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Draft Indian Standard

MEASUREMENT OF ENVIRONMENTAL TRITIUM IN NATURAL WATER FOR HYDROLOGICAL STUDIES

ICS 13.280

Nuclear Energy for Peaceful Application Sectional Committee, CHD 30
Last date of comments:

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FOREWORD

(*Formal clause shall be added later*)

Tritium is one of the naturally occurring isotopes of hydrogen and is radioactive. There are 18 isotopologues of water one of which is HTO. Thus, making tritium an integral part of water molecule. Tritium is produced in stratosphere by spallation reaction of nitrogen with cosmic ray neutrons. The steady state inventory of tritium is about 11g/day. The produced tritium is oxidised and leads to formation of tritiated water which reaches troposphere through the mixing layer between stratosphere and troposphere. This process is specially enhanced during the spring season and is known as spring leak. The time taken by the tritium from its production to enter the hydrological cycle is about 30 days. The environmental input of tritium is very low, hence, for measurement of tritium in natural waters preconcentration of tritium is essential. Environmental tritium plays an important role in estimating the residence time of water and evaluating the groundwater dynamics. The half-life of tritium is 12.43 years and with the available measurement techniques groundwater ages up to 50 years can be estimated. The residence time estimation provides a helpful insight into the aquifer longevity, thus helping in managing the aquifers sustainably.

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022 ‘Rules for rounding off numerical values (*second revision*).

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MEASUREMENT OF ENVIRONMENTAL TRITIUM IN NATURAL WATER FOR HYDROLOGICAL STUDIES

1 Scope

This standard prescribes the method of this document helps in understanding the key aspects like sampling for tritium, its preconcentration, measurement and calculating its content in a given sample.

2 REFERENCES

The standards listed below contain provisions which, through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revisions, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards listed below:

IS No.	*Title*

3 TERMINOLOGY

For the purpose of this standard, the definitions given below shall apply.

3.1 Isotopologues — Isotopologues are molecules that differ only in their isotopic composition. For example, water, whose hydrogen-related isotopologues are: “light water” (H_2O), “semi-heavy water” with the deuterium isotope in equal proportion to protium (HDO), “heavy water” with two deuterium isotopes of hydrogen per molecule (D_2O) and “super-heavy water” or tritiated water (T_2O as well as HTO and DTO).

3.2 Spallation Reaction — Spallation is a violent reaction in which a target is bombarded by very high-energy particles. The incident particle, such as a proton, disintegrates the nucleus through inelastic nuclear reactions. The result is the emission of protons, neutrons, α-particles, and other particles.

3.3 Half-Life — Time required for a quantity of radioactive substance to reduce to half of its initial value.

3.4 Aquifer — An aquifer is a body of rock and/or sediment that holds groundwater.

3.5 Distillation — It is a process involving the conversion of a liquid into vapour that is subsequently condensed back to liquid form.

3.6 Isotopic Fractionation — Isotopic fractionation is defined as the relative partitioning of the heavier and lighter isotopes between two coexisting phases in a natural system

3.7 Electrical Conductivity — It is a measure of a material's ability to carry an electrical current. The SI unit of electrical conductivity is siemens per metre (S/m).

3.8 Electrolysis — Electrolysis is the process of using electricity to split water into hydrogen and oxygen

3.9 Stainless Steel 304 — The most common stainless steel. The steel contains both chromium (between 18% and 20%) and nickel (between 8% and 10.5%) combined with a maximum of 0.08% carbon.

3.10 Cathode — It is the metallic electrode on which reduction takes place.

3.11 Anode — It is the metallic electrode where oxidation takes place.

3.12 Scintillator — It is a substance that emit fluorescence when exposed to radiation. It can be liquid

3.13 Tritium Unit — Tritium activities are commonly described in terms of tritium units (TU), where 1 TU = 1 atom of tritium per 10^{18} atoms of hydrogen or 1 TU = 7.19 DPML^{-1} of water = 0.118 Bq L^{-1} of water.

3.14 Figure of Merit — A numerical expression taken as representing the performance or efficiency of a given device

4 SAMPLING

There are very few geochemical processes in nature that can alter the tritium content hence the sampling of environmental tritium is quite simple. In the field, samples are collected from water bodies like river, lakes and pond, dug wells, borewells, handpumps etc. For obtaining the representative water sample the wells are purged for 30 minutes or till a constant temperature is obtained. Then, water is collected in a 1 L bottle preferably having inner cap and brought to the laboratory for measurement. The sample need not be prefiltered nor any preservative need to be added for sampling water for tritium analysis

5 PROCEDURE

5.1 Sample preparation for tritium counting involves four main steps. The first step is distillation of the collected water sample. About 500 ml of the sample is poured in a double neck with 24/29 and 26/19 joint, glass round bottom flask (borosil make). Small glass and ceramic beads are added into the flask to avoid bumping. The 26/19 joint of the round bottom is blocked with glass cork and the 24/29 joint is connected to the glass (borosil make) condenser. The other end is of the condenser is connected to the 500 ml glass reagent bottle (borosil make). The small opening in condenser is connected to silicon trap to release any excess pressure developed during distillation through a pin hole in silicon trap. This setup (Fig. 1) ensures close system distillation making the losses due to fractionation minimum and ensures less chances of pressure bursting of the glassware.

FIG. 1 DISTILLATION SETUP

5.2 The distillate is collected in a separate bottle and electrical conductivity (EC) is measured using pre-calibrated EC meter. EC of 10 µS/cm or below is ensured by repeating the distillation if needed. This step ensures that all the inorganic impurities are removed from the water samples so that the electrolytic cell does not corrode during electrolysis.

5.3 The next step is the addition of sodium peroxide (90 % purity) to make the water conducting. Sodium peroxide (0.5 g) is added to 250 ml of distilled water samples. This addition leads to the release of oxygen gas and the resultant solution becomes alkaline. The reaction involved is given in equation below

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

5.4 250 g by weight of this solution is added to electrolytic cells. A typical electrolytic cell consists of a perforated mild steel cathode of developed surfaces and a stainless-steel anode (SS-304). It is concentric in type and tubular in shape. The outer anode holds the sample while the perforated cathode is placed inside it and the two are electrically insulated from each other with a PTFE spacer at the bottom. At the top, the two cells are sealed together with a rubber O-ring which is smeared with a little silicon oil. The cathode is fitted with an outlet at the top for venting the hydrogen and oxygen gases generated during electrolysis. An actual image of a cell is given in Fig. 2. The difference in the cathode surface before and after development is shown in Fig. 3.

5.5 The selective enrichment of tritium is defined by separation factor given as

$$\beta = \frac{[T/H]_{electrolyte}}{[T/H]_{evolved\ hydrogen}}$$

FIG. 2 ANODE AND DEVELOPED CATHODE ELECTROLYTIC CELL

FIG. 3 CATHODE WITH AND WITHOUT DEVELOPMENT

5.6 Enrichment is done in the batch of twenty cells (*see* Fig. 4) out of these three are the standard spiked solution of known concentration, three are local water samples and fourteen are the sample cells. The cells are placed in Polystat Cole Parmer make chiller and are connected in series to a DC regulated power supply. The chillier unit is to keep the temperature of the system maintained to ~1-4 ˚C so the evaporation losses due to heat generation can be minimized. The constant current of ~5 A is applied at the beginning of electrolysis and the voltage of the system being ~76 V. As the volume reduces the current is reduced to avoid overheating. During the processes of electrolysis 250 ml of the solution is reduced to 13ml, the enrichment factor of ~19 is achieved. As, 2.975 45 AH is required to reduce 1 ml of water, a total of 705 AH are required for the complete process and this is achieved in approximately 7 days.

The reactions of electrolytic enrichment process are given in

Anode (+): $2OH^- \rightarrow H_2O + 1/2\ O_2 + 2e^-$

Cathode (-): $2H^+ + 2e^- \rightarrow H_2$

Fig. 1 Electrolysis setup for tritium enrichment

5.7 During the process of electrolysis, there is generation of gases like hydrogen and oxygen which are explosive. Hence, they need to be removed safely from the system. So, the generated gas is passed through the bubbler setup containing silicon oil and released into the environment. Secondly, the two electrodes are fitted with O-ring so if the pressure increases the joint pop-out and releases the pressure. As solution reduces hence the concentration of alkali increases. So before counting the alkali needs to be neutralized as it causes quenching of the scintillator. The sample is transferred into a 50 ml glass round bottom flask. To this ~2 g lead chloride (99% purity) is added to neutralise the increased alkalinity. The governing equation is:

$$2NaOH + PbCl_2 \rightarrow 2NaCl + Pb(OH)_2$$

FIG. 5 NEUTRALISATION SETUP FOR SAMPLES POST ELECTROLYSIS

5.8 This solution is heated at ~150 ˚C and the condensate is collected through closed system setup (Fig. 5). 14 ml of Optiphase Hisafe scintillator (Perkin Elmer make) is added to the 8 g of the enriched sample in high-density polythene scintillation vials and counted in Quantallus 1 220 liquid scintillator (Fig. 6).

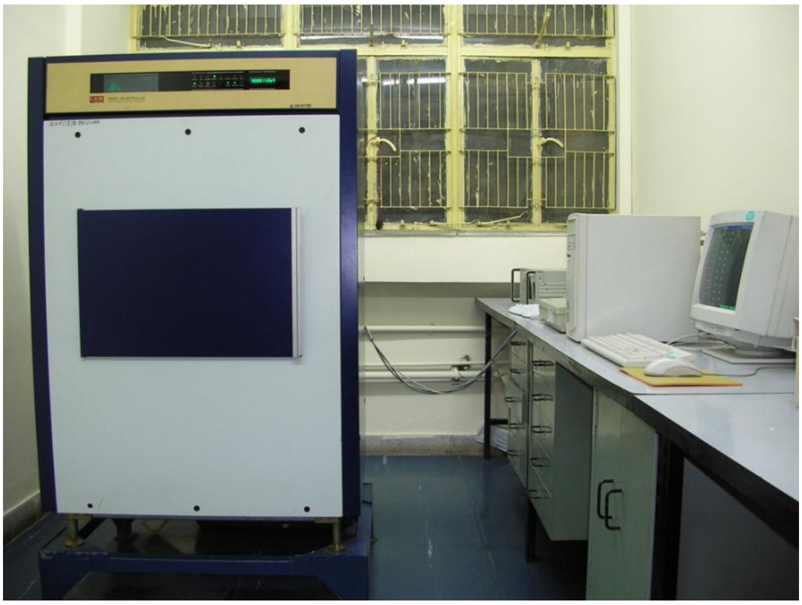

FIG. 6 LKB QUANTALLUS 1 220

5.9 The sample is counted for 500 min. each (50 min each sample for 10 cycles). After counting, the cpm values are obtained by selecting the channel that has the best figure of merits (square of efficiency /background).

5.10 For quality assurance of the lab generated data in every batch spiked samples and distilled water samples are added to keep the check on the consistency of measurement. The tritium values are reported in terms of tritium Units (TU) where 1 TU is equal to 0.118 Bq/Kg or 3.19 pCi/Kg

6 CALCULATION

The spikes cells are used to calculate the enrichment parameter E_P using the formula given by

$$E_P = W_e \times E = (W_o - W) \times \frac{\ln Z_s}{\ln N_s}$$

Where,

W_e = wt. of electrolyzed sample, W_0 = wt. of initial sample = 250 g

W = wt. of final sample = net wt. of electrolyzed sample - 0.4gm

Z_s = enrichment factor which is calculated using the following equation

$$Z_s = \frac{cpm_{spike}}{cpm_{std}} \times D.F.$$

D.F. = dilution factor (total volume/std added, for spike preparation)

$N_s = W_0 / W$ = mass reduction factor

cpm_{spike} = background corrected counts for spike solution.

Enrichment Factor of an individual cell can be calculated using E_P

$$Z = \exp\left[\frac{(E_P \times \ln N)}{(W_o - W)}\right]$$

Tritium value in terms of TU (tritium unit) can be calculated by using the following formula

$$TU_{sample} = \frac{cpm_{sample} \times TU_{std}}{Z \times cpm_{std}}$$

7 ERROR ESTIMATION

7.1 Errors in tritium measurement can be of three types

a) Counting Error,
b) Error due to enrichment,
c) Error due to pipetting and weighing etc. this is generally taken as 1%.

For example, if for a sample of net count rate, A ± a. the corresponding errors would be as follows

Counting error (a_1) = a/A * 100%

Enrichment error (a_2) = σ_{EP} x ln Z

σ_{EP} = percentage standard deviation in enrichment parameter from the standard.

a_3 = 1%.

Therefore, total error = $\pm (a_1^2 + a_2^2 + a_3^2)^{1/2}$

For tritium when reported in terms of TU the error will be given as

$$TU_{error} = \frac{Error\%_{sample} \times TU_{std}}{Z \times 100 \times cpm_{std}}$$

Relevant References

1. IAEA technical document 246
2. Tritium enrichment of environmental water by electrolysis: development of cathode exhibiting high isotopic separation and precise measurement of tritium enrichment factors by C.B. Taylor, IAEA Vienna