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Tritium Concentration Study of Surface and Ground Water with a Specially Designed Proportional-counting Technique

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Abstract: The design and performance of a system for the measurement of very low tritium concentrations in natural waters are described and discussed in the light of analytical and accuracy. The system consists of a sensitive flow-type proportional counter with a controllable inlet gas. Along with this counter, a reliable method for preparation of the samples has been used. Low tritium concentrations are determined on samples that have been preconcentrated electrolytically, necessitating samples of about 300 mL at least to allow for repeated measurements. Water samples were converted to hydrogen gas and then reacted with ethylene to yield ethane. A special proportional counter of about 1.9 L was designed and constructed for this purpose. Appropriate electronic equipment allowed the registration of tritium counts and background below and mainly background above about 15 keV. Water samples were collected from two ground sources and two main rivers and in two different seasons. The rivers' concentrations were higher in summer than in winter. The ground water concentrations were of about a factor of two smaller than the river concentration in summer.

Key words: Tritium concentration, surface and ground water, proportional counter

INTRODUCTION

It is now established that useful hydrological and meteorological information can be obtained from measurements of the natural tritium content of precipitation, surface water and underground water (IAEA., 1963, 1964; Cameron, 1965). Projects in which natural tritium is used generally entail the measurement of large numbers of samples and consequently the assay system should be designed to measure a maximum of samples.

In the northern hemisphere, tritium concentrations in precipitation vary from a few hundred to a few thousand TU; in surface water, concentrations are slightly lower than current precipitation due to dilution with older ground water, while ground water concentrations range from zero to several hundred TU. In the southern hemisphere, tritium concentrations are lower by a factor of about one hundred (Brown and Grummit, 1956).

From published details of counting systems (Geyh, 1972; Hufen *et al.*, 1974; Theodorsson and Part, 1991; Theodorsson, 1991, 1992, 1996, 1999), the minimum detectable concentrations measurable with typical gas and scintillation counters are about 5 and 500 TU, respectively. Thus with a system giving a concentration factor of 10, many northern hemisphere samples could be measured with a liquid scintillation counter and almost all could be measured with a gas counter.

For routine operation at maximum efficiency, the preparation and measurement of the samples should be independent. A gas which has a low vapor pressure at liquid air temperature has the advantage that it can readily be transferred by freezing from reaction vessels to storage vessels and the counter can be filled at high pressure without any complicated pumps. It can also be freed from undesirable impurities by freezing and pumping. We have decided to use ethane as the counting gas. The ethane is synthesized using hydrogen from the sample and ethylene tank.

As the volume and pressure of gas in gas counter can be such that an amount of hydrogen equivalent to 10 mL of water can be introduced, an electrolysis system giving a final volume of about 15 mL is required. To achieve a concentration factor of 10, a reduction in volume by a factor of about 15 is required. Hence the initial volume of water in the electrolysis cell should be about 250 mL. For routine operation, robust metal cells and minimum handling and subsidiary measurements are desirable. A sensitive flow-type proportional counter of about 1.9 L has been designed and constructed. The total length of counter is 609.2 mm, the distance between the anode holders is 574.4 mm, the inner cathode diameter is 62.3 mm and the anode is of tungsten and 0.023 mm of diameter (Fig. 1). The sensitivity of the counter was examined with ^{14}C with low activity.



Fig. 1: Top: View of the specially designed glass tubes and bottom: Mg-furnace with water cooled Pd-asbestos catalyst to produce hydrogen gas

The counter responded remarkably well to the samples with activities greater than 0.5 TU with an accuracy of about 5% or 0.5 TU.

MATERIALS AND METHODS

Sample preparation: The water samples were collected from Tehran undergrounds and rivers during two seasons in 2004-2005 and distilled to dryness. An aliquot of 10 mL is transferred to a vacuum line, frozen and the air removed. A previously degreed Mg-furnace is heated to 500°C, the water warmed to 60°C and the vapor allowed to react with the Mg (Fig. 1). The efficiency of the conversion to hydrogen gas is larger than 97%. The gas is purified by passing it through Pd-metal at 420°C and then transferred to a 30 L storage vessel. Both vessels are connected through a tube containing a water-cooled Pd-asbestos catalyst. For cooling, the cell is placed in a metal tank filled with water together with an appropriate fraction of antifreeze to avoid ice formation in the tank at the temperature of -5°C. The position of the cell with respect to the tank is fixed by means of a heavy plastic covered lid 5 cm thick with a hole in it through which the cell is inserted to dip into the cooling tanks underneath. The head of the cell rests on the top of the lid. A



Fig. 2: View of the whole electrolysis system; battery charger, automatic current control system, 30 L storage vessel and metal tank

battery charger (Fig. 2) supplies a current of 10 amperes at about 2.3 volts. An automatic servo-system was designed to maintain the current fixed at 10 amperes during electrolysis.

A ring is completed over an automatic rotary pump which circulates the mixture over the catalyst to yield ethane. When the conversion efficiency exceeds 98%, the circulation is stopped and the gas product transferred into the counter. For routine measurements, the pressure in the counter is 750 mm Hg. The complete procedure of water reduction and ethane preparation took about two days. Even though the product may contain a small amount of higher hydrocarbons, leaving some hydrogen unreacted; it behaves as a good counter gas. The amount of hydrogen sample in the gas is in any case given by the number of operation potentials of the counter.

Procedure: Initially, the cell is filled with 250 mL of the sample water containing 1% by weight of Na_2O_2 . The cell is then placed in the corresponding cooling tank and is supplied with 2.3 volts by a battery charger. The initial temperature of the cooling tank is about $\pm 1^\circ\text{C}$ and the cell is left to cool for about 15 min before switching on the supply. The electrolysis current was controlled by a servo-electronic system and the cooling tank was maintained within $\pm 1^\circ\text{C}$ throughout the run.

A total charge of 700 ampere-hours reduces the sample volume from 250 mL to about 15 mL. From the electro-chemical equipment of hydrogen (26.6 amp h/g), about 687 amp h is needed theoretically for a volume

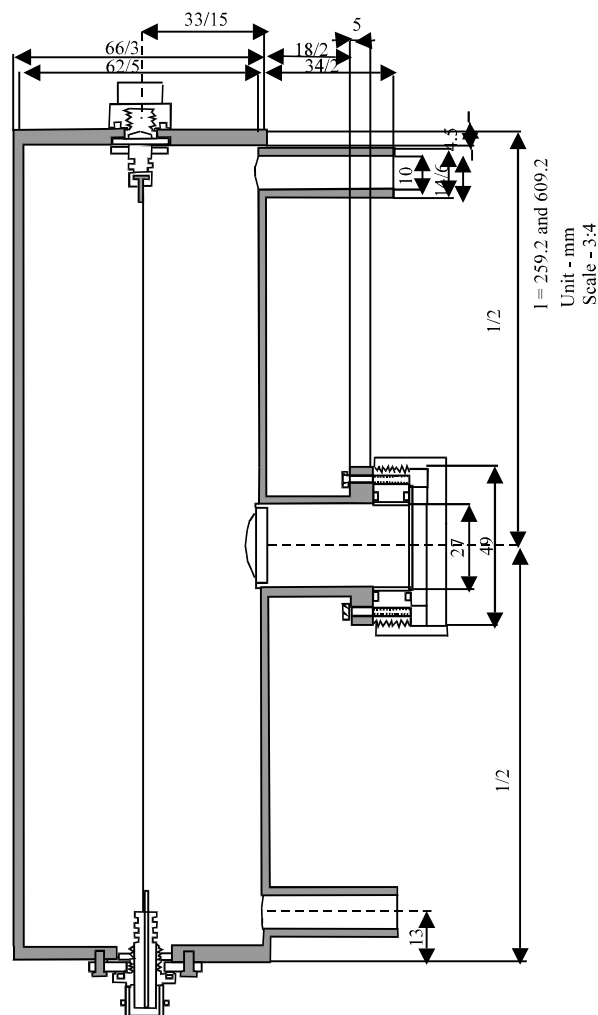


Fig. 3: Schematic view of the proportional counter. All numeric data in millimeters.

reduction of 236 mL (250-14 mL). There is, therefore no significant loss of sample as spray or by evaporation under the present working conditions.

Once the necessary charge has passed through the cell, the supply is switched off and the cell is disconnected to prevent reverse current passing through the cell as this has been found to damage the cathode surface. The cell is then removed from the tank and the enriched sample poured out of the cell into stainless steel flask and distilled without neutralizing it.

Gas preparation: The water sample was first reduced to hydrogen and then a stoichiometric mixture of hydrogen and tritium-free ethylene is converted to ethane using a palladium catalyst, according to the reaction.

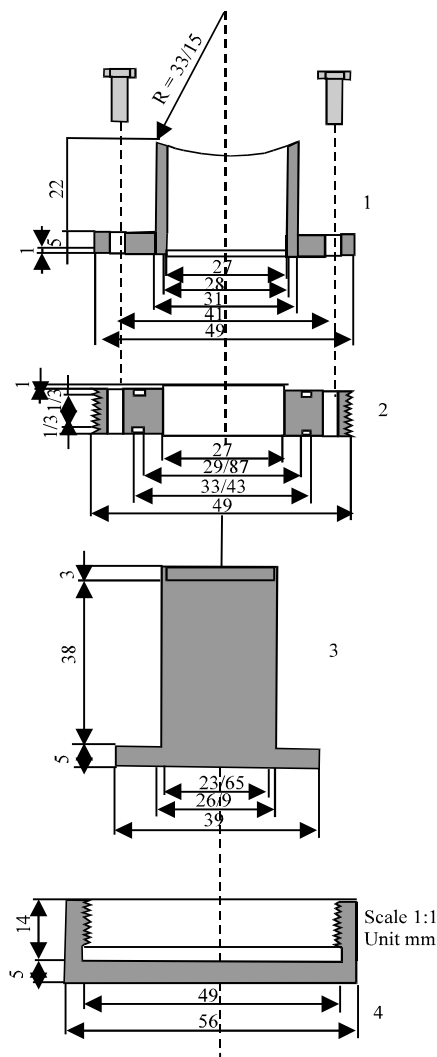
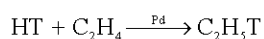


Fig. 4: Schematic view of the central hole with corresponding: (1)hole, (2) cap holder with proper vacuum O ring, (3) bench for sample tray, (4) cap for bench holding

Counting system: A flow type proportional counter sensitive to low energy beta has been designed and constructed. The counter has a total volume of 1.9 L and the center part volume (cross section area time length of anode wire) of 1.7 L (Fig. 3). The anode wire is of tungsten of 0.023 mm of diameter. The counter was placed horizontally inside an iron shield surrounded by a 10 cm layer of 85% paraffin, 15% boric acid and again iron layer. The whole mantle arrangement was surrounded by lead bricks.

The counter has the possibility to count very low energy alpha and beta particles by putting the sample on a standard tray and on a bench provided at the middle of the counter (Fig. 4). Excellent plateau up to 700 volts long



Fig. 5: Set-up for counter calibration, plateau and sensitivity determination

and of slope less than 0.5% per 100 volts are obtained in total count versus voltage curve. The curve relating voltage to anticoincidence count rate with high activity sample is flat over about 650 volts, when no pulse height selection is used. The set-up for accomplishing the calibration and plateau and sensitivity determination is shown in Fig. 5.

RESULTS AND DISCUSSION

The pulse height selection was used to count only pulses in the region of tritium energy spectrum. As such, backgrounds obtained with tritium-free water were 2.85 counts per minute, but with pulse height selection the backgrounds were reduced to 2.5 ± 0.03 counts/min. This small reduction in background gained by using pulse height selection was not considered sufficiently worthwhile as additional time is needed each time a sample is filled in order to adjust the gas gain and the reduction in counting time for the normal sample activity is very small.

In routine counting, after adjusting the flow of the gas with a flow meter (Fig. 5), the plateau was checked by taking a 1 min count every 200 volts in the total count rate in the counter, in order to check that the slope and starting voltage were normal. The voltage was then set at 850 volts and the sample counted as long as was needed to give the desired statistical accuracy.

With this apparatus, the tritium activity of Tehran main Rivers such as Karaj and Haraz and ground waters such as Cheshmeh Ali and Farmanfarmaeian were counted. Present experimental errors were; statistical

Table 1: TU measurements \pm SD in two different seasons

Seasons of sample counting	Rivers		Ground waters	
	Haraz	Karaj	Cheshmeh Ali	Farmafarmaian
Winter (March)	244 \pm 21	285 \pm 23	225 \pm 21	303 \pm 21
Summer (August)	532 \pm 22	673 \pm 25	277 \pm 23	323 \pm 25

counting error about 2%, errors due to temperature and pressure reading as well as uncertainties in the exact gas composition about 0.6% and errors in the counter calibration 2%.

Present results show variation of the tritium concentration in rivers as compared with the tritium concentration of the ground water. However, the concentration in rivers exhibited less seasonal variation. This is because the melting snow water from the Alborz adds winter rain to the Haraz and Karaj rivers in the summer, thus flattening the summer peak. Furthermore, a large fraction of the river water derives from ground water which has been underground for several years. Nevertheless, the rivers' concentrations are about two times the ground concentrations (Table 1).

The results achieved are reasonable and the method of measurement, although being simple, but is reliable. The system is established for continuous measurements during the year and monitoring the tritium activity during different seasons to monitor the seasonal variations of the tritium concentration in different Iranian surface and ground waters. This investigation needs a remarkable financial support that hopefully will be provided by the authorities of Research Council.

Future activities: Future plans include systematic measurements of rain, ground and river waters in different seasons to better understand the dynamics of the distribution of tritium in different regions and in different seasons.

CONCLUSIONS

Instrumentation employed for low concentration tritium can with no doubt be used for high tritium contaminated water environment. The method of tritium concentration is simple and reliable with a very good efficiency. The proportional counter is constructed in such manner that can be used as normal fixed one by vacuuming and charging the P10 mixture at any pressure. It has the advantage of counting very low energy samples by putting them on a bench provided by the middle of the counter. The instrumentation is so that the permanent measurements during the whole year can readily be accomplished.

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