Environmental isotopes in New Zealand hydrology

2 Standards, measurement techniques, and reporting of measurements for oxygen-18, deuterium, and tritium in water

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Abstract The present internationally adopted measurement scales and standards for $^{18}O/^{16}O$, D/H, and T/H in environmental waters are defined and explained. Present measurement techniques at Institute of Nuclear Sciences, DSIR, Lower Hutt, are summarised with appropriate reference to earlier procedures. For $^{18}O/^{16}O$ determination, water samples are equilibrated with CO_2 gas which is then analysed by mass spectrometry. For D/H measurement, the water is reduced to hydrogen which is also analysed by mass spectrometry. Levels of T/H in waters of the South Pacific region are so low that β-particle counting must be preceded by electrolytic enrichment to attain good accuracy. Sampling procedures are described.

Keywords Stable isotopes; hydrology; water; mass spectroscopy; oxygen-18; deuterium; tritium; measurement; samples; sampling; standards; scintillation counters.

INTRODUCTION

This paper, the second in the series, describes our techniques for measurement of the relative abundances of the stable isotopes, oxygen-18 and deuterium, and the radioactive isotope, tritium, in water. Of the utmost importance are the international standards and measurement scales which enable results from different laboratories to be compared, and the procedures used within our laboratory to keep the measurements standardised.

Received 19 November 1980; accepted 13 April 1981

In environmental waters, $^{18}O/^{16}O$ ratios vary in the range (1900–2000) ppma, while for D/H the range is (80–160) ppma (where ppma is atomic parts per million). Most waters lie within the upper 20% of these ranges, the lower 80% being occupied only by upper tropospheric–stratospheric water vapour and polar snow and ice. For effective application in hydrological studies, measurement accuracy of c. 0.2 ppma is required for both isotopes. This accuracy is not obtained on a routine basis by attempting to make absolute measurements; but the *differences* between the isotopic ratios of gases can be determined with the required precision in mass spectrometers of a suitable type; unknown gas samples can be related to laboratory reference gases, which have themselves been accurately calibrated against internationally accepted standards and measurement scales. It is for this reason that oxygen-18 and deuterium contents are normally expressed as fractional differences from an international standard water (see definitions below). The mass-spectrometric comparison with the reference gas is made by alternately switching between the sample and reference gases admitted, at equal pressures, to the analysis chamber and recording the differences between the collector currents for the ions containing the minor isotopes.

Because the measurement gas must be far away from its condensation temperature, water vapour is not suitable as a mass-spectrometric gas; an additional complication is the difficulty of achieving selective ionisation to H_2O^+ without interference due to the formation of ions such as OH^+ and O^+. It is therefore necessary to perform chemical preparations which produce more suitable measurement gases whose isotopic composition is accurately related to that of the water sample. For $^{18}O/^{16}O$ measurement, carbon dioxide is equilibrated with the water sample and then admitted to the mass spectrometer; for D/H analysis, the water is quantitatively reduced to hydrogen.

Thermonuclear tritium has been the dominant source of HTO in the environment since 1954–55, and concentrations in New Zealand precipitation peaked at a yearly average of TR = 38 in 1964–65 (where TR = Tritium Ratio, and TR = 1 corresponds to a T/H ratio of 10^{-18}). Levels have

since steadily declined as the thermonuclear HTO is removed from the atmosphere to the much larger, and consequently very tritium-diluted, ocean reservoir. Special significance attaches to the range below TR = 1; here one tries to determine whether predominantly very old waters contain any newer water at all. Old in this sense refers to the period elapsed since recharge: this is important in establishing the time scale of vertical ocean mixing, recharge and changes in flow patterns in geothermal areas, and the circulation patterns of many groundwaters. The range below TR = 1 poses special measurement problems which are discussed in the following sections.

The quality of the sample is determined by the sample collection procedures. These are described below.

STABLE ISOTOPE MEASUREMENT

International standards and measurement scales

The presently accepted international standards and measurement scale for $^{18}O/^{16}O$ and D/H in waters were established following a Consultants' Meeting on Stable Isotope Standards and Intercalibration in Hydrology and Geochemistry, held at the International Atomic Energy Agency (IAEA), Vienna, in 1976 (Gonfiantini 1978). A linear measurement scale is used, bounded by 2 distilled-water standards V-SMOW (Vienna Standard Mean Ocean Water) and SLAP (Standard Light Antarctic Precipitation), which respectively lie close to the highest and lowest $^{18}O/^{16}O$ and D/H ratios encountered in environmental waters.

Before the 2-standard scale was introduced, stable isotope ratios R (= $^{18}O/^{16}O$ or D/H) were conveniently expressed as δ values, representing the difference in parts per thousand between the isotope ratio of a sample and that of the single standard V-SMOW, according to

$$\delta_{\text{V-SMOW}} = \left(\frac{R_{\text{sample}}}{R_{\text{V-SMOW}}} - 1 \right) \times 1000 \qquad (1)$$

A linear δ scale therefore corresponds to a linear isotope ratio scale. From this point the subscript 'V-SMOW' will be dropped, and δ signifies $\delta_{\text{V-SMOW}}$ defined by Equation 1.

The change to the scale based on the 2 standards V-SMOW and SLAP was made because evidence of intercomparison data showed that it improved the coherence of results obtained by different laboratories. At each laboratory, a combination of experimental factors causes measured δ values (δ_m) to differ systematically from the true values defined by Equation 1; δ_m is related to δ by a factor k close to unity, which is essentially constant throughout the entire range of δ encountered, but which may vary between mass spectrometers

$$\delta = k\delta_m \qquad (2)$$

The adoption of assigned δ values for SLAP allows a laboratory constant k' to be determined from control measurements of V-SMOW and SLAP according to

$$\delta'(\text{SLAP}) = k'\delta_m(\text{SLAP}) \qquad (3)$$

where δ'(SLAP) is the assigned δ value. The corrected result for a sample (δ') is obtained by substituting this value of k' in Equation 2.

The selected values $\delta^{18}O(\text{SLAP}) = -55.5‰$ and $\delta D(\text{SLAP}) = -428‰$ are based on results submitted by many laboratories (Gonfiantini 1978).

The following absolute isotope ratio measurements have been reported for V-SMOW and SLAP (Hagemann et al. 1970, Baertschi 1976):

$^{18}O/^{16}O$ of V-SMOW = $(2005.20 \pm 0.45) \times 10^{-6}$
D/H of V-SMOW = $(155.76 \pm 0.05) \times 10^{-6}$
D/H of SLAP = $(89.02 \pm 0.05) \times 10^{-6}$

The value δD(SLAP) obtained from these results is -428.5 ± 0.1, but the meaning of the error is unclear.

To fill a practical need for a third reference water sample with isotopic composition approximately midway between V-SMOW and SLAP, another water was prepared by IAEA in 1977, and named GISP (Greenland Ice Sheet Precipitation). Mean values from many laboratories for this standard are $\delta^{18}O(\text{GISP}) = -24.82‰$ and $\delta D(\text{GISP}) = -189.9‰$ (Gonfiantini pers. comm. 1981).

Internal laboratory standardisation

The international standards V-SMOW and SLAP are now distributed in sealed glass vials containing aliquots of c. 25 mL; this quantity is too small for use in routine calibrations. Each measuring laboratory must therefore prepare adequate supplies of its own laboratory standard waters, which should be carefully compared with V-SMOW and SLAP every 3 years or so.

We presently use 4 working standards in routine measurements: INS-3 (prepared 1971) is a distilled ocean water and therefore very close to V-SMOW in isotopic composition; INS-5 (1971) is distilled Antarctic plateau snow, close to SLAP; INS-4 (1971) is distilled Antarctic coastal snow, close to GISP; INS-8 (1974) is a distilled Hutt Valley tap water used in routine deuterium measurement. A new working standard, INS-9, will shortly replace INS-4 which is now in short supply. Results of our measurements in 1972 and 1977 of these standards, SLAP, and GISP relative to V-SMOW are given in Table 1.

Table 1 Results of stable isotope measurements of INS and international water standards relative to V-SMOW. Standard deviations and numbers of measurements (in parentheses) are shown.

Standard	1972 $\delta_o D$ (‰)	1977 $\delta_o D$ (‰)	1977 δD (normalised)	1972 $\delta^{18}_o O$ (‰)	1977 $\delta^{18}_o O$ (‰)	1977 $\delta^{18}O$ (normalised)
INS-3	2.0±0.7 (20)	1.2±0.4 (7)	1.2	0.54±0.10 (8)	0.10±0.01 (8)	0.10
INS-4	-255.7±2.1 (11)	-256.2±0.6 (8)	-257.8	-32.46±0.06 (8)	-32.59±0.11 (8)	-32.50
INS-5	-396.8±2.4 (12)	-390.6±0.9 (4)	-393.0	-50.72±0.08 (8)	-50.46±0.10 (8)	-50.31
INS-8	-	-48.3±0.6 (4)	-48.7	-	-	-
INS-9	-	-130.9±0.4 (5)	-131.7	-	-17.52±0.07 (8)	-17.46
GISP	-	-188.7±0.9 (8)	-189.9	-	-24.84±0.02 (8)	-24.77
SLAP	-428.3±2.3 (16)	-425.4±0.7 (7)	(-428)	-55.95±0.15 (8)	-55.66±0.02 (8)	(-55.5)
NBS-1	-45.8±0.8	-	-	-7.89±0.07	-	-
NBS-1A	-183.7±1.6	-	-	-24.44±0.06	-	-

All results submitted for publication after 1977 are on the 2-standard scale (shown by 1977 normalised results in Table 1).

The bulk supplies of the above working standards are stored in sealed glass containers of up to 20 litre capacity. As required, smaller quantities are removed from these containers for routine use. This procedure guards against any shifts or drifts in the isotopic composition of our laboratory standards.

Origin of international standards

SMOW was originally a defined standard, whose isotopic composition was close to mean ocean water, but defined relative to the actual reference water NBS-1 (Craig 1961). Craig later prepared an actual ocean water standard by mixing distilled ocean water with small amounts of other waters to bring the isotopic composition as close as possible to that of defined SMOW; this water has the same $^{18}O/^{16}O$ ratio as defined SMOW, but a slightly lower D/H ratio (by 0.2‰). The discrepancy in D/H is 5 to 10 times lower than the routine experimental error in most laboratories; therefore this water, which was transferred to IAEA in 1968 for storage and distribution, and is now known as V-SMOW, is for all practical purposes identical to the old defined SMOW.

To ensure continuity, sealed portions of V-SMOW, SLAP, and GISP are now held by IAEA at 2 separate locations in Vienna, and also at the U.S. National Bureau of Standards in Washington, D.C.

Oxygen-18 measurement technique

Sample preparation

Water vapour is so close to its condensation temperature that it is unsuitable as a mass spectrometric analysis gas; an additional problem is unwanted production of OH^+ and O^+ ions in the ion source. Epstein & Mayeda (1953) introduced a technique by which CO_2 is equilibrated with sample water at constant temperature, and the equilibrated CO_2 is then introduced to the spectrometer for $\delta^{18}O$ determination; the oxygen exchange between CO_2 and H_2O occurs through the reactions

$$CO_2(\text{gas}) \rightleftharpoons CO_2(\text{dissolved})$$

$$CO_2(\text{dissolved}) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

In a non-shaking system, the reaction rate is controlled by the time constant of the gas exchange reaction, and isotopic equlibrium is typically reached over many hours. If the system is shaken, the hydration reaction is rate-controlling and isotopic equilibrium takes less than an hour. Within any set of samples, the $^{18}O/^{16}O$ ratios between CO_2(gas) and water differ by the same factor for all samples, including a number of laboratory standard waters in all sets. The difference in $^{18}O/^{16}O$ is then established in the mass spectrometer between each equilibrated CO_2 and a reference CO_2; the end result of the measurements is a set of measured $\delta^{18}O$ values (relative to V-SMOW) for the unknown samples, supported and calibrated by control values for the laboratory standard waters.

We presently use a non-shaking equilibration system in which twenty 5 mL water samples (including usually 2 each of 2 laboratory standard waters of widely differing δ values) can be run simultaneously (Fig. 1). Full details of the principles of the equilibration method and the procedures are given in Taylor (1973).

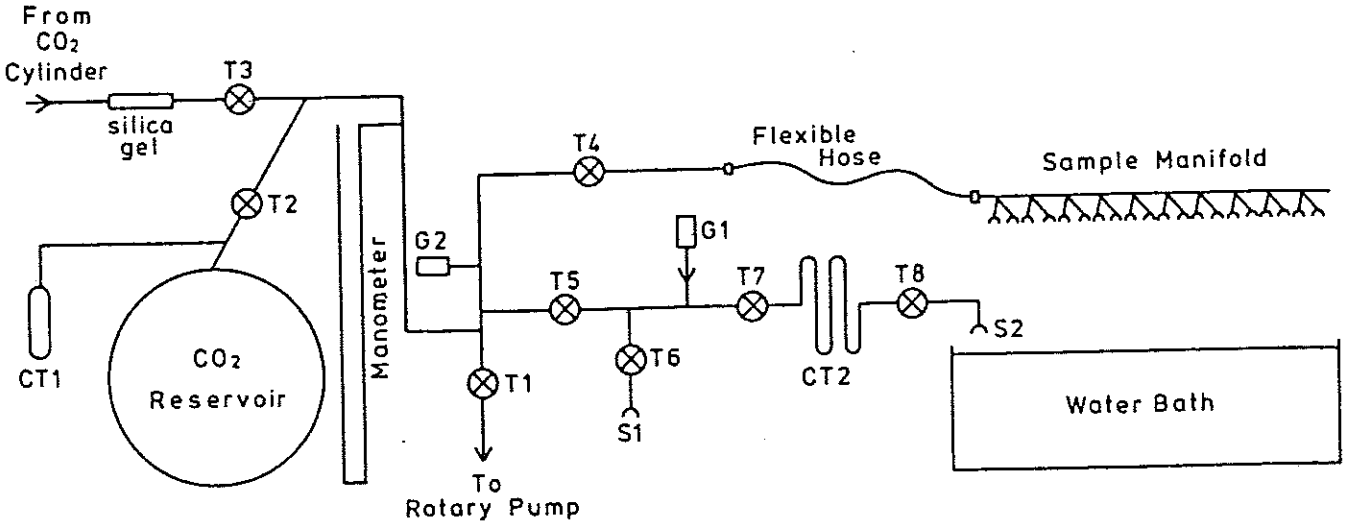

Fig. 1 Schematic diagrams of the vacuum system for equilibration of CO_2 and H_2O for $^{18}O/^{16}O$ ratio measurement. T1–T8 are vacuum valves; G1, G2 are Pirani pressure gauges; CT1, CT2 are cold traps; and S1, S2 are take-off points. CO_2 from the CO_2 reservoir is added to water samples in the 20 bottles attached to the sample manifold. The water bath keeps the bottles at constant temperature. After 2 days, each bottle in turn is attached to S2, and a sample of the CO_2 is extracted for mass spectrometric analysis.

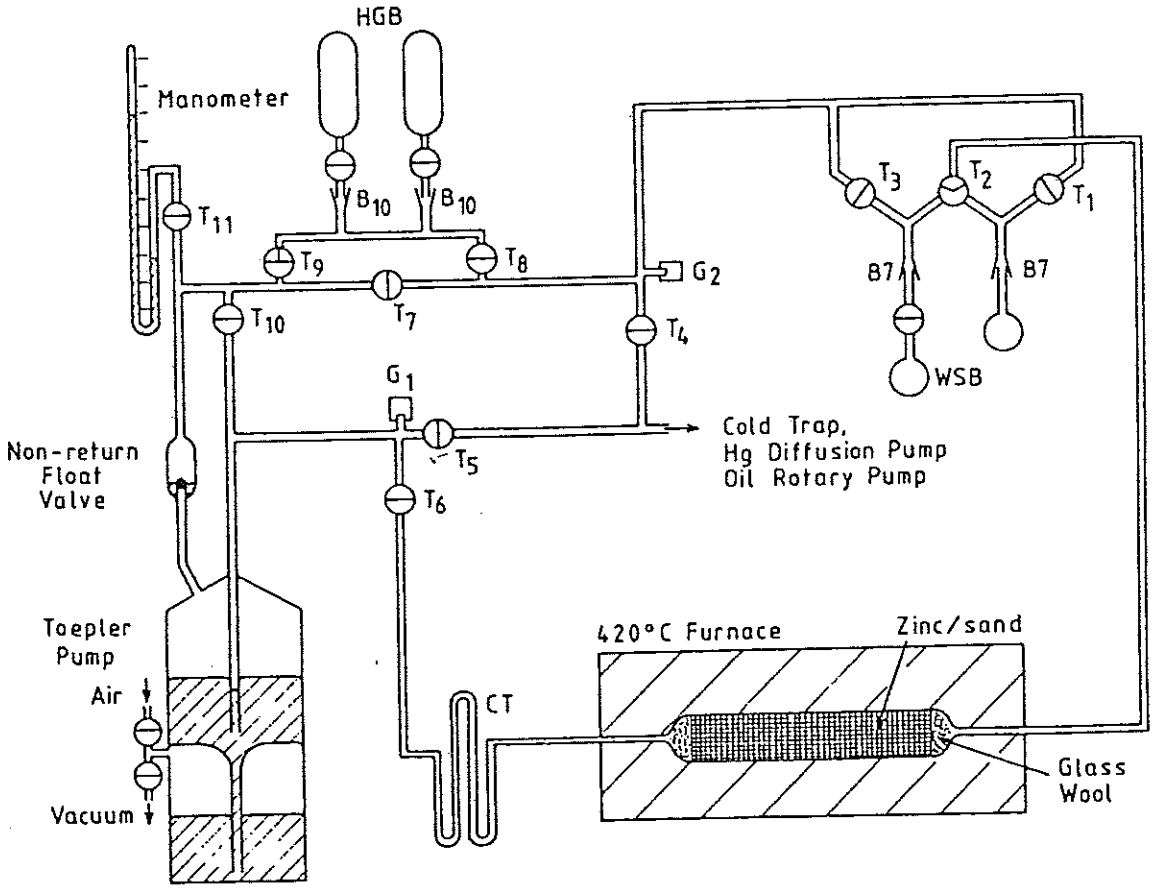

Fig. 2 Schematic diagram of the vacuum system for conversion of H_2O to H_2 for D/H ratio measurement by mass spectrometry. T1–T11 are vacuum valves; WSB is a water sample bulb; HGB are hydrogen gas bottles; G1, G2 are thermocouple vacuum gauges; and CT is a cold trap. Water is allowed to expand across the zinc/sand mixture from WSB and the resulting hydrogen is pumped by the Toepler pump into HGB.

Mass spectrometry

The mass spectrometer uses the double collection technique (Nier 1947), with rapid switching between sample and reference gas admitted at equal pressures to the analysing chamber (McKinney et al. 1950). At present we can measure mass 44 ($^{12}C^{16}O^{16}O$) simultaneously with either mass 45 ($^{13}C^{16}O^{16}O$ + $^{12}C^{16}O^{17}O$) or mass 46 ($^{12}C^{16}O^{18}O$ + $^{13}C^{16}O^{17}O$), but we plan to install a triple collector for simultaneous measurement of all 3 masses. (In $\delta^{18}O$ measurements, mass 45 enters only in correction terms.)

Peak height differences between sample and reference CO_2 are measured over approximately 10 min. The method and procedures are discussed in detail by Taylor & Hulston (1972); since then the only changes have been the installation of microprocessor control (Spedding & Plummer 1980; Stewart & Hulston 1980) to replace the calculator previously used for data acquisition (Hulston et al. 1973), and minor changes in the calculation procedures. In our method the isotopic composition of the reference gas on the mass spectrometer is not an important parameter; the reference gas can be any pure CO_2 gas which remains essentially constant in isotopic composition over the measurement period of a set of samples and is reasonably close in $^{18}O/^{16}O$ ratio to the unknown samples. The critical reference parameters for any set of samples are those of the CO_2 gas after equilibration with the laboratory standard waters.

Deuterium measurement technique

Sample preparation

About 15 μL of water is quantitatively reduced to hydrogen in a glass vacuum system (see Fig. 2) by slow evaporation through a zinc/sand matrix in a cylindrical Pyrex tube heated to 420–440°C (Friedman 1953; Lyon & Cox 1980). We use a 2/3 by weight mixture of Fisher zinc granules, 30 mesh, and BDH "sand purified by acid", 40–72 mesh. Operation in the temperature range above the zinc melting point (419.4°C) allows all the zinc to participate in the reaction; below the melting point only a surface layer of zinc participates, and the lifetime of a tube filling is much shorter. In the range 420–440°C, the just-molten zinc does not drain through the sand, and the whole matrix presents a uniform gas flow resistance which smoothly controls the reaction rate. The pressure gradient through the Zn/sand matrix is maintained by Toepler-pumping the hydrogen into an evacuated glass bottle. After completion of the reaction, the hydrogen gas is partially recirculated to ensure complete isotopic mixing, and is then pumped back into the glass bottle. This precaution is required because the slowly evaporating water becomes steadily enriched in deuterium; therefore, at the end of the reaction, the small residue of hydrogen on the reaction tube side of the Toepler-pump is substantially enriched in deuterium and must be mixed again with the hydrogen in the sample bottle to ensure that the latter has the same D/H ratio as the initial water sample. The complete reaction takes about 40 min.

Uranium has been used in several laboratories for the reduction reaction, and we have just finished testing a new preparation system based on uranium (Stewart & James 1981). 5 μL samples of water are syringed into the system, distilled, allowed to react with uranium turnings at 700°C (in a tube of Vycor glass), and the hydrogen produced is adsorbed onto charcoal cooled by liquid nitrogen. With this system, sample throughput has increased, and 'memory' between samples has decreased.

Mass spectrometry

The mass spectrometric procedure is in most respects very similar to that used in the $\delta^{18}O$ measurements, with mass-2 (H_2^+) and mass-3 (HD^+ + H_3^+) being collected simultaneously. The presence of H_3^+ necessitates a correction procedure; H_3^+ is produced by hydrogen attachment to H_2^+ in the ion source, and therefore increases with H_2 pressure. The correction procedure involves measurement of the mass-3 signal at several pressures and extrapolation back to zero pressure. The H_3^+ contribution can be minimised by special design of the ion source, with a positive ion repeller voltage which repels the H_2^+ ions as rapidly as possible out of the ionisation region to reduce hydrogen attachment to H_2^+. In our Micromass 602C spectrometer, the H_3^+ contribution is about 5% at the routine measurement pressure; in the INS-built instrument (Hulston 1962) used prior to 1975, the contribution was 30%. The current instrument has microprocessor control.

On-line sample processing

A sample system on-line with the mass spectrometer has been investigated (Stewart & Hulston 1977). Water vapour derived from a hot probe (Thurston 1971) is passed over zinc or uranium, and the H_2 is fed directly into the mass spectrometer for D/H analysis. A much greater sample throughput should be obtainable when this method is developed.

TRITIUM MEASUREMENTS

Measurement methods

Environmental tritium can be measured either by gas or liquid scintillation counting of the decay electrons, or alternatively by accumulating the

daughter ^{3}He atoms over a period of weeks or months and then measuring these in a specially designed mass spectrometer (Clarke et al. 1976). The latter method was only recently developed; while it offers certain advantages, it is extremely expensive to establish. Tritium measurements have been made at INS since about 1960; we still use the counting method. For many years Geiger-counting of hydrogen gas was preceded by a 3-stage electrolytic enrichment (Taylor et al. 1963). Our present technique, described below, comprises a single electrolytic enrichment stage, followed by liquid scintillation counting.

Measurement units

Until recently, tritium concentrations in environmental waters were predominantly expressed as Tritium Units (TU) at the date of sample collection t_c, where 1 TU is defined as a T/H ratio of 10^{-18}. Although the inconsistency of using the word 'Unit' to express a ratio has long been recognised, a recommendation of the International Commission of Radiological Units and Measurements (1963) to use instead the term Tritium Ratio (TR) was never followed, perhaps because it was recognised that the inclusion of the constant 10^{-18} in the definition of TR means that it is not strictly a ratio either. Adoption of SI specific activity units (Bq/(kg H_2O)), used now in health physics and other fields, is not favoured by most workers in environmental studies, because of the problems of relating new data to the large body of data already published and well-understood in TU. Following consideration of the problem by an advisory panel at IAEA, Vienna (1979), Taylor & Roether (1981) have recommended a switch from TU to TR as being the best choice in the circumstances. This shift is one of nomenclature only; no numerical conversions are involved.

Conversion from TR (or TU) to SI specific activity units is achieved using

$$R(t_c) = 10^{18} \times \frac{M}{2L} \times \frac{a(t_c)}{\lambda} \qquad (4)$$

where $R(t_c)$ = Tritium Ratio, M = molecular weight of the water, L = Avogadro constant, $a(t_c)$ = specific activity, λ = tritium decay constant.

Tritium measurement scale

Calibration of tritium measurements in waters is achieved by subjecting tritiated-water standards to the same measurement procedure. Tritiated-water standards are usually certified in specific activity units $a_s(t_0)$, at a specified calibration date t_0 (in the following pages, subscript s denotes the standard). At any later date t, the specific activity $a_s(t)$ is assumed to be

$$a_s(t) = a_s(t_0)\exp[-\lambda(t-t_0)] \qquad (5)$$

λ is the assigned decay constant = $\ln 2/T_{1/2}$ where $T_{1/2}$ is the assigned tritium half-life.

The 3 parameters $a_s(t_0)$, t_0, and $T_{1/2}$ uniquely determine a laboratory's tritium scale. In order to promote uniformity in measurement and reporting of low-level tritium, Taylor & Roether (1981) have recommended general adoption of a tritium scale based on U.S. National Bureau of Standards (NBS) tritiated-water standard SRM-4926C, with certified specific activity 3.406×10^6 Bq/(kg H_2O) at 3 September 1978, and half-life 4540 d (12.43 a). All our results released since January 1980 are expressed in TR on this scale.

All our results released (in TU) before January 1980 used an earlier NBS tritated water SRM-4926 with certified specific activity 8.780×10^6 Bq/(kg H_2O) on 3 September 1961, and half-life 12.262 a. To convert to TR on the new scale, our old results should be multiplied by the factor

$$0.3879 \times \frac{\exp[-\lambda^*(t_c - t^*_0)]}{\exp[-\lambda(t_c - t_0)]}$$

with t_0 = 3 September 1961, t^*_0 = 3 September 1978, $\lambda = 1.5477\times10^{-4}$ d^{-1}, $\lambda^* = \ln 2/4540 = 1.5268\times10^{-4}$d^{-1}. (Full details of measurement scales and inter-scale corrections are given in Taylor & Roether (1981).)

The following conversion factors apply to the new measurement scale if M = 0.018015 kg/mol:

1 TR $\equiv$ 6.686×10^7 tritium atoms/(kg H_2O)
1 TR $\equiv$ 3.193 pCi/(kg H_2O)
8.464 TR $\equiv$ 1 Bq/(kg H_2O)

Enrichment requirement

The main difficulty of tritium measurement in the New Zealand environment lies in the necessity to provide an enriched sample for counting in order to achieve a sample count rate which can be resolved above the counter background. At the time of maximum thermonuclear HTO fallout (1964–65), an unenriched New Zealand rainwater would have yielded only about 1 net count per minute (cpm) in a sensitive gas proportional counter; present rainwater would yield only about 0.1 cpm. Counter backgrounds are typically a few cpm.

Electrolytic enrichment is favoured for routine tritium measurement: this concentrates the tritium from a large water sample to a sample size matching the counter requirement. In our present enrichment cells, sample volume is reduced from 1 litre to (8.5–10.0) mL; more than 70% of the original HTO is

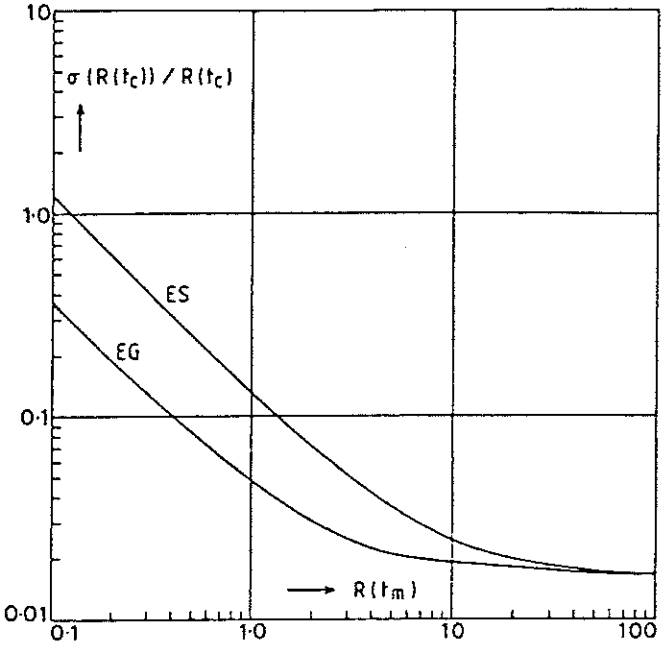

Fig. 3 Fractional tritium measurement error $\sigma(R(t_c))/R(t_c)$ plotted as a function of measured Tritium Ratio $R(t_m)$ for different measurement procedures. Curve ES approximates to the present INS enrichment cells when used in conjunction with liquid scintillation counting. Curve EG typifies the improvement which can be obtained with a low-background proportional gas counter.

retained, although 99% of H_2O has been electrolytically dissociated. In our present low-level liquid scintillation counter, the count rates after enrichment are about 1 net cpm for TR = 1 in the original sample, with background about 6 cpm. A proportional gas-counting facility is being developed which should double the net count rate, with substantially reduced background; this will provide the improved detection sensitivity necessary for detection within the critical range below 1 TR (see Fig. 3).

Measurement sensitivity

The sensitivity of the tritium detection method is expressed by evaluating the fractional standard measurement error, given by

$$\frac{\sigma(R(t_c))}{R(t_c)} = \frac{\sigma(R(t_m))}{R(t_m)}$$

$$= \sqrt{\left(\frac{\sigma^2(n)+\sigma^2(n_B)}{(n-n_B)^2} + \frac{\sigma^2(n_s)}{n_s^2} + \frac{\sigma^2(Z)}{Z^2}\right)} \quad (6)$$

where n, n_B, n_s : $\sigma(n)$, $\sigma(n_B)$, $\sigma(n_s)$ are respectively the net count rates per unit mass of water at the measurement date t_m : standard errors of these count rates, for the enriched sample, enriched tritium-free water (blank), and tritiated-water-standard (diluted) used to calibrate the counter, and Z, $\sigma(Z)$ are the electrolytic enrichment factor (final tritium concentration/initial concentration) and its standard error. In this error estimation, the Poisson distribution inherent in the counting observations is considered to be adequately approximated by a normal distribution, allowing the incorporation of other random errors (e.g., in sample quantity, dilution of standard) in assessing the errors of count rates and enrichment factor.

Because the net sample count rate $(n-n_B)$ is proportional to $ZR(t_m)$, the fractional measurement error given by Equation 6 depends on $R(t_m)$; different measurement methods may therefore be compared by plotting $\sigma(R(t_c))/R(t_c)$ against $R(t_m)$ over the expected range of $R(t_m)$. Fig. 3 is an example of such a diagram. Curve ES indicates the potential sensitivity of our present system involving enrichment followed by liquid scintillation counting; curve EG approximately indicates the improvement to be expected if the enriched samples can be counted in a good proportional gas-counting system.

The form of the curves in Fig. 3 is typical of such sensitivity diagrams: at the left-hand end, the fractional measurement error is determined by the high fractional statistical error of the net count rate, while at the right-hand end it tends towards the enrichment error $\sigma(Z)/Z$.

Summary of present tritium measurement technique

After sample collection, exchange with atmospheric HTO must be avoided, so the samples are stored in tightly closed plastic or glass bottles. Samples are weighed exactly in their arrival condition, and again 1 week later, to ensure that the containers were evaporation-free before arrival at the laboratory; following this check, further weighing controls monitor possible evaporation through the period of storage, distillation, and further storage until measurement. At present, 1 g of evaporation from a full 2 litre storage bottle stored in an outside shed has been found to raise the tritium content of a tritium-free water by about 0.01 TR by exchange with atmospheric water vapour. The controls are only critical in regard to waters of very low tritium content, but are carried through routinely for all samples because the procedure supplies essential control information on practical problems of contamination-free handling. Because the laboratory atmosphere can acquire contamination from various causes (e.g., tritium-emitting luminous watch dials, inadvertent transport of tracer tritium from other laboratories) samples are always stored in an outside shed. Vapour samples of the

laboratory atmosphere are taken at regular intervals; over recent years they have not indicated any significant episodes of contamination.

Efficient electrolytic tritium enrichment depends on a developed and highly sensitive cathode catalytic surface layer; this places stringent requirements on sample purity. All samples are distilled before electrolysis, and must pass a resistivity test.

For the electrolytic enrichment, 1 litre of the distilled sample is mixed with 1.2 g of Analar-grade Na_2O_2. In the enrichment cells (Taylor 1981a, b), the volume is reduced over 10–11 days to c. 20 mL, 20 cells being connected in series at currents up to 13 A. For the final stages of volume reduction down to (8–10) mL, each cell is coupled to its own control circuit, which supplies 2.0 A, and responds to changes in the current distribution between 2 separate cathodes by shutting off the current automatically as the required final volume is reached. The cells operate in a cooling bath set at 0°C to minimise loss of HTO by evaporation. Enrichment is calibrated by running 3–4 cells with a tritiated-water sub-standard prepared by diluting NBS-standard to suitable concentration level; principles and other details of this calibration method were already fully discussed in an earlier paper (Taylor 1977). Another cell contains an essentially tritium-free water, run as a contamination check. The cells are operated on a 2-week cycle, corresponding to a processing rate of 15–16 samples per fortnight.

At the completion of electrolysis, the cells are transferred to a vacuum distillation line, where neutralisation (by CO_2 gas) of the electrolyte is followed by quantitative distillation (to within 20 mg) from all 20 cells simultaneously; distillation temperature is raised to 110°C to remove the last water of crystallisation from the Na_2CO_3 remaining after the excess CO_2 gas has been pumped away. It is important to recover and measure accurately all the residual hydrogen as water, because this quantity must be known to determine the enrichment factor reliably. After the neutralisation–distillation procedure, the enriched, distilled-water sample is ready for liquid scintillation counting.

The presently used liquid scintillation cocktail comprises 8 mL of distilled water sample and 12 mL of Packard Insta-gel liquid scintillation cocktail. The polyethylene counting vials have much lower background than glass vials, but can only be counted for up to 10 days, because the counting efficiency then deteriorates rapidly due to diffusion loss of Insta-gel components through the vial wall. This cocktail is counted at about 7°C to give stable, low background. Identical standard cocktails (usually 3, prepared from tritium-free distilled water) are circulated with the enriched samples, and sealed-in-glass standard and background samples are also included in each set to monitor any changes in sensitivity and counter background. The complete set of vials is cycled repeatedly, with counting time per vial being 50 min. in each cycle. By cycling the vials in this manner, the small effects of variable counter sensitivity (about ±0.5%) and background (a mainly neutron-induced component that depends on atmospheric pressure) are minimised. With the above-mentioned cocktails, sensitivity at present is about 1 net cpm/70 TR in the water; background is about 6 cpm.

Calculation of results

The basic formula for calculating the result of a tritium assay using the counting method is

$$R(t_c) = 10^{18} \times \frac{M}{2L} \times \frac{a_s(t_0)}{\lambda} \times \frac{1}{Z} \times \times \frac{n(t_m)}{n_s(t_m)} \times \exp[-\lambda(t_c - t_0)] \qquad (7)$$

SAMPLING PROCEDURES

Measurement of $\delta^{18}O$, δD, and TR in environmental water samples must be preceded by careful sample selection and collection. Selection is made after consideration of the problem to be investigated and review of available and feasible sampling sites. The waters actually collected should exactly correspond to the intended concept. This requirement may sound obvious, but we have found that it is all too easy to collect samples which do not fit this criterion. Samples can be of numerous different categories: they may be rain, snow or ice, atmospheric vapour samples, river water, groundwater, ocean water, hot springs or geothermal wells, lake water, soil moisture. A large number of effects may easily interfere with the collection of an isotopically representative sample, as is shown by the following examples:

(1) precipitation begins to evaporate as soon as it reaches many types of collector; any significant evaporation tends to shift the isotopic composition;
(2) vapour samplers may not be 100% efficient, in terms of collection or recovery of collected water;
(3) mixing lengths in rivers are often surprisingly great, so that many sampling points may not yield water representative of the entire cross-section of flow;
(4) stagnant wells or bores will not yield representative samples until thoroughly flushed with water from the sampling horizon;

(5) bore-casings may be damaged, admitting water from unwanted horizons;
(6) separation of steam and water fractions in geothermal samples may not be easily controllable;
(7) ocean sampling bottles may leak during raising;
(8) lakes may be non-uniform in isotopic composition, both horizontally and vertically ;
(9) in the case of tritium, sample bottles or other gear, and even the water to be collected, may be affected by contamination; e.g., many oceanographic ships use tracer tritium in seagoing experiments;
(10) collection of water during drilling operations is made very difficult by penetration of drilling fluid into the surrounding water horizons.

Supplementary collection details must usually be taken as part of the investigation, and these may also be useful in assessing the quality of the isotope sample. These would normally include weather conditions, water temperature, collection time or period, map references, description of sample location or installation, well-logs, identity of person doing sampling, depth in lake or ocean, details of other measurements performed or to be performed on samples from same location, and any unusual circumstances.

The sample storage bottle must fulfil the requirement that there should be negligible evaporation of the sample during the period between collection and measurement (Stewart 1981). Amongst the available bottle–cap combinations, the number which fulfil the evaporation criterion is surprisingly small. The usual problem lies with insecure caps or permeable washers. For ^{18}O and D samples we use 30 mL McArtney vials—a glass bottle with metal screw cap fitted with a neoprene washer. 2 L plastic bottles are usually used for tritium samples, but glass bottles are preferable for samples expected to yield very low tritium concentration. Hot water is best collected in Pyrex bottles, but may be transferred to other bottles after cooling. It is often a good idea to collect 2 bottles for each sample, and then to hold the duplicates until safe receipt of the samples is advised by our laboratory.

At the time of collection, bottle and cap should first be thoroughly rinsed with the water to be sampled, before filling the bottle to the neck, but not overflowing. The cap must be screwed on securely. Sampling details should be noted in a field notebook, but adequate identification and the sampling date must be marked indelibly on the bottle or on a label securely fixed to the bottle.

Precipitation sampling presents a special problem: global variations of $\delta^{18}O$, δD, and TR are assessed by monthly samples from a network organised by IAEA/WMO. The usual procedure is to empty the rain gauge daily at the time of the daily reading, the daily quantities being combined to form a monthly cumulate sample; but in many circumstances special adaptations may have to be made to standard gauges to minimise evaporation in the case of D and ^{18}O. Slight evaporation of precipitation samples is not so critical for tritium; the usual procedure is to accumulate the precipitation below a suitably sized funnel for the entire month, and to record the quantity of precipitation nearby using a standard rain-gauge.

In precipitation measurements, recording of precipitation totals allows amount-weighted averages to be determined, which is important in assessing the flux of isotopes to the ground surface. Amount-averaging may also be applicable in river studies, requiring sampling at carefully selected time intervals and locations complemented by flow measurements. Indeed, the isotope sampling is generally only one of a number of samplings and observations which has to be made at any location.

SUMMARY

In this paper, we have briefly summarised our present measurement procedures for oxygen-18, deuterium, and tritium in waters with mention of earlier procedures. The reader is referred to INS reports for more detailed information on many of these techniques. We have covered in more detail the standardisation procedures used in our laboratory for these measurements and conclude with a description of approved sample collection techniques.

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