currently employed: electrolysis, thermal diffusion, distillation, and gas chromatography. Fractional electrol-

ysis is the method most commonly used and is the method used in the tritium laboratory.

The electrolysis is performed in cells of the type shown in figure 1. At present, cells of 1-liter and 250-, 40-, and 10-milliliter capacity are used, the size of the cell being determined by the degree of enrichment required. As a general proposition, samples are enriched according to their estimated original tritium concentrations as follows:

Concentration (tritium units)	Volume reduction (milliliters)
>1,000	None measurable directly.
100–1,000	40–4
10–100	250–4
<10	1,000–4

These ranges are flexible and may be adjusted according to the amount of time available for counting a sample. For example, a sample containing 400 TU may be measured directly but this requires a long counting time and monopolizes the counting equipment unnecessarily.

The electrodes are constructed from uniform steel and nickel tubing, and the two segments are separated by a Teflon spacer of uniform
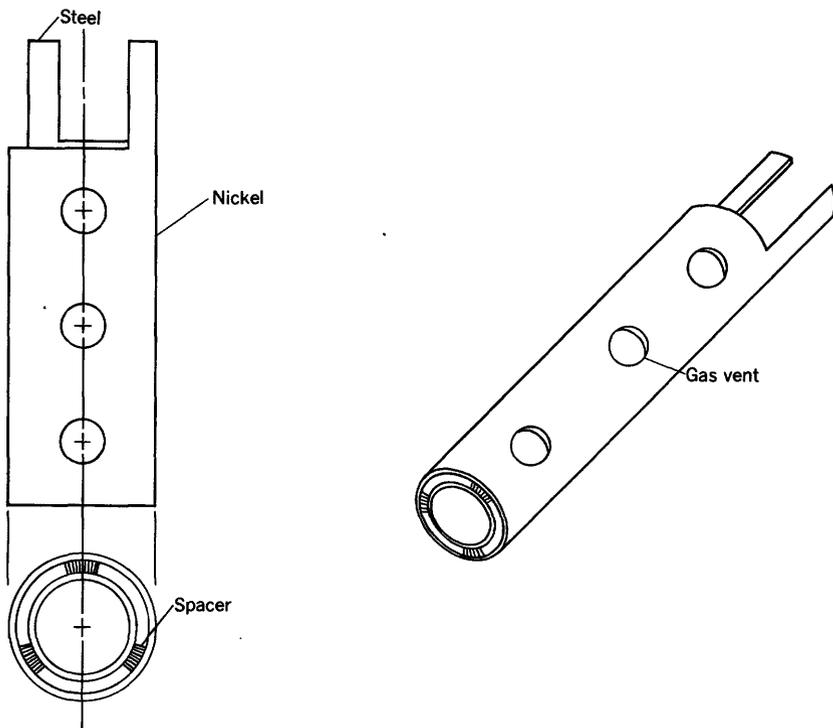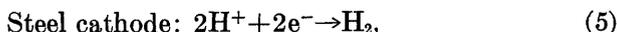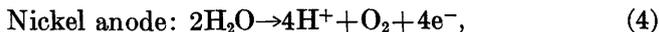

FIGURE 1.—Nickel-steel electrode for electrolytic enrichment process.

thickness. The cells are fitted with stoppers to eliminate cross contamination and a gas outlet to allow the H_2 and O_2 produced during electrolysis to escape.

The reactions that occur at the electrodes are

$$\text{Nickel anode: } 2H_2O \rightarrow 4H^+ + O_2 + 4e^-, \tag{4}$$

$$\text{Steel cathode: } 2H^+ + 2e^- \rightarrow H_2, \tag{5}$$

where H may be protium (H^1), deuterium (H^2), or tritium (H^3).

Nickel and steel are used as electrode materials because of the good separation efficiency obtained (that is, the reduction of protium in reaction (5) is more rapid than the reduction of tritium), their corrosion resistant character, and their ready availability.

FACTORS INFLUENCING SEPARATION EFFICIENCY

Factors that adversely affect the separation efficiency during the electrolysis are:

1. Variation in interelectrode spacing and associated current density differences.
2. High temperatures in the electrolysis cell which produces water vapor losses.
3. Irregularities on electrode surface.
4. High salt concentrations which react with the electrodes.

During electrolysis, protium is preferentially reduced and discharged at the cathode, and the solution surrounding the cathode increases in tritium concentration relative to the rest of the solution. This condition is undesirable since a larger proportion of tritium is available for reduction at the cathode, and the separation efficiency of the process is reduced. This concentration gradient is eliminated to some extent by diffusion, convection caused by thermal differentials, and mixing through gas evolution (Urey, 1933). If irregularities are present on the electrode surface, electrolysis takes place in the electrode cavities since gas bubbles tend to form on the projections. Bubbles held in this manner decrease the stirring effect, and the tritium concentration increases near the cathode surface, thus unfavorably increasing the concentration gradient and decreasing the separation efficiency.

To have the electrolysis proceed at a reasonable rate, an electrolyte is added to the water sample. The solution is made alkaline by the addition of Na_2O_2:

$$Na_2O_2 + H_2O \rightarrow 2NaOH + \tfrac{1}{2}O_2 \tag{6}$$
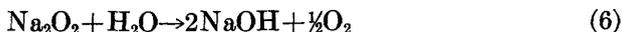
An alkaline, rather than acidic, electrolyte is used because of the competing hydrogen gas the metal-acid combination would produce. The Na_2O_2, unlike the acid, contains no hydrogen and reduces the possibility of contamination. Electrolytes such as NaCl are undesirable because they attack the electrodes, making them unsuitable for extended use. For this reason, the conductance of the sample is measured prior to analysis, and if the salt concentration is too high, the sample is quantitatively distilled.

During electrolysis, a fractionation decrease, and hence a separation efficiency decrease, occurs as cell temperature increases because the ratio P_{H_2O}/P_{T_2O} (where P is the vapor pressure) decreases with increasing temperature. It is desirable to maximize this ratio by cooling the electrolysis cell to improve the separation efficiency. The cooling bath is a converted deepfreeze unit fitted with a thermoswitch-relay temperature control, a centrifugal circulating pump, and an exhaust duct. Power for the electrolysis cells is furnished by low-ripple battery eliminators.

Carlston and Thatcher (1962) in a study of the parameters involved in the electrolysis process found that low-temperature and low-current density conditions are desirable for good recovery. Table 1 shows the effect of temperature and current on tritium recovery.

TABLE 1.—*Effect of temperature and current on tritium recovery*

[After Carlston and Thatcher, 1962]

Temperature (°C)	Applied volts	Average current (amperes)	Percent recovery
8	} 2. 6	1	{ 83
25			73
8	} 3. 1	{ 3	58
25		{ 4	48

MULTISTAGE ENRICHMENTS

When the NaOH concentration is between 1 and 20 percent during the electrolysis (Ostlund and Werner, 1962), the most rapid electrolysis rate is achieved and the recovery is reproducible. If a high degree of enrichment is to be achieved, a sample must be electrolyzed in a number of stages to maintain this optimum range. When transferring a sample from stage to stage, the partially enriched water sample is first neutralized by slowly bubbling CO_2 gas through the solution. Neutralization liberates any hydrogen bound in the OH^- by forming sodium carbonate and water, and speeds up the distillation process:

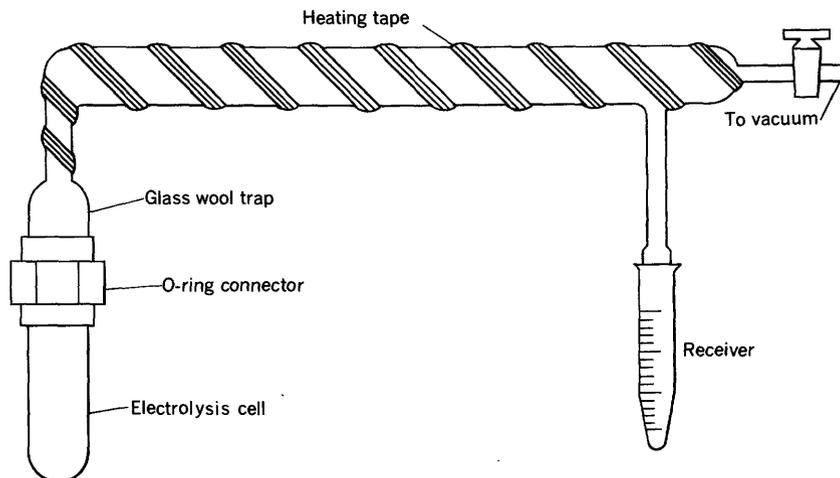$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \qquad (7)$$
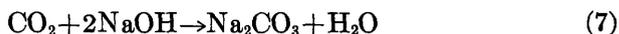
FIGURE 2.—Vacuum distillation apparatus for the quantitative recovery of sample.

Neutralized samples are vacuum distilled using the apparatus shown in figure 2. Heat is supplied with a Variac controlled heating tape (only partly shown), and a glass wool trap helps prevent salt particles from passing through the system to the receiver bulb. After quantitative distillation, the sample is again made alkaline by the addition of Na_2O_2 and the enrichment continued in the next electrolysis stage.

COUNTING PROCEDURES

GAS PHASE TECHNIQUE

The tritium content of an enriched sample is determined by gas phase counting. Although the method offers high sensitivity and efficiency in measuring the beta decay, it has the disadvantage that a skilled technician is needed to prepare the sample for counting. The sample is counted as hydrogen gas, and the tritium recovery is quantitative, thus eliminating fractionation effects.

The gas production apparatus is shown in figure 3. An aliquot of the enriched water sample, approximately 0.6 ml, is placed in bulb E where it is frozen with liquid nitrogen, and the system evacuated to remove all the gaseous impurities. This bulb is then warmed and the water vapor allowed to pass through the hot zinc column. The water vapor reacts with the zinc to form hydrogen gas and zinc oxide:

$$Zn + H_2O \xrightarrow{400° C} ZnO + H_2. \tag{8}$$
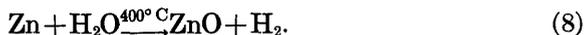
The bulb to trap any unreacted water vapor is cooled with liquid nitrogen during this reaction. This water vapor may be subse-

quently recycled through the hot zinc to effect a complete reaction. As the hydrogen is formed by reaction (8), it is forced into the detector tube by a Toëpler pump and there mixes with a measured quantity of previously added toluene vapor.   The amount of hydrogen may be calculated from the pressure observed on the mercury manometer because the volume of the detector is known.

Toluene acts as a quench gas and eliminates multiple discharges and cascading.   Several gasses have been investigated for suitability as quenching agents, and toluene and ethylamine were found to have exceptionally good counting characteristics.   Plateaus of 800 volts and $<$3 percent slope are obtained by using toluene that has been frozen with liquid nitrogen and then purified by pumping off the gaseous impurities prior to adding the pure quench to the sample detector.   A toluene to hydrogen pressure ratio is approximately 1:40 at 40 cm (centimeters) of mercury pressure, but this ratio is not critical.   Although a satisfactory quench gas, ethylamine rapidly attacks the detector Plexiglas endpieces and makes the unit unsuitable for further use after a short time.
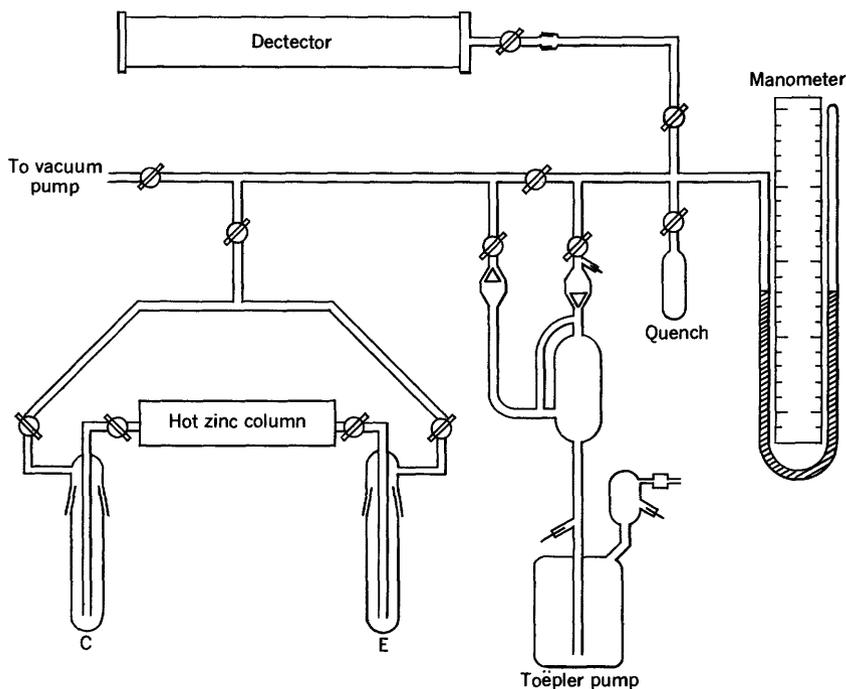

FIGURE 3.—Gas production apparatus used to prepare H_2 from water.   C bulb for trapping any unreacted water vapor; enriched water sample is added to bulb E.

A cross section of the Geiger-Mueller detector is shown in figure 4. A gas-tight seal is obtained between the body wall and the endpieces with epoxy cement. The inner surface of the tube must be clean and smooth, and great care must be taken to center the stainless steel anode wire properly.

Since the count rate may be low for even enriched samples, it is necessary to reduce the high natural background to a statistically usable level. The counting array shown in figure 5 serves this purpose. The array consists of a mercury shield, an anticoincidence ring, and the mercury shroud inside of which the detector is placed. The mercury shield is a large stainless steel tank filled with 5,000 pounds of purified mercury metal which forms a 4-inch-thick mercury wall surrounding the detector. This dense metal absorbs a large part of the cosmic radiation naturally present. The anticoincidence ring is a multiple anode Geiger detector which reduces the background by eliminating pulses that are simultaneously triggered in the ring and sample detector. The mercury shroud is similar in construction to the large shield and serves to reduce the background count still further by absorbing radiation which passes through the anticoincidence ring without triggering a pulse and by absorbing radiation produced by impurities in the metal of the anticoincidence ring. This counting array reduces the unshielded background count of 350 cpm (counts per minute) to a background of 2.5 cpm. The background value is determined by filling the detector with a tritium-free electrolytic hydrogen and quench mixture and counting it in the array.

The tritium soft beta emission is measured by a Sharp's Laboratory Low Beta System, which consists of the anticoincidence ring and detector preamps, high voltage supply, main electronics console and dual printout registers. The console houses the logic circuits, main amplifiers and scalers. A block diagram of the system is shown in figure 6.
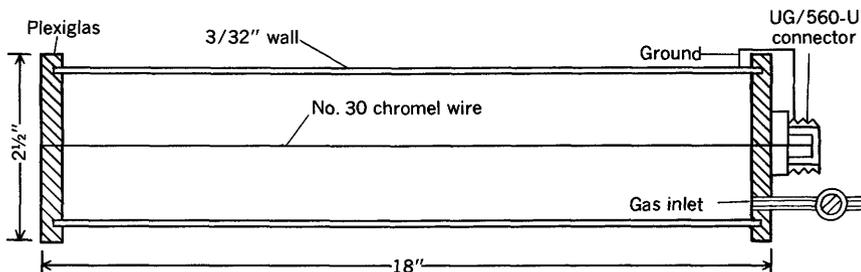

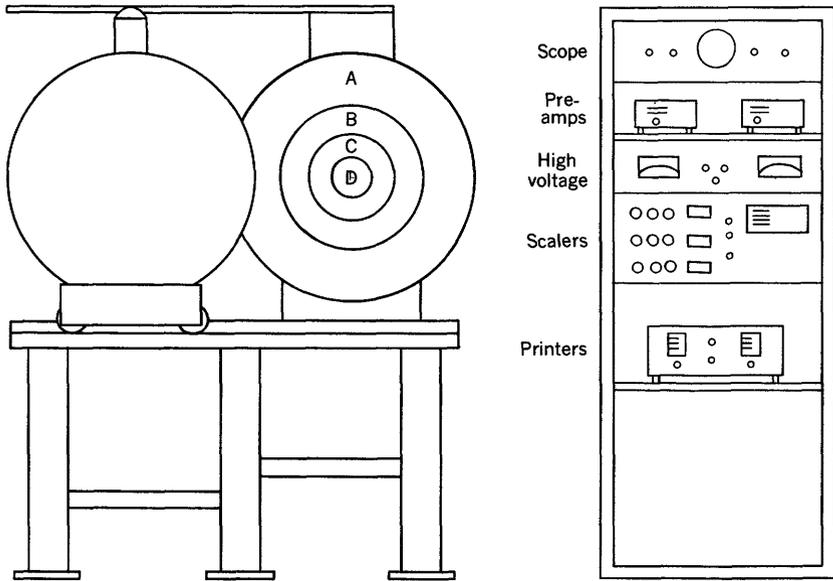FIGURE 4.—Internal sample Geiger-Mueller detector.

FIGURE 5.—Counting array: A, mercury shield; B, anticoincidence ring; C, mercury shroud; D, cavity in which detector is placed.
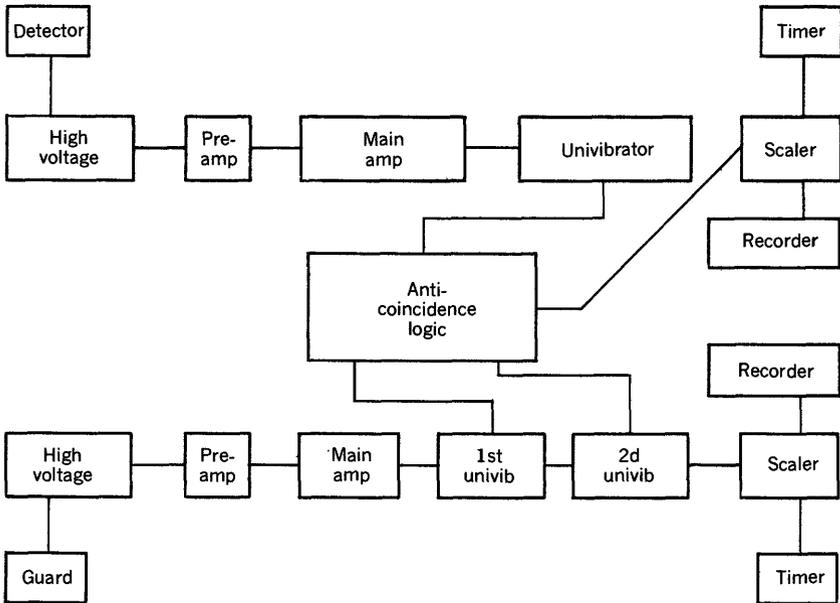

FIGURE 6.—Block diagram of electronic circuitry.

LIQUID SCINTILLATION TECHNIQUE

If tritium is present in sufficient amounts, the tritium concentration may be determined directly by use of a liquid scintillation spectrometer. An aliquot of water sample is mixed with a scintillator solution in a polyethylene vial and placed between two photomultiplier tubes in the spectrometer. As the tritium decays, the emitted beta particles excite the scintillator solution generating light pulses that are detected and amplified by the photomultiplier tubes and electronically sorted according to pulse energy into the appropriate scaler channel (Bell and Hayes, 1958). The window on the analyzer channel is adjusted to accept the major part of the tritium spectrum while excluding excessive background noise and the higher part of the energy spectrum.

The spectrophotometer used was fitted with a 200-position sample changer, automatic printout, and a time base modified to extend the counting time to 1,000 minutes. The dioxane cocktail used is basically that described by Werbin, Chaikoff, and Imada (1959). They found that optimum counting results were obtained with 100 grams naphthalene, 10 grams 2,5-diphenyloxazole, and 0.25 grams 1,4-bis-2(5-phenyloxazolyl)-benzene per liter of spectroquality dioxane. These investigators cited as optimum a dioxane-naphthalene-water ternary of 20 percent water having an efficiency of 8.6 percent. However, this laboratory found optimum conditions to be a 10-percent-water ternary in a 20-ml plastic vial yielding a counting efficiency of 24 percent and a background of 16 cpm. Although the efficiency of the system increases with decreasing water content (because of an internal pulse-height-attenuation process called quenching), this increase in efficiency from 8.6 to 24 percent is due mainly to refinements in electronics.

The liquid scintillation method has some disadvantages not found in the gas phase technique. The high background of the liquid scintillation spectrometer (16 cpm for liquid scintillation versus 2 cpm for gas phase) is a distinct disadvantage. This background is due to thermal noise within the photomultiplier tubes and to small conccentrations of K–40 or other radioactive impurities in the glass sheath of the phototubes. The photomultiplier tube faces are made of quartz to reduce the K–40 background.

Chemical quenching and quenching due to matter or coloration in the water sample present a problem since they hinder the transfer of light and decrease the counting efficiency. High-activity samples are corrected for quenching by using the channel-ratio method (Bush, p. 1024), in which the relative spectrum shift for the analyzer and monitor channels is correlated to a quench correction factor,

Q. A curve is prepared by quenching a standard with chloroform and plotting Q versus the monitor to analyzer ratio.

Quenching due to the formation of peroxides also occurs as the dioxane cocktail ages and it is inadvisable to prepare more scintillator solution than can be used within a few days after preparation.

It is necessary to minimize exposure of the sample cocktail to light since the phosphors become excited, causing an initial high count rate. The samples are allowed to cool in the darkened freezer unit at least 30 minutes prior to counting.

ENRICHMENT CALCULATIONS

An enrichment efficiency factor, E, based on NBS (National Bureau of Standards) tritium standards is used to calculate the amount of enrichment:

$$E = \frac{TV}{T^oV^o} \tag{9}$$

where

V^o=initial volume,
V=final volume,
T^o=initial TU,
T=final TU.

Most recent precipitation samples only require a single stage of enrichment to obtain measurable levels, and the use of E to calculate enrichment is convenient.

When high enrichment is necessary, the deuterium enrichment can be measured and the tritium enrichment computed by the method described in the section on "Theory and Calculations."

Normally, the final deuterium concentrations are measured with the falling drop apparatus shown in figure 7. The constant temperature bath is filled with a large volume of water (about 10 gal) for thermal stability, and the temperature is maintained by a thermoswitch and heating system. The falling tube, filled with isobutyl benzoate (a water insoluble substance having a density close to that of water), is thus kept at a constant temperature in the mechanically stirred bath. Heat reflectors keep the infrared radiation of the heating lamps from directly striking the falling tube.

A small amount of sample is drawn into a micropipet assembly, and the time required for a drop of measured volume to pass between two marks on the falling tube is measured by a timer. The first mark is positioned low enough on the tube so that the drop reaches its terminal velocity before timing is begun. Since Stoke's Law is obeyed and the density of the drop is proportional to the deuterium concentration, the
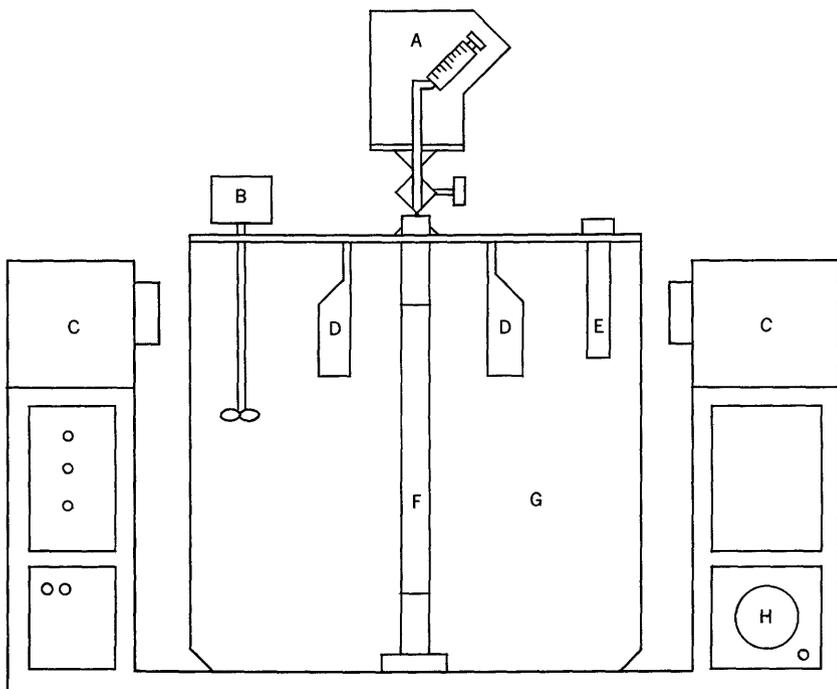
FIGURE 7.—Falling drop apparatus for measuring deuterium in water. A, Micropipet assembly; B, motor-driven stirrer; C, heating system; D, heat reflectors; E, thermoswitch; F, falling tube; G, constant temperature bath; H, timer.
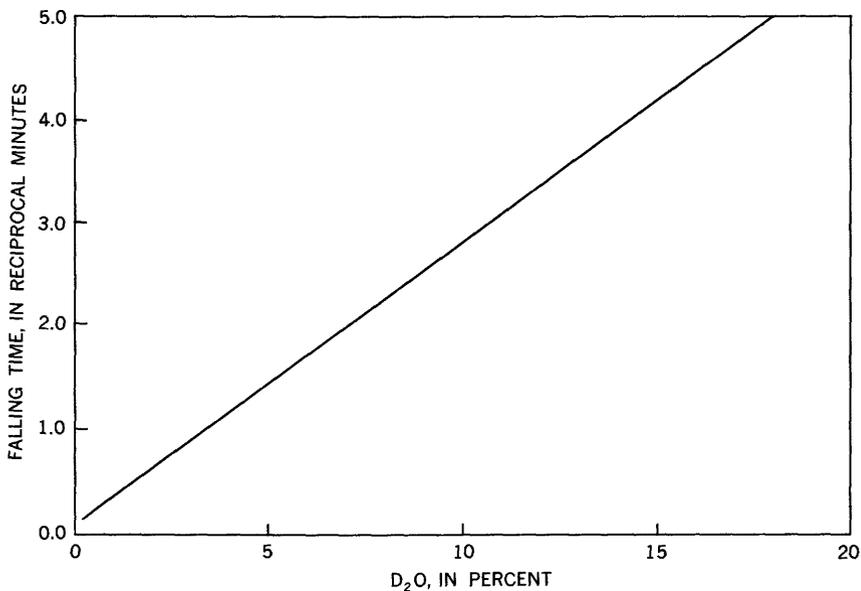

FIGURE 8.—Falling time of sample droplet as a function of the D_2O content.

deuterium content may be measured by comparing a sample's falling time to those of a series of standards. A standard curve is shown in figure 8, in which the reciprocal of the falling time in minutes is plotted versus percent D_2O.

THEORY AND CALCULATIONS

During the electrolysis process, the enrichment of the isotopes relative to each other are related by the equation:

$$\frac{dp}{p} = \alpha \frac{dd}{d} = \beta \frac{dt}{t}, \tag{10}$$

where α and β are enrichment factors and p, d and t are the number of moles of protium, deuterium and tritium, respectively. The enrichment factors may be defined as the ratio of concentrations of the isotopes in the gas phase to those in the liquid phase:

$$\alpha = \frac{(p/d) \text{ gas}}{(p/d) \text{ liquid}}, \tag{11}$$

$$\beta = \frac{(p/t) \text{ gas}}{(p/t) \text{ liquid}}, \tag{12}$$

$$\gamma = \frac{(d/t) \text{ gas}}{(d/t) \text{ liquid}}. \tag{13}$$

As the value of γ apparently decreases with increasing temperature (Roy, 1962), the ratio of log β/log α appears to be quite constant at 1.40 ± 0.01 (Kaufman and Libby, 1954; Bigeleisen, 1960). An expression for the original tritium concentration of the enriched water may be derived from the relationship found in equation (10):

$$\int_{p^o}^{p} \frac{dp}{p} = \int_{d^o}^{d} \alpha \frac{dd}{d} = \int_{t^o}^{t} \beta \frac{dt}{t},$$

where the superscript ^{o} indicates initial conditions.

Assuming that $t \ll d \ll p$, then

$$\frac{V}{V^o} = \left(\frac{d}{d^o}\right)^\alpha = \left(\frac{t}{t_o}\right)^\beta, \tag{14}$$

or, letting X signify the mole fraction,

$$X_t^o = X_t \cdot \frac{V}{V^o} \left[\frac{X_d^o V^o}{X_d V}\right]^{\alpha/\beta}. \tag{15}$$

The original tritium concentration, X_t^o, is calculated using equation (15).

The final tritium concentration, X_t, is calculated from sample activity, detector efficiency, eff_{det}, and observed hydrogen pressure, P_{obs}, to give disintegrations per minute per milliliter

$$\frac{(\text{cpm})\, P}{(\text{eff}_{det})\, P_{obs}} = \text{dpm/ml} \tag{16}$$

where P is a water equivalency factor that relates hydrogen pressure in the detector to milliliters of water, and

$$\frac{\text{dpm/ml}}{7.2 \times 10^{-3}\ \text{dpm/ml/TU}} = X_t \text{ expressed in TU.} \tag{17}$$

The enrichment factor ratio α/β is determined by preparing standard s of known initial deuterium and tritium concentrations, measurin g these concentrations after enrichment, and substituting these valu es into equation (14).

ANALYTICAL ERRORS

The measurement of such physical quantities as pressure, weight, and volume are negligible sources of error. A pressure readin g error of 1 mm for a total mercury pressure of 60 cm would introd uce an error of ± 0.17 percent, whereas the volumetric error of a 40-ml pipet is on the order of ± 0.05 percent. Losses in transfer op erations are small and have been shown to be about ± 0.1 percent.

Cross contamination and detector memory effect may present a problem after the analysis of an active sample, but if the distil-lation equipment is properly dried and the detector evacuated to a low pressure, then cross contamination may be regarded as an in-significant error factor. This intersample contamination is no t important for liquid scintillation counting since new vials are use d for each sample and pipets are cleaned and completely dried in a n oven prior to use.

There is a possibility of erratic performance of the counting equip-ment due to such factors as excessive line noise, electronic oscillations or component breakdown. This source of error is indeterminate and is best guarded against by frequent equipment checks using blanks, standards and a printer set for short count times.

Table 2 shows the analytical results for a variety of samples. These data indicate the effect of enrichment on the assay and gives a comparison between counting systems for a range of tritium concentrations.

TABLE 2.—*Analytical results of tritium concentration measurements*

Sample		Date collected	Enrichment factor	Tritium units	
Type	Location			Gas counting	Liquid scintillation counting
Surface water____	Sacramento River, Sacramento, Calif.	July 27, 1964_____	5. 65	240	212
	Brown Creek, Polkton, N.C____	_____	5. 20	110	96
	Mississippi River, Anoka, Minn.	July 1963_____	0	_____	920
	Mississippi River, Anoka, Minn.	July 1963_____	5. 57	950	_____
	Missouri River, Nebraska City, Nebr.	June 1963_____	0	2,440	2,240
Precipitation____	Denver, Colo _____ ___	May 5–18, 1963_.	0	12,950	12,550
Standard_____	IAEA* (Vienna) [1]_____	August 1962_____	6. 10	119	_____
	_____do.[2]_____	October 1962____	0	_____	1,430
Unknown_____	_____do.[3]_____	_____	39. 79	45±4	43±6
	_____do.[4]_____	_____	11. 43	558±30	495±31
	_____do_____	_____	0	4,050±200	4,130±200

[1] 112 TU.
[2] 1,448 TU.
[3] <100 TU.
[4] 200–800 TU.
*International Atomic Energy Agency.

COMPARATIVE SENSITIVITIES OF COUNTING TECHNIQUES

A comparison between the detection limits of the gas phase system and the liquid scintillation technique shows the greater sensitivity of the gas phase method.

Based on 2σ statistics, a 500-minute count time, a background of 2.20 cpm, and a water equivalent of 0.61 ml, the lower limit of detectability for the gas phase system would be 46 TU.

A similar calculation for a 2-ml water sample, a counting efficiency of 23.75 percent, and a background of 16.20 indicates that the sensitivity for the liquid scintillation spectrometer would be 149 TU.

These concentrations are the minimum tritium that must be present to be detectable above the statistical background of the system under the described conditions. It would not be possible to measure these minimum concentrations with any accuracy, however.

COUNTING STATISTICS

The counting error is statistical since radioactive decay is a random quantity, and the frequency of the measured events follows a bell-shaped normal distribution curve. A common measure of the analytical precision is the standard deviation, σ, which is expressed as

$$\sigma = \left[\frac{\sum\limits_{1}^{N} (X - \overline{X})^2}{N-1} \right]^{1/2} \tag{18}$$

where X is the measured value in a set of N measurements and $\overline{X}$ is the arithmetic mean of the set of N measurements. For a normal distribution curve, a probability of 68.3 percent exists that a single measured value X will have a maximum deviation of 1σ. For a 2σ deviation, the probability is 95.5 percent.

When a single measurement is made that produces a statistically significant number of counts, the standard deviation for a large number of counts is equal to the square root of the total counts, N_T. To convert these results into counts per minute, both the total counts, N_T, and the square root of the total counts, $N_T^{1/2}$, are divided by the time in minutes, t. Thus, for a 1σ deviation and a 68.3-percent chance that the measurement is correct, the activity of the sample may be expressed as

$$\frac{N_T}{t} \pm \frac{(N_T)^{1/2}}{t}.$$

To make the most efficient use of the counting equipment and maximize the number of samples analyzed, the total counting time needed to make a measurement within the desired probable error limits is predetermined from the approximate sample activity.

The series of curves shown in figure 9 were calculated for the liquid scintillation spectrometer and were based on a background of
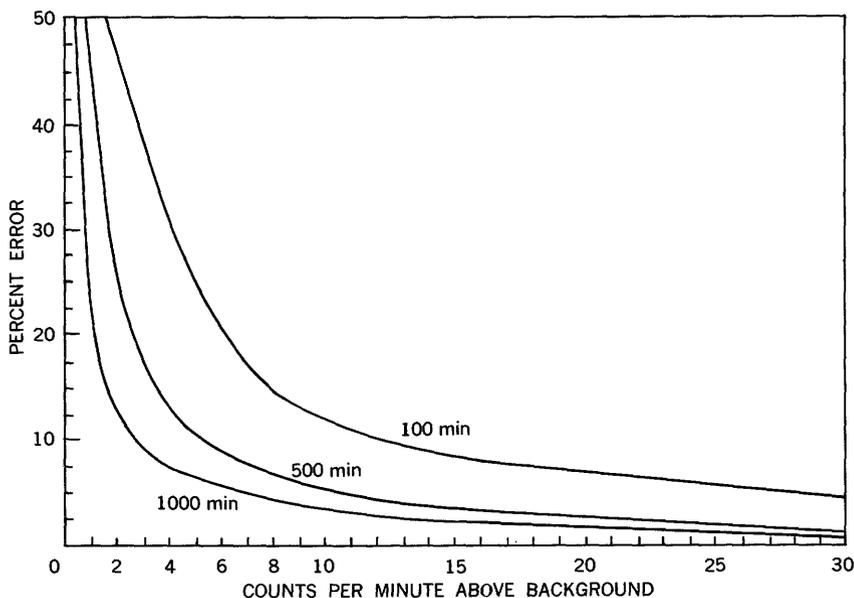

FIGURE 9.—Percent error, sample activity, and counting time relationships for the liquid scintillation system.

16 cpm and 2σ statistics. For example, if the sample had an activity of 10 cpm above background and was counted for a total of 500 minutes, the probable error for the measurement would be about 5 percent. Since 1 cpm above background equals 292 TU for the liquid scintillation system, there would be a 95.5 percent chance that the tritium concentration of the sample would be

$$X_t = 2,920 \pm 150\,TU.$$

SUMMARY

The tritium content of water samples is determined by either of two methods: gas phase counting or liquid scintillation techniques. In the gas phase method, hydrogen from the water molecule is reduced to H_2 gas; this gas is placed in a detector tube, and the activity of the sample is measured under anticoincidence counting. The liquid scintillation technique involves mixing an aliquot of enriched sample with a dioxane scintillator solution and counting the resulting cocktail in a dual channel liquid scintillation spectrometer.

Prehydrogen bomb tritium concentrations in precipitations were low and not directly measurable; therefore fractional electrolysis was used to increase the tritium concentration to easily measurable levels. Samples are placed in a cell fitted with nickel and stainless steel electrodes and a potential placed across the cells results in H_2 and O_2 evolution at the electrode surfaces. Since protium is preferentially reduced, tritium tends to be enriched in the solution. The increase of tritium in solution thus becomes a function of volume reduction during electrolysis, and the overall tritium increase is expressed in an enrichment factor. Knowledge of the enriched sample's activity and the enrichment factor permits calculation of the original tritium concentration of the water sample.

The natural production of tritium in the atmosphere and its subsequent incorporation into the water molecule gives the hydrologist a useful tool for ground-water dating and associated studies. The low concentrations of this natural tritium requires a reproducible enrichment process and a sensitive means of detecting the low energy beta emission. The process described fulfills these requirements and is readily adaptable to low cost analysis and large-scale production.

REFERENCES

Alvarez, L. W., and Cornog, R., 1939, He[3] in helium: Phys. Rev., v. 56, p. 613.

Bell, C. G., Jr., and Hayes, F. N., 1958, Liquid scintillation counting: New York, Pergamon Press, p. 3–6.

Bigeleisen, Jacob, 1960, Correlation of tritium and deuterium isotope effects: Brookhaven Natl. Lab. 5314.

Bush, E. T. [no date], General applicability of the channels ratio method: Anal. Chemistry, v. 35, p. 1024.

Carlston, C. W., and Thatcher, L. L., 1962, Tritium studies in the United States Geological Survey, *in* Tritium in the physical and biological sciences, v. 1, *of* Symposium on the detection and use of tritium in the physical and biological sciences, Vienna 1961, Proc.: Internat. Atomic Energy Agency, p. 75–81.

Faltings, V., and Harteck, P., 1950, Tritium content of the atmosphere: Zeitschr. Naturforschung, v. 5a, p. 438–439.

Kaufman, S., and Libby, W. F., 1954, Natural distribution of tritium: Phys. Rev., v. 93, p. 1337.

Ostlund, H. G., and Werner, O. E., 1962, The electrolytic enrichment of tritium and deuterium for natural tritium measurements, *in* Tritium in the physical and biological sciences, v. 1, *of* Symposium on the detection and use of tritium in physical and biological sciences, Vienna 1961, Proc.: Internat. Atomic Energy Agency, p. 95–103.

Roy, L. P., 1962, Influence of temperature on the electrolytic separation factor of hydrogen isotopes: Canadian Jour. Chemistry, v. 40, p. 1452.

Urey, H. S., 1933, Separation and properties of the isotopes of hydrogen: Sci., v. 78, p. 566.

Werbin, Harold, Chaikoff, I. L., Imada, M. R., 1959, A rapid and sensitive method for determining H³-water in body fluids by liquid scintillation spectrometry: Soc. Experimental Biology Medicine Proc., v. 102, p. 8.

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