

LIQUID SCINTILLATION COUNTING
RECENT APPLICATIONS AND DEVELOPMENT
VOLUME II. SAMPLE PREPARATION AND APPLICATIONS

A COMPUTER ALGORITHM TO CALCULATE
TRITIUM CONCENTRATIONS IN
ENVIRONMENTAL WATER

Charles N. Cawley

Department of Design and Environmental Analysis
Cornell University
Ithaca, New York

Ervin J. Fenyves
D. Blair Spitzberg

Graduate Program in Environmental Sciences
University of Texas at Dallas
Richardson, Texas

An algorithm implemented in PL/1 to calculate tritium concentrations in environmental waters using a new method recently developed by the authors is described in detail. The new liquid scintillation counting method is a double isotope, external standard count procedure which eliminates the background by measuring tritium free water samples and applying a difference methods. The computer program developed for this method calculates from the count rates measured in two channels (tritium and carbon-14 channels) and the external standard count rates the concentration of tritium in the samples together with the associated statistical error.

I. INTRODUCTION

Precise liquid scintillation counting (LSC) methods to measure environmental tritium concentrations generally require enrichment of the samples (Ampur, 1974, Brown and Grummitt, 1956, Gentry *et al.*, 1973, Sauzay and Schell, 1972, Theodorsson, 1974). Enrichment by either electrolytic or

thermal diffusion methods require the construction of rather large and expensive equipment and their operation requires substantial energy. Ion exchange columns and fractionalization process have been used also (Calf, 1969, Shigematsu, 1969, Taylor and Schwarz, 1977, Tomono *et al.*, 1972). If enrichment is used, estimating the degree of enrichment becomes a problem, particularly when using the latter methods.

A new method for measuring environmental tritium levels without enrichment was recently developed by the authors (Cawley *et al.*, 1980). This method is basically a double isotope, external standard count procedure which eliminates the background by measuring tritium free water samples ("dead water" samples) and applying a difference method.

II. DESCRIPTION OF THE METHOD

During this investigation a Packard Tricarb Model 3380 Liquid Scintillation Counter has been used. In order to minimize any differences due either to reagents or to preparation of the liquid scintillator, a proprietary product, "Monophase-40" by Packard Instrument Company has been selected. Because of the long count periods and the problems of scintillant migration into and through the walls of plastic vials, low potassium glass vials have been used throughout the investigation. To improve the statistics of the measurement, 15 vials of the sample are counted. In order to remove natural quenching agents and heavy metal radionuclides from the environmental waters (particularly, lead-210 which emits a beta particle which has a maximum energy comparable to tritium), the samples are doubly glass distilled. Therefore, it is assumed that the only radionuclides present in the sample plus cocktail are tritium and carbon-14.

Sample preparation consists of:

1. Adding 4.0 ml of doubly distilled water to 16.0 ml of "Monophase-40" and
2. Mixing thoroughly before dark conditioning for a minimum of four hours in the refrigerated counter.

To determine if periodicity or drift is detectable in the count rate, samples have been counted with readouts every ten minutes for up to three weeks. A detailed analysis

of the data using chi-square, runs tests, and Fourier analysis showed that neither drift nor periodicity is present in the instrument.

The efficiency of the counter was determined by using external standards. To measure the efficiency for counting tritium and carbon-14 quenched tritium and carbon-14 standards were used and the external count rates vs. gain curves have been plotted varying the spectral ranges of both isotopes (Figure 1). From these curves the optimal range and gain settings for counting tritium and carbon-14 in two separate channels were determined as:

1. In Channel I (tritium channel), discriminator settings of 100-300 and a gain of 100 percent, and
2. In Channel II (carbon-14 channel), discriminator settings of 100-1000 and a gain of 6 percent.

Thus, in order to minimize the contribution of carbon-14 to the count rate in Channel I, a narrow, low-energy region of the tritium spectrum is being counted (Figure 2).

The most delicate part of the method developed to measure environmental tritium levels is the elimination of the background. A difference method has been applied for this purpose using "dead water" samples, i.e. tritium free water samples obtained from National Bureau of Standards.

The environmental and dead water samples exhibit quenching characteristics falling into the range of 0.5 - 0.6 quenched standards (Packard Instrument Co.) for tritium and carbon-14. During each cycle an efficiency calibration using the quenched standards is made. A cycle consists of counting the 15 sample vials, 2 or more vials of dead water, and the 4 quenched standards (two carbon-14 and two tritium standards). The selected count period is 20 minutes.

A set of four equations describe the contribution of tritium and carbon-14 to the total count rates in the channels optimized for counting each of the two isotopes.

Channel I (tritium channel):

$$A = \epsilon_H^I \left[e_H + d_H \right] + \epsilon_C^I \left[a_C + b_C \right] \quad (1)$$

$$B = d\epsilon_H^I \left[d_H \right] + d\epsilon_C^I \left[a_C + c_C \right] \quad (2)$$

Channel II (carbon-14 channel):

$$C = \epsilon_C^{II} \left[a_C + b_C \right] \quad (3)$$

$$D = d\epsilon_C^{II} \left[a_C + c_C \right] \quad (4)$$

where

- A = count rate in Channel I for sample,
 B = count rate in Channel I for dead water,
 C = count rate in Channel II for sample,
 D = count rate in Channel II for dead water,
 a_C = contribution of carbon-14 to the count rate in the scintillator and vial,
 b_C = contribution of carbon-14 to the count rate in the sample,
 c_C = contribution of carbon-14 to the count rate from the dead water,
 d_H = contribution of tritium to the count rate in the scintillator and vial,
 e_H = contribution of tritium to the count rate in the sample to be measured,
 ϵ_H = efficiency for counting tritium in Channel I in sample,
 ϵ_H^I = efficiency for counting carbon-14 in Channel I in sample,
 ϵ_C^I = efficiency for counting carbon-14 in Channel II in sample,
 $d\epsilon_H^I$ = efficiency for counting tritium in Channel I in dead water,
 $d\epsilon_C^I$ = efficiency for counting tritium in Channel I in dead water,
 $d\epsilon_C^{II}$ = efficiency for counting carbon-14 in Channel II in dead water.

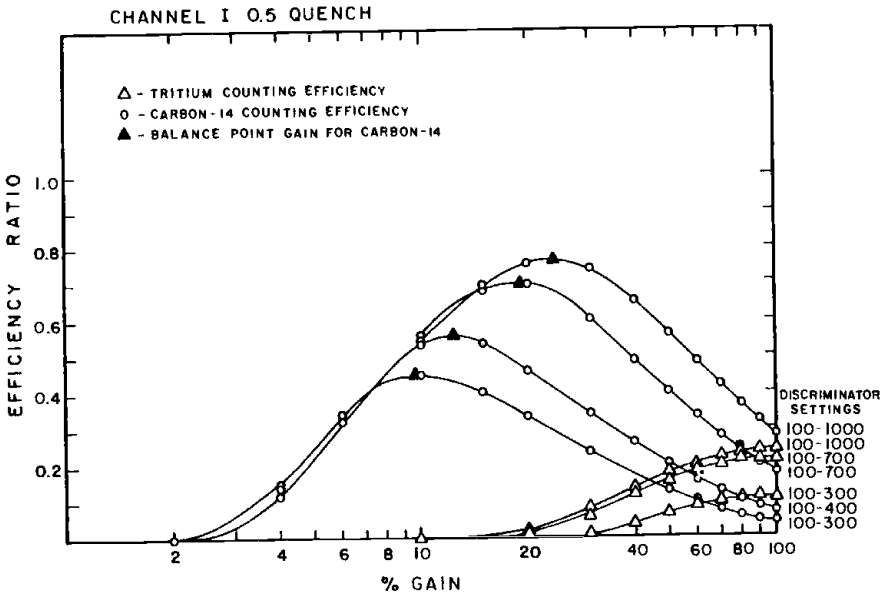


FIGURE 1: Tritium and Carbon-14 Efficiencies for the 0.5 Quenched Standards as a Function of Discriminators and Gain Settings

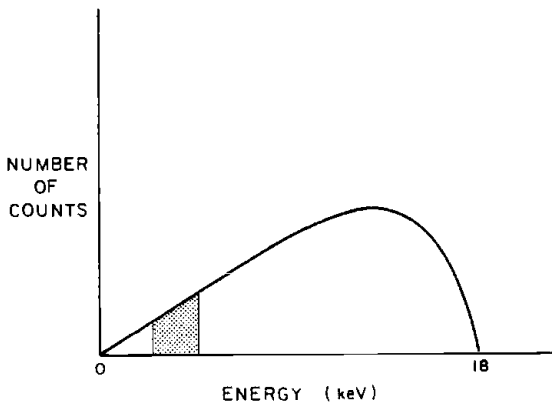


FIGURE 2: Low Energy Region of Tritium Spectrum by Discriminators and Gain Settings

Solving the above equations for e_H ,

$$e_H = \frac{1}{\epsilon_H^I} \left[A - \frac{1}{d\epsilon_H^I} \left(\epsilon_H^I \cdot B - \frac{\epsilon_H^I \cdot d\epsilon_C^I \cdot D}{d\epsilon_H^I} \right) - \frac{\epsilon_C^I \cdot C}{\epsilon_C^{II}} \right] \quad (5)$$

Each of the count rates, A, B, C, and D in the preceding equation has an associated error, $\delta A, \delta B, \delta C$ and δD . From the errors, the combined error for the tritium count rate, δe_H , is calculated as:

$$\delta e_H = \frac{1}{\epsilon_H^I} \left[(\delta A)^2 + \left(\frac{\epsilon_H^I}{d\epsilon_H^I} \right)^2 \cdot (\delta B)^2 + \left(\frac{\epsilon_H^I \cdot d\epsilon_C^I}{d\epsilon_H^I \cdot d\epsilon_C^{II}} \right)^2 \cdot (\delta D)^2 + \left(\frac{\epsilon_C^I}{\epsilon_C^{II}} \right)^2 \cdot (\delta C)^2 \right]^{1/2} \quad (6)$$

The errors associated with estimating the efficiencies in each channel are much smaller than the errors associated with the count rates in each channel. Therefore, the errors of the efficiencies are neglected. It is assumed that the tritium content of the dead water is zero (National Bureau of Standards certifies that it is less than .6 pCi/l).

This method of measuring environmental tritium requires neither the large capital costs nor the large operating expenses of the enrichment techniques. While counting times may be long, the sample requires minimal preparation.

It is a simple, reliable and inexpensive method to estimate environmental tritium with acceptable precision (Table I).

TABLE I: Selected Measurements of Tritium Concentration in the Brazos River Basin

Sample Locatio	Tritium concentration (in pCi/l)	Measurement Time (in Minutes)
Brazos River at Glen Rose	160 ± 40	12500
Brazos River Above Lake Whitney	382 ± 42	9750
Commanche Peak Reservoir	117 ± 25	20300

III. DESCRIPTION OF ALGORITHM

The count rates used in Eqs. (1 - 6) are the weighted averages of the count rates obtained by measuring 15 vials for each sample for multiple 20 minute count periods. This calculation, the efficiency calibration, and the relatively complicated evaluation of the tritium count rate and its error using Eqs. (5 - 6) justifies the development of a computer algorithm.

A. Data Organization

The numerous short counting periods, the large number of vials coupled with the efficiency calibration data from the external standard count, the quenched standards, and the vials with mixtures of either scintillator-sample or scintillator-dead water make this a program of data organization and reduction. To eliminate the need to change the source program due to different numbers of observations from one sample run to another, the PL/1 feature of dynamic allocation of storage has been used. This allows the user to define the dimensions of the arrays for the input data. It is not uncommon for the arrays for the quenched standards, the dead water, and the sample data to have different dimensions.

B. *Arrays for the Quenched Standards*

Observations for the quenched tritium standards are placed in arrays: the external standard count (ESC), the counting time, and the counts in Channel I. For the quenched carbon-14 standards, the arrays are: ESC, the counting time, the counts in Channel I, and the counts in Channel II.

C. *Initial Computations*

The data from the quenched standards and the AES for the sample and dead water are used to calculate the efficiency of the system for counting:

1. Tritium in Channel I
2. Carbon-14 in Channel I and
3. Carbon-14 in Channel II

Through the external standard counts of the quenched standards and those of the dead water and of the sample, the counting efficiencies are calculated by subroutine calls.

Once the efficiencies for the sample and the dead water and their respective count rates in Channels I and II are determined, the tritium concentrations in pico-Curies per liter and the associated error may be calculated for each sample vial.

D. *Final Computations*

The structure of the algorithm is a section of preliminary calculations followed by an iterative loop which calculates the measurement and the associated error for each vial. At the end of the loop, preliminary calculations are made to measure the contribution each vial makes to the weighted average and error for the sample. The last program segment calculates the weighted average and error (Cochran, 1954, Cochran and Carroll, 1953, Hinkley, 1979, James, 1956).

E. *Program Format*

Figure 3 is a detailed flow chart of the algorithm. The only problems in implementing the algorithm are those related to intermediate storage of the variables. Eq. (5) the expansion for e_H , the tritium count rate has a rather complex form.

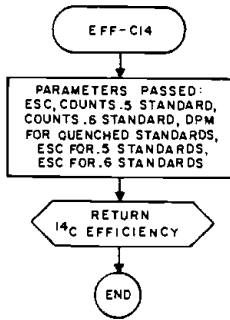
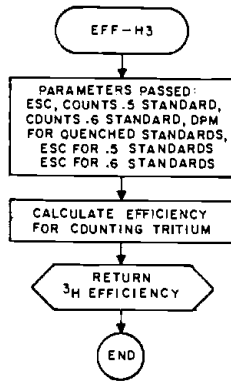


FIGURE 3B: Computer Algorithm (Subroutine to Calculate Counting Efficiencies)

To solve the problems of intermediate storage, Eq. (1) is expressed by using components P, R and S.

$$P = \left[\frac{\epsilon_H^I}{d\epsilon_H^I} \right] B \quad (9)$$

$$R = \frac{\begin{bmatrix} \epsilon_H^I \\ \epsilon_C^I \end{bmatrix} \begin{bmatrix} d\epsilon_C^I \\ d\epsilon_H^I \end{bmatrix}}{\begin{bmatrix} d\epsilon_H^I \\ d\epsilon_C^I \end{bmatrix} \begin{bmatrix} \epsilon_C^{II} \\ \epsilon_H^{II} \end{bmatrix}} D \quad (10)$$

$$S = \frac{\begin{bmatrix} \epsilon_C^I \\ \epsilon_C^{II} \end{bmatrix}}{\begin{bmatrix} \epsilon_C^I \\ \epsilon_C^{II} \end{bmatrix}} C \quad (11)$$

Eq. (5), thus, becomes:

$$e_H = \frac{A - (P - R) - S}{\epsilon_H^I} \quad (12)$$

Using this form for calculating e_H removes the errors related to the storage of intermediate variables.

REFERENCES

- Ampur, S. (1974). *Int. J. of Appl. Rad. Isotopes* 25, 573.
 Brown, R. M. and Grummitt, W. E. (1956). *Can. J. Chem.* 34, 220.
 Calf, G. E. (1969). *Int. J. of Appl. Rad. Isotopes*, 26, 177.
 Cawley, C. N., Fenyves, E. J., Spitzberg, D. B., and Wiorkowski, J. (1980) To be published.
 Cochran, W. G. (1954) *Biometrics* 10, 101.
 Cochran, W. G. and Carroll, S. P. (1953). *Biometrics* 9, 447.
 Gentry, C., Schott, R., LeFevre, H., Froment, G., and Sanson, C. (1973). In *Tritium* (A. A. Moghissi and M. W. Carter, eds.) Messenger Graphics, Phoenix, Arizona.
 Hinkley, D. V. (1979) *Scan. J. Stat.* 6, 37.
 James, G. S. (1956) *Biometrika* 43, 301.
 Sauzay, G. and Schell, W. R. (1972). *Int. J. of Appl. Rad. Isotopes* 23, 25.
 Shigematsu, A., Toyohara, M. and Tomono, K. (1969). *Nuc. Instr. Meth.* 76, 301.

- Taylor, C.B. and Schwarz, P. (1977). *Int. J. of Appl. Rad. Isotopes* 28, 605.
- Theodorsson, P. (1974). *Int. J. of Appl. Rad. Isotopes* 25, 97.
- Tomono, K., Tokunaga, N., Koyana, A., Toyohara, M., and Shigematsu, A. (1972). *Nuc. Instr. Meth.* 102, 257.