CONCENTRATION OF TRITIUM IN LIQUID SAMPLES BY ELECTROLYSIS

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In today's environmental world, tritium, with a half-life of 12.3 years, is ubiquitous. The heavy hydrogen decays entirely through the emission of a beta particle into stable ^{3}He. The beta-max for the decay is 18.6 KeV, with an average energy of 5.7 keV, which normally requires separation from other beta emitters. In groundwater-hydrology and oceanography tritium concentrations are generally given as TU (Tritium Unit), equivalent to a concentration of 10^{-18}. Other disciplines may report the radioactivity in Bq (Bequerel) or mBq, related to TU by:

$$1TU = 0.118 \text{ Bq/L of water } (= 3.19 \text{ pCi/L})$$
$$\text{or: } 1 \text{ Bq/L} = 8.47 \text{ TU}$$

Sources of tritium production include:
1)   Cosmogenic; naturally produced in the upper atmosphere as cosmic-rays interact with atmospheric nitrogen and oxygen (Spallation).   The major reaction involved is that of thermal neutrons with nitrogen:

$$^{14}N(n, ^3H) \rightarrow ^{12}C$$
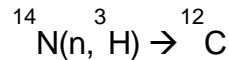
2)   Atmospheric nuclear weapons testing in the 1940s through the 1970s; Figure 1 shows the tritium concentration in monthly precipitation from Ottawa, Canada. In the spring of 1963, the peak tritium concentration in precipitation in the northern hemisphere was about 5000 TU [(NCRP) 1979].
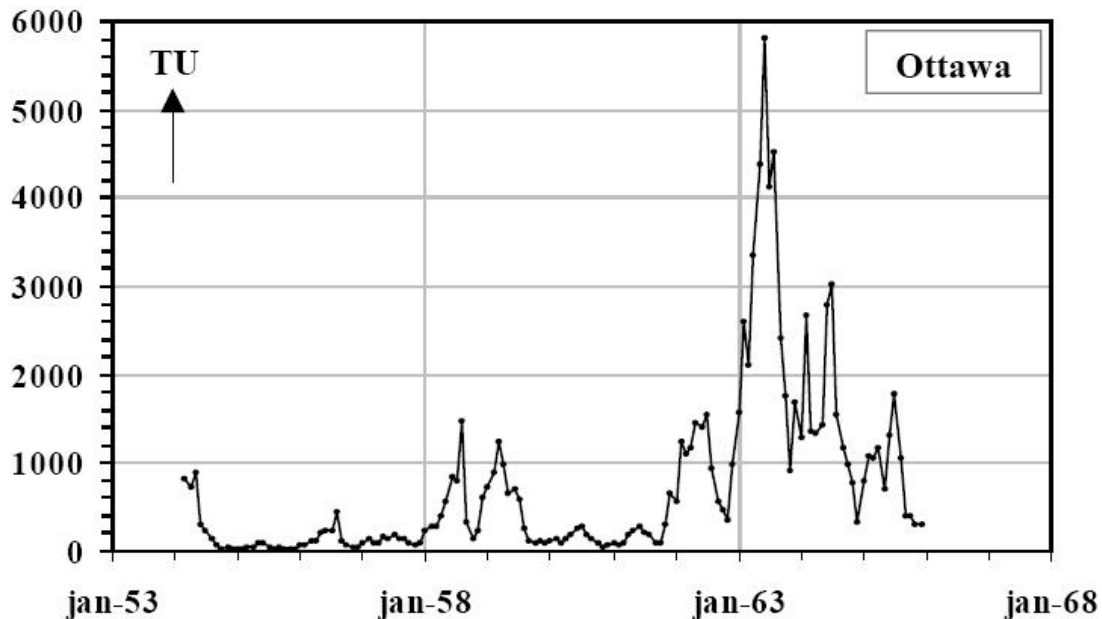

fig. 1

Anthropogenic sources of tritium in recent decades have far exceeded natural sources. It is estimated that, in the 1990's, the legacy of the nuclear weapons

test of the 1950's and 1960's is an additional 52×10^{18} Bq of tritium in the current global inventory [Okada and Momoshima, 1993].

3)   As a by product in nuclear powers reactors; Most of the tritium produced in a reactor is from the absorption of neutrons by boron. Boron is a good absorber of neutrons, which nuclear reactors use to help control the fission-chain reaction. Toward that end, boron either is added directly to the coolant water or is used in the control rods to control the chain reaction. The primary sources of tritium in the reactor coolant system in a PWR are: (1) diffusion of tritium from the fuel through the zircaloy cladding; (2) neutron activation of boron in the burnable poison rods and subsequent tritium diffusion through the stainless steel cladding; and (3) neutron activation of boron, deuterium and ^{6}Li in the reactor coolant. Two major neutron reactions with boron resulting in tritium production are:

$$^{10}B \text{ (n,2a)} \rightarrow {}^3T$$
$$^{10}B \text{ (n,a)} \rightarrow {}^7Li \text{ (n,na)}^3T$$
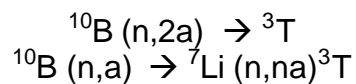
4)   When neutrons are absorbed by other chemicals (e.g., lithium or heavy water) in the coolant water. Lithium hydroxide is used for pH control in the primary coolant in some PWRs. The principal reactions are:

$$7Li(n,na) \rightarrow 3H$$
$$8Li(n,a) \rightarrow 3H$$
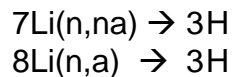
5)   Or tritium can also be produced (to a lesser extent) from the fission process itself, where the fission yield of tritium for U-238 is ~0.01%.

Normal releases of tritium from nuclear facilities are estimated to produce 0.02×10^{18} Bq/y and off-normal releases an additional 0.001×10^{18} Bq/y with a resultant steady-state buildup of 0.4×10^{18} Bq globally [Okada and Momoshima, 1993].
The combined global inventory of natural and human tritium emissions is about 50 times greater than tritium levels from natural sources alone. The resulting estimated average concentration of tritiated water in the earth's waters is 0.00000027 Ci/m3 (or 10 Bq/L).

Regulatory Limits
Under the authority of the Safe Drinking Water Act, EPA sets the Federal legal limits for contaminants in drinking water. These limits are called maximum contaminant levels, and water suppliers must provide water that meets these standards. EPA's drinking water standards do not apply to private drinking water wells, such as those that may be impacted by tritium that is inadvertently released from nuclear power plants. However, many State authorities have adopted the EPA's drinking water standards as legally enforceable groundwater protection standards, and those standards are often used in assessing laboratory test results of water from private wells.

In 1976, EPA established a dose-based drinking water standard of 4 mrem per year to avoid the undesirable future contamination of public water supplies as a result of controllable human activities. In so doing, EPA set a maximum contaminant level of 20,000 picocuries per liter (pCi/L) for tritium. This level is assumed to yield a dose of 4 mrem per year. If other similar radioactive materials are present in the drinking water, in addition to tritium, the sum of the annual dose from all radionuclides shall not exceed 4 mrem per year. Water treatment plant operators use this drinking water standard, along with monitoring requirements, to remain vigilant regarding the amount of radioactivity in drinking water and provide a means to gauge if the concentration of contaminants in finished drinking water is increasing or decreasing over time.

Biological Retention
Human studies indicate that, generally, tritium retention can be characterized by a three-component exponential function. These three components have biological half-lives of 6 to 12 days, 10 to 34 days, and 130 to 550 days, with respective median values of 9, 22, and 340 days [Hill and Johnson, 1993]. The first biological half-life is for the body water metabolism of hydrogen and reflects the turnover of water within the pool of body water. The second half-life appears to be related to tritium involved in carbon-tritium bonds, and the last is for tritium incorporated into organic molecules having very slow turnover rates [Hill and Johnson, 1993].

Perception vs. Risk
On September 3, 2006 the Decatur Daily carried the headline, "Nuke plant leaks cited, Group says TVA, NRC are 'flippant'."
ATHENS — The head of a nuclear watchdog group says news of tritium leaks at three Valley power plants is disconcerting because of how "flippant TVA and the NRC are" about the contamination.
The Tennessee Valley Authority's three nuclear power plants, including Browns Ferry, near Athens, have leaked tritium into the groundwater, according to TVA and Nuclear Regulatory Commission documents.

A series of newspaper articles suggest that power reactors are tainting the drinking water with tritium:

Guardian Newspaper Jan 25, 2006, BRACEVILLE, Illinois – After higher that normal tritium levels were found in groundwater near the Braidwook nuclear reactor 60 miles southwest of Chicago, Exelon Corporation, owner of the reactors, have (*sic*) bought out one property owner and is presently negotiating financial settlements with 14 other neighbors.

Morris Daily Herald, Feb 21, 2006, A tritium leak that began in Dec 2004 at Dresden, east of Morris, Ill., may be still on-going. Levels of tritium 25 times the allowable drinking water limits set by the U.S.E.P.A. were found in a test well near the center of Dresden property….

Herald News, Feb 16, 2006. Inside concrete vaults set into the ground where several valves are located, employees at Byron found standing water with tritium levels four times about the EPA limit.

The Arizona Republic, Jan 17, 2006. Arizona Public Service Co (APS), owner of Palo Verde's three reactors, notified the Arizona Department of Environmental Quality March 4, that a tritium leak may impact the groundwater.

Hartford Courant, Nov 4 & 8, 2005. HADDAM, Conn. – No one knows when the leak began but a few gallons of contaminated water per day breached a 6-foot-thick concrete wall. The water contains cesium, cobalt, strontium and tritium.

Journal News, January 7, 2006 Buchanan, New York – Six on-site wells contained contaminated water, with one registering seven times the EPA's approved level for drinking water
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Recognition of Need
In late 2006, GEL Labs recognized the need to develop a procedure for the quantitative determination of tritium below 150 – 200 pCi/L. The need was based on customer concerns and the demand for a reliable method with well defined turn-around-times, and GEL's reputation for quality service. Both DOE and NRC programs are recognized as the prime customers for this service.

Concentration of Tritium by Electrolysis
Tritium and hydrogen are interchangeable in most molecules and compounds; however, because of the difference in the physical properties of tritium, e.g., weight, spatial configuration, and charge density, tritiated molecules and compounds may exhibit slight but demonstrable differences. One of these tendencies is exploited here. The molecule of water containing hydrogen is more likely to be dissociated by electrolysis than the molecule of water containing tritium. The electrolytic enrichment is preformed over a two week period while immersed in a cold-water bath to minimize evaporative losses.

A 300-400 mL sample will be required for the most sensitive analysis. The sample will first be analyzed in our lab in Charleston to verify the absence of extraneous radioactivity and to detect 'high' concentrations of tritium, i.e. > ~200 pCi/L. The sample will then be shipped to our facility in Richland Washington for the electrolysis enrichment.

As part of the initial method development, the environment of a commercial radiochemistry laboratory was investigated. During a given operational day, literally hundreds of liters of tritiated water may be evaporated as part of analytical procedures. While most of the tritiated vapor is exhausted to the ambient environment, it is impossible to guarantee complete elimination of tritium from the working environment. In order to reach the detection levels possible with this procedure, the ambient environment must be free from possible contamination by external tritium. In addition, the generally humid environment in

the Southeastern United States produces ambient conditions more prone to contamination by extraneous tritium. For this reason, the majority of the procedure is completed in the Richland Service Center (RSC), in Richland Washington which is free from routine radiochemistry activities and lies geographically in a dry high-desert atmosphere.

The sample is shipped overnight to RSC, where it is then distilled to provide a sample free from other contaminates.

An aliquant of 250 mL is used for the electrolysis step, to which is added sodium hydroxide to act as the basic electrolyte. The mixture is added to an electrolysis cell for enrichment.
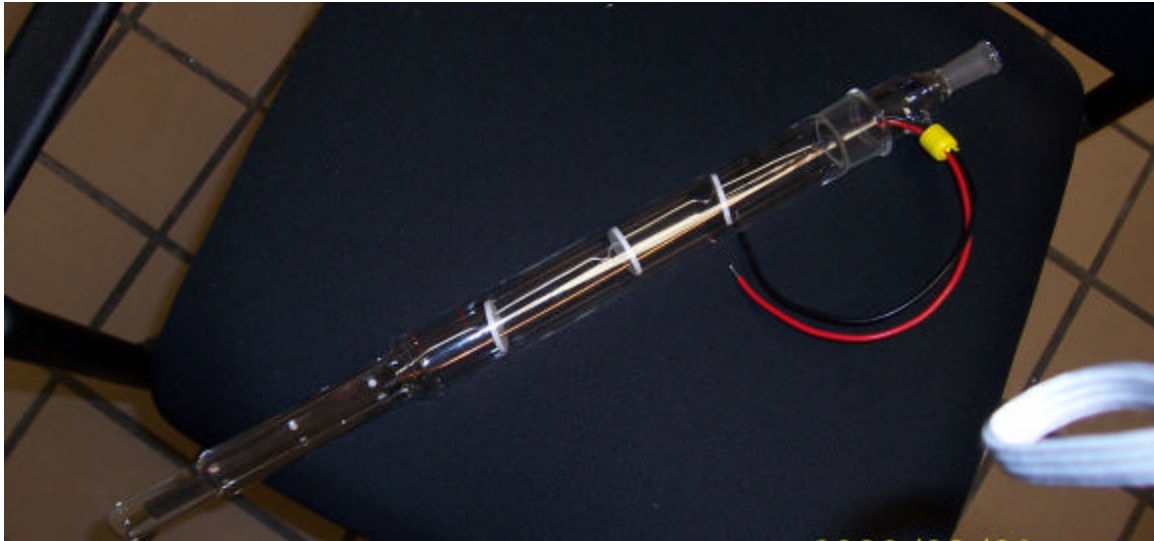
A batch may include up to 12 samples, 2 background samples and 2 spiked 'dead' water samples to act as laboratory control samples (LCS). The spiked samples contain 50 to 200 pCi of a NIST-traceable tritium standard depending on the expected sample concentration. The 'dead' water is collected from a 1400 foot deep aquifer containing 100,000 year old water.

The assembled electrolysis cells containing the sample, the two background samples, and the two LCS samples are placed in a cold-water bath to minimize evaporative loss of tritium during the two week enrichment process. The cold-water bath is maintained around 5° C. A chest-freezer is filled with water and used as the cold-water bath by using a thermocouple to cycle the power on at 4°C and off at 6°C. A constant current to the electrolysis cells is maintained until the volume is reduced to approximately 25 mL. The current is then reduced for the final volume reduction to 12-15 mL. The entire volume reduction requires 12 – 14 days.

The enriched sample is then removed from the cell by vacuum distillation. A distillation trap is partially immersed in liquid nitrogen while the contents of the electrolysis cell are distilled under vacuum. The trap is then allowed to equilibrate with the ambient temperature and then weighted to determine the mass (volume) of the enriched sample.

The enriched sample is then quantitatively transferred to a liquid-scintillation vial and sealed for shipment to Charleston for counting.

The results of the LCS standards are used to determine the relationship between the volume reduction and the tritium enrichment. The volume reduction factor for each standard sample is

$$X = V_i / V_f$$

where V_i and V_f are the initial and final volumes.

The tritium enrichment factor is

$$Y = C_f/C_i$$

Where C_f and C_i are the final and initial tritium concentrations.

MARLAP Approach
The Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP) Manual addresses the need for a nationally consistent approach to producing radioanalytical laboratory data that meet a project's or program's data requirements. MARLAP provides guidance for the planning, implementation, and assessment phases of those projects that require the laboratory analysis of radionuclides. The guidance provided by MARLAP is both scientifically rigorous and flexible enough to be applied to a diversity of projects and programs. This guidance is intended for project planners, managers, and laboratory personnel. MARLAP provides the necessary guidance for using a performance-based approach to meet a project's analytical data requirements. In a performance-based approach, the project-specific analytical data requirements that are determined during directed planning serve as measurement performance criteria for analytical selections and decisions. The project-specific analytical data requirements also are used for the initial, ongoing, and final evaluation of the

laboratory's performance and the laboratory's data. MARLAP provides guidance for using a performance-based approach for all three phases of the data life-cycle for those projects that require radioanalytical laboratory data. This involves not only using a performance-based approach for selecting an analytical protocol, but also using a performance-based approach for other project activities, such as developing acceptance criteria for laboratory quality control samples, laboratory evaluations, data verification, data validation, and data quality assessment.

Method Validation
MARLAP suggests that without reliable analytical methods, all the efforts of the project may be jeopardized. Financial resources, timeliness, and public perception and confidence are at risk, should the data later be called into question. Proof that the method used is applicable to the analyte and sample matrix of concern is paramount for defensibility. The project manager should ensure the methods used in the analyses of the material are technically sound and legally defensible.

The method selected and proposed by the laboratory must be based on sound scientific principles and must be demonstrated to produce repeatable results under a variety of sample variations. Each step of the method should have been evaluated and tested by a qualified expert (radioanalytical specialist) in order to understand the limits of each step and the overall method in terms of the MQOs. These steps may involve well-known and characterized sample digestion, analyte purification and decontamination steps that use ion exchange, solvent extraction, precipitation and/or oxidation /reduction applications. Method validation will independently test the scientific basis of the method selected for a given analyte and sample matrix.

Newly Developed or Adapted Methods
MARLAP also recommends that methods developed by the laboratory or adapted from the literature that have not been previously validated for a project be validated according to Levels D or E of Table 1. These levels provide the most comprehensive testing of method performance. Levels D and E have an increased number of replicates and the data obtained should provide the best estimate of the precision and bias of the method. When the matrix under consideration is unique, the method should be validated using the same matrix (e.g., MVRM) as determined in Level E. This is extremely important for process/effluent waters versus laboratory deionized water and for various heavy metal radionuclides in soils or sediments when compared to spiked sand or commercial topsoil. For site-specific materials containing severe chemical and radionuclides interferences, many methods have been unable to properly address the magnitude of interferences.

Validation Level	Applications	Sample Type[1]	Acceptance Criteria[2]	Levels[3] (Concentrations)	Replicates	No. of Analyses
A Without Additional Validation	Existing Validated Method	———	Method Previously Validated B thru E	———	———	———
B	Same or similar Matrix	Internal PT	Measured Value Within ±2.8μ_{MR} or ±2.8f $_{MR}$ Known Value	3	3	9
C	Similar Matrix/ New Application	Internal or external PT	Measured Value Within ±2.9μ_{MR} or ±2.9f $_{MR}$ Known Value	3	3	15
D	Newly Developed or Adapted Method	Internal or external PT	Measured Value Within ±3.0μ_{MR} or ±3.0f $_{MR}$ Known Value	3	3	21
E	Newly Developed or Adapted Method	MVRM* Samples	Measured Value Within ±3.0μ_{MR} or ±3.0f $_{MR}$ Known Value	3	3	21

Table 1

* Method Validation Reference Material
uMR . . . . required absolute method uncertainty
f MR . . . . required relative method uncertainty

[1] PT and MVRM samples should be traceable to a national standards body, such as NIST in the United States. Internal PT samples are prepared by the laboratory. External PT samples may be obtained from a performance evaluation program or from a commercial radioactive source producer that has traceability to a national standards body. Blank samples should be representative of the matrix type being validated.

[2] The acceptance criterion is applied to each analysis in the method validation, not to the mean of the analyses. u_{MR} is the required absolute method uncertainty for analyte concentrations at or below the action level and f $_{MR}$ is the required relative method uncertainty for analyte concentrations above the action level. The acceptance criteria are chosen to give a false rejection rate of ~5% when the measurement process is unbiased, with a standard deviation equal to the required method uncertainty (u_{MR} or f $_{MR}$). The stated multiplier, k, for the required method uncertainty was calculated using the formula $k \simeq z$ where N is the number of measurements, a is the desired false rejection rate, and, for any p, $z_{p\ 0.5\ \%\ 0.5(1\ \&\ a)_{1/N}}$ denotes the p-quantile ($0 < p < 1$) of the standard normal distribution.

[3] Concentration levels should cover the expected analyte concentration range for a project including the action level concentration. A set of five appropriate blanks (not considered a level) should be analyzed during the method validation process. The blank data and the estimated absolute bias in the mean blank concentration value (see Attachment 6A in this chapter for applicable statistical tests) shall be reported as part of the method validation documentation.

Determination of Uncertainty

The data collected from the method validation will be used to estimate the method uncertainty. The method uncertainty will then be one component of the uncertainty menu for the individual sample uncertainty. Other menu components used to calculate the combined standard uncertainty include the liquid scintillation counting uncertainties, the uncertainty associated with the background samples when subtracted from the result. A control chart will be developed from the X (enrichment factor) and Y (volume reduction) over a period time. Control limits will be derived from the data and used to establish acceptable performance criteria.

References

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