

**State of Idaho**

---

**INEL**      Oversight  
                Program

**TRITIUM ENRICHMENT PROGRAM**

**RESEARCH AND DEVELOPMENT GRANT #4**

**JANUARY 16, 1994**

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**MASTER**

*S*

**DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED**

#### **ACKNOWLEDGMENT**

**A research project was performed by Idaho State University-Environmental Monitoring Laboratory (EML) to improve the sensitivity for tritium analysis. This report was generated by the EML under contract #211-032-59 for the INEL Oversight Program.**

**The Oversight Program submitted this report to the Department of Energy in support of the Research and Development Grant #4: Independent Testing of Air Quality Data.**

## **Contents**

I.	Introduction.....	1
II.	Methods.....	3
III.	Results.....	4
IV.	Conclusions.....	5
V.	References.....	6
	Appendix A: H-3 Enrichment procedure.....	11
	Appendix B: Required Materials.....	13
	Appendix C: Tritium Enrichment factor.....	14

## **Tables**

Table 1.	Calibration Results.....	8
Table 2.	Comparison of Conventional and Enhanced Tritium Analysis.....	9

## **Figures**

Figure 1.	H-3 Enrichment Standard Curve.....	10
-----------	------------------------------------	----

## I. INTRODUCTION

Tritium ( $^3\text{H}$  or T), the heaviest and only radioactive isotope of hydrogen, was discovered in 1939 by Alvarez and Cornog (NCRP, 1979). Tritium is known to have a physical half-life of 12.3 years with the mode of decay being a 0.018 MeV (maximum) beta emission.

The biological half life of tritium in the aqueous (HTO) form is approximately 10 days and because the human body metabolizes tritiated water similar to normal water, the critical organ is the whole body (Eisenbud, 1987).

Tritium is introduced into the environment through several mechanisms, the most significant of which are natural production, release from nuclear reactors, fuel reprocessing and atomic weapon detonation. Gaseous tritium at room temperature combines with gaseous hydrogen (H) to form HT, that readily forms a vapor of HTO.

Tritium is produced in the earth's atmosphere at a rate of 4MCi y-1 in the process of spallation (NCRP, 1979). Spallation is defined as the removal of nucleons from an atom nucleus thereby changing its mass number. Tritium is produced from the spallation of nitrogen and oxygen. (Dorfman and Hemmer, 1954)

Tritium is also introduced into the environment by the operation of nuclear reactors. Tritium is generated in two ways. The first results from fission production at a rate of approximately 1 atom per 10,000 fissions (Albenesius, 1959). The second method produces large amounts of tritium from spallation following neutron irradiation of boron ( $^{10}\text{B}$ ). Boron is present in the reactor system as a neutron poison controlling the fission rate during operation. Containment of the fuel and its byproducts prevents large quantities of radionuclides, including tritium, from being directly released into the environment (Moghissi et al, 1986).

Tritium that is enveloped within the fuel can be released into the environment during several phases of the nuclear fuel reprocessing. The first point at which tritium is most likely to escape to the environment is in the fuel-receiving and storing phase. The release is due to fuel-cladding failure where the tritium is vented into the off-gas system and a slow accumulation occurs in the storage pool water. Another important source of tritium comes from the extraction, separation, and purification processes of the fuel where the HTO is incorporated into the aqueous waste streams (Kullen et al, 1975).

Tritium is also produced and released in the detonation of nuclear devices. The amount of tritium produced depends upon the spectrum of fission and fusion energy yields, the type of explosive and the characteristics of the explosion site. (NCRP, 1979)

Once HTO becomes accessible to the environment two dispersal paths become available. The HTO can be retained in the atmosphere for a period of time or it can quickly become deposited onto the earth's surface.

Once deposited on the ground, the soil acts as a transport media until the HTO becomes part of the ground water system. This process occurs when movement of the HTO in the soil moves vertically through the soil column where it eventually reaches the ground water table.

Water in soil can be classified into two categories: free water and capillary water. Unobstructed water percolates relatively quickly through the soil. The rate of percolation is governed by the soil texture and structure. Fractures such as holes caused by insects, worms, mammal activity and lumens created by decaying biological tissue also expedite the distribution of the free water (IAEA, 1981).

Capillary water constitutes water held as a thin layer on the surface of soil particles or in capillaries formed between soil particles. Water movement occurs when there is a water potential difference in the capillary system, or through the molecular diffusion mechanism. This type of dispersal does cause a spread of the contaminated water but is not as rapid as free water movement (IAEA, 1981).

The amount of time before HTO passes through the soil into the ground water system is highly variable. Dependents include velocity flows, hydrodynamic dispersion, permeabilities and soil composition. All of these are a factor in predicting the dispersion models and rate of transport which in turn effect the final concentration entering into the ground water system (NCRP, 1979).

Activities occurring at the Idaho National Engineering Laboratory (INEL) have directly led to the introduction of tritium into the environment. Data clearly suggest that wastewater disposal practices at the INEL have increased tritium concentrations in ground water. Background concentrations of tritium in ground water in Idaho generally range from 75 to 150 pCi/L (Michel, 1989). Ground water samples that were collected in 1987 from 81 wells on the INEL showed concentrations of tritium ranging from -300 to 80,600 pCi/L (negative values are a relict of the analysis methodology) with a mean concentration of 8,190 pCi/L (Knobel and Mann, 1988). A large portion of the contamination has come from the injection of wastewater directly into the aquifer at the Idaho Chemical Processing Plant (ICPP) and the percolation of wastewater from the disposal ponds at the Test Reactor Area (TRA). The plume of tritium generally follows the southwesterly direction of ground water movement in the Snake River Plain Aquifer (fig. 1) (Pittman et al, 1988).

Tritium has migrated approximately 8.3 miles downgradient from the ICPP injection well and 9.1 miles downgradient from the TRA disposal ponds since the 1950's. The arrival of tritium in the ground water at the Radioactive Waste Management Complex (RWMC) was first detected in 1975. In 1985 tritium above typical background concentrations was detected in water wells #103, #105 and #108 near the southern boundary of the INEL. Estimates have been made that the tritium migration rate ranges from 4 to 5 ft/day (Pittman et al., 1988).

Information about tritium concentrations in ground water is useful in determining time and location of plumes, and flow dynamics of groundwater following diffusion patterns of other radioactive materials and organic compounds. For this information to be useful it is important to be able to detect levels of tritium below typical background levels ranging from 50 to 200 pCi/L (Background levels found in site well waters in 1951). Using standard water analysis procedures (liquid scintillation counting) a Lower Level of Detection (LLD) of approximately 400 pCi/L can be achieved. To decrease the LLD the Idaho State University Monitoring Program has adopted a Tritium Enhancement procedure that can decrease the LLD to approximately 50 pCi/L.

## II. METHODS

Fractionation between tritium and the common isotope of hydrogen, protium, are high, making it possible to enhance the sample before counting. Various methods exist for enhancement of tritium in water including gas chromatography, thermal diffusion and electrolysis (NCRP, 1979).

Gas chromatography is accomplished by utilizing a water sample of up to 40 grams and slowly bypassing the sample through hot magnesium to reduce it to hydrogen. The hydrogen is then introduced into a system of ovens containing a palladium sponge which dissolves the hydrogen. The ovens are alternately heated and cooled absorbing and releasing the gas sequentially. The advantages of this method include a high degree of enrichment. About 80 percent of tritium from the original sample can be contained in approximately 700 cc of hydrogen gas. Moreover the procedure is relatively quick, only taking a few hours. Disadvantages include: the complicated instrumentation; some degree of danger with creating hydrogen gas; and large amounts of water that are not easily handled (Hayes and Hoy, 1973).

A second method of enrichment is thermal diffusion. Twelve liters of hydrogen gas are needed from the water sample which is obtained by reduction through zinc or hot magnesium. The apparatus tube is filled with the gas sample where a center wire is heated while the outer cylinder wall is cooled. The gas being cooled and

condensed is enriched in heavier molecules while the lighter elements stay close to the hot wire. This method has proven to be highly useful for enrichment because of the molecular weight difference between HT and H<sub>2</sub>. Another advantage is that the end product is enriched ten-times with greater than 95 percent recovery possible in about 20 hours. This method may be less desirable when dealing with a sample size larger than 20 grams (Verhagen, 1967).

Enrichment can also be achieved through electrolysis. This process takes advantage of susceptibility of H<sub>2</sub>O verses HTO in an electrolytic cell. When subjected to a current H<sub>2</sub>O disassociates faster than the heavier tritium molecule. Disintegration of water molecules is achieved by using an electric current with the introduction of an electrolyte, which allows for a fractionation factor of about 25 in favor of protium to occur (Kaufman and Libbey, 1954). Two different preparation techniques are available for electrolysis; acid and alkaline.

As with methods for enrichment, various methods of detecting tritium exist. The most familiar method is liquid scintillation. Other methods for detecting the presence of tritium include: measurement of bremsstrahlung, mass spectrometry and gas chromatography. While not all of these methods are suitable for all situations, they do have the potential for further development.

### III. RESULTS

The Environmental Monitoring Laboratory (EML), Idaho State University (ISU), initiated a project to improve the sensitivity of analysis for <sup>3</sup>H. The EML tried both the acid and base electrolysis methods using the procedures modified published procedures (HASL 300).

Acid electrolysis was accomplished by completely distilling the sample in the presence of potassium permanganate (KMnO<sub>4</sub>) thus eliminating solids and any organic material. The sample was then enriched by electrolysis in a sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) medium at a high current for approximately 40 hours to reduce the initial sample volume of 50 mL to 6-8 mL. The final volume is then determined on a known aliquot by titration of the sulfuric acid. The degree of enrichment is determined by a calibration of enrichment against volume reduction. Acid electrolysis provided an LLD of about 100 pCi/L. These initial trials with the acid electrolysis procedure indicated that this method did not adequately meet the needs of the EML.

Alkaline electrolysis was accomplished by completely distilling the sample in the presence of potassium permanganate ( $\text{KMnO}_4$ ) thus eliminating solids and existing organic material. An initial volume of 150 mL sample in the presence of sodium hydroxide ( $\text{NaOH}$ ) was electrolyzed at a rate of 1 mL per hour at 3 amps. The electrolytic cells were maintained at a temperature of approximately 5 degrees Celsius in a water bath fabricated from a chest type food freezer and a large plastic tub. Approximately 25 mL of aliquot was added daily while reducing the cell current to 0.3 amps for the final 50 mL. This procedure yielded a final volume of approximately 10 mL from an intial volume of 250 mL in 14 days. The final volume was then directly distilled from the electrolyte out of the electrolysis cell, and the degree of enrichment was calculated. An LLD as low as 20 pCi/L can be easily achieved with this method. The alkaline aliquot method was selected as a more suitable procedure. The procedure is given in Appendix A. The list of materials needed to accomplish the procedure is located in Appendix 2.

Table 1 indicates the results of nine samples of standard solution electrolyzed to varying final volumes. The  ${}^3\text{H}$  concentrations in the standard solutions were about 300 pCi/L. Initial volumes were 250 mL. The method of calculation for the enrichment factor is given in Appendix C. A plot of data is shown in Figure 1. The least square fit of the data yielded the equation:

$$Y = .53 * X + 4.70$$

This equation was used as the calibration curve for the subsequent analysis of environmental samples at an initial volume of 250 mL. Thirteen sample were analyzed by conventional methods and again by the electrolysis method outlined in Appendix A. A comparison of results is given in the table 2.

#### IV. CONCLUSIONS

A procedure to measure tritium in water samples at concentrations as low as 20 pCi/L has been perfected at the ISU-EMP. The procedure is now considered to be routine and will be used when required.

The EMP at Idaho State University has a need to have the ability to accurately measure concentrations of tritium at concentrations less than 50 pCi/L. This level of detection will allow the measurement of anthropogenic tritium in ground water. It will also allow the detection of minor variations of tritium concentrations in surface water, precipitation or water vapor.

The normal measurement of water samples for tritium allows for an LLD of approximately 350 pCi/L to be obtained. The LLD for tritium in water samples can be lowered to about 20 pCi/L using modified methods that are standard and well documented. The method which uses alkaline electrolysis enriches the ratio of tritiated water to protonated water in the measured sample. The sample with the concentrated or enriched tritium radioactivity is then measured using normal methods. There are only two real disadvantages to this tritium enrichment technique. The procedure is complex and requires an individual to be well trained. The electrolysis process also takes about 14 days and requires the use of specialized glassware and equipment.

#### V. REFERENCES

- Albenesius, E., 1959. Tritium as a Product of Fission. Phys. Rev. Lett. **3**, 6, 274-275.
- Dorfmann, L, and B. Hemmer, 1954. Ion-Pair Yield of the Tritium-Oxygen Reaction. J. Chem. Phys. **22**, 9, 1555-1558.
- Eisenbud, M, 1987. Environmental Radioactivity From Natural, Industrial, and Military Sources. Academic Press, Inc., San Diego, California.
- HASL-300 Procedures Manual, 1990. Tritium in Water-Acid Electrolysis. Environmental Measurements Laboratory U.S. Department of Energy, New York, New York.
- Hayes, D. and J. Hoy, 1973. "A Chromatographic System for the Enrichment and Analysis of Low Level Tritium Samples", in Tritium, Moghissi, A. and M. Carter, eds. Messenger Graphics, Phoenix, Arizona.
- International Atomic Energy Agency, 1981. Tritium in Some Typical Ecosystems, IAEA Technical Report Series No. 207. International Atomic Energy Agency, Vienna, Austria.
- Kaufman, S. and W. Libbey, 1954. The Natural Distribution of Tritium. Phys. Rev. **93**, 6, 1337-1344.
- Knobel, L. and L. Mann, 1988. Radionuclides in Ground Water at the Idaho National Engineering Laboratory, Idaho. U.S. Geological Survey Open-File Report 88-731. DOE/ID-22077.
- Kullen, B. L. Trevorrow, and M. Steindler, 1975. Tritium and Noble-Gas Fission Products in the Nuclear Fuel Cycle. II. Fuel Reprocessing Plants, Report No. ANL-8135. Argonne

National Laboratory, Argonne, Illinois.

Michel, R., 1989. Tritium Deposition in the Continental United States, 1953-1983. U.S. Geological Survey Water-Resources Investigation Report 89-4072.

Moghissi, A., H. Godbee and S. Hobart, 1986. Radioactive Waste Technology. The American Society of Mechanical Engineers, New York, New York.

National Council on Radiation Protection, 1979. Tritium in the Environment, NCRP Report No. 62. National Council on Radiation Protection and Measurements, Bethesda, Maryland.

Pittman, J., R. Jensen, and P. Fischer, 1988. Hydrological Conditions at the Idaho National Engineering Laboratory 1982 to 1985. U.S. Geological Survey Water-Resources Investigations Report 89-4008. DOE/ID-22078.

Verhagen, B, 1967. "Rapid Isotope Enrichment of Gases by Thermal Diffusion for Nuclear Dating" in Radioactive Dating and Methods of Low-Level Counting. International Atomic Energy Agency, Vienna, Austria.

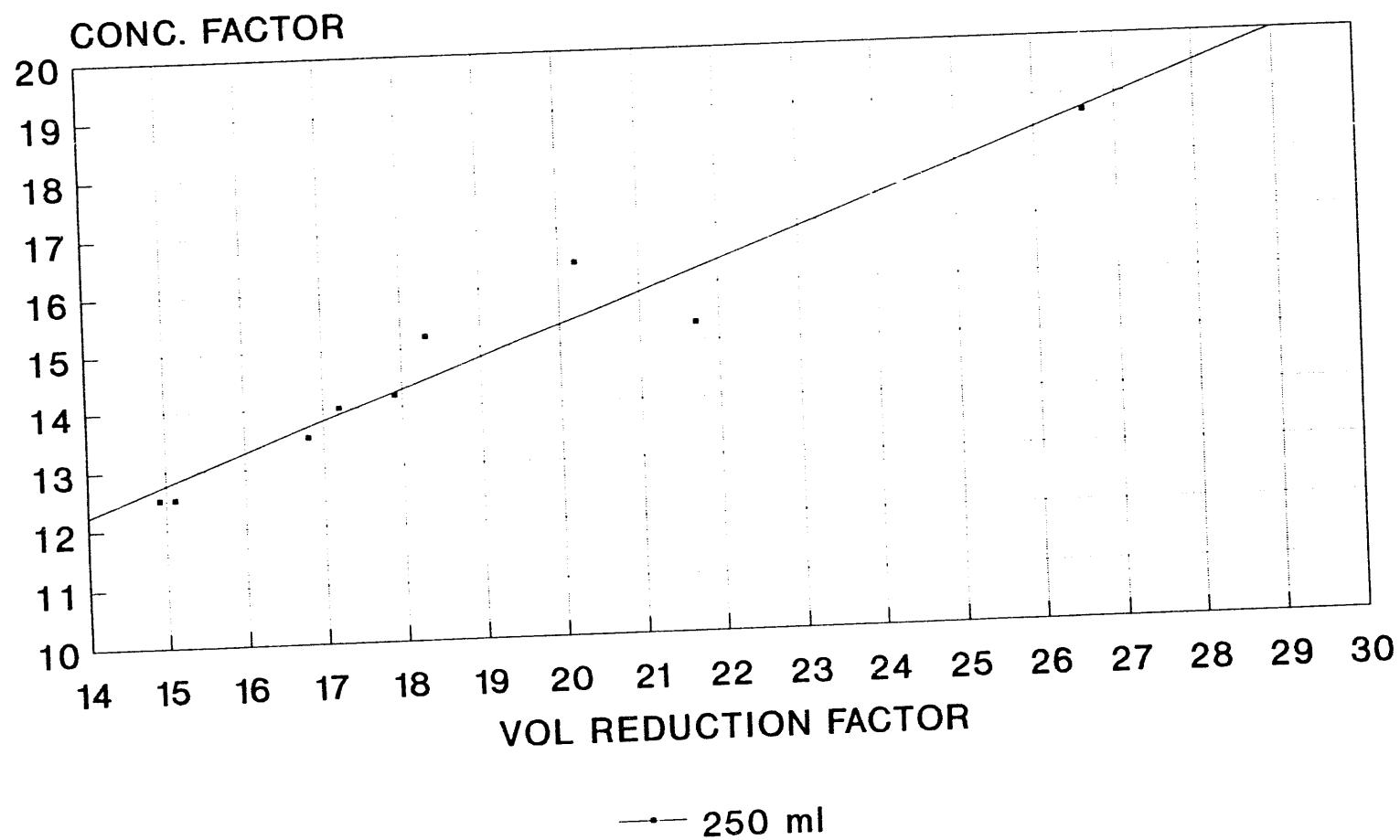
TABLE 1. CALIBRATION RESULTS

Volume Reduction X	H-3 Enrichment Factor Y	% Recovery H-3
14.9	12.5	83.9
15.1	12.5	82.8
16.8	13.5	80.4
17.2	14.0	81.4
17.9	14.2	79.3
18.3	15.2	83.1
20.2	16.4	81.2
21.7	15.3	70.5
26.6	18.7	70.3

**TABLE 2. Comparison of Conventional and Enhanced Tritium Analysis**  
**(results in pCi/mL +/- 1sd)**

SAMPLE #	ENHANCED RESULT RESULT	CONVENTIONAL RESULT
RS2959	0.02 +/- 0.01	-0.1 +/- 0.1
RS3300	0.01 +/- 0.01	-0.1 +/- 0.1
RS3082	0.03 +/- 0.01	-0.2 +/- 0.1
RS3083	0.19 +/- 0.01	0.1 +/- 0.1
RS3084	0.18 +/- 0.01	0.0 +/- 0.1
RS3087	0.09 +/- 0.01	-0.1 +/- 0.1
RS3119	0.02 +/- 0.01	-0.4 +/- 0.1
RS3179	0.07 +/- 0.01	-0.1 +/- 0.1
RS3294	0.03 +/- 0.01	0.0 +/- 0.1
RS3295	0.04 +/- 0.01	-0.2 +/- 0.1
RS3297	0.76 +/- 0.01	0.7 +/- 0.1
RS3298	0.01 +/- 0.01	-0.1 +/- 0.1
RS3299	0.09 +/- 0.01	0.0 +/- 0.1

# H-3 ENRICHMENT STD CURVE



5-3-93

## APPENDIX A: H-3 ENRICHMENT PROCEDURE

1. The sample is initially prepared distillation in the presence of potassium permanganate ( $KMnO_4$ ). This process eliminates solids and existing organic material. Distill at least to a volume of 250 mL and store in a suitable container.
2. Measure exactly 250 mL of the prepared distillate.
3. Add about 400mg of NaOH (two average size pellets) and 5-10 mL of the distilled sample to a clean electrolysis cell and let stand for approximately 1 hour. Gently shake until the pellets are completely dissolved.
4. Add more distilled sample to make the volume 150 mL.
5. Insert the electrode assembly and place the cell in an ice bath. The ice bath should be maintained at a temp 5-10 degree C. The ice bath has been fabricated from a chest type freezer and a large plastic tub.

*The ice bath is used to avoid evaporative losses because tritiated water evaporates at the same rate as stable water. Excessive evaporation will lead to poor tritium recovery relative to the original concentration.*

6. Connect the cells to the power supply. The red lead is the nickel anode and is connected to positive. The black lead is the iron cathode which is connected to negative. The cells are connected in series so that the red lead from the first cell is connected to the positive pole of the power supply. The black lead of the first cell is connected to the red lead of the second cell and the black lead of the second cell is connected to the negative pole of the power supply.
7. The power supply (Fisher Scientific) is set to the 3 amps. At 3 amps, electrolysis will proceed at a little over 1 mL per hour.
8. The cell is run until about 25 mL remains (approximately 5 days) and stopped. Another 25 mL of sample is added and the cells are restarted. This procedure is repeated until a total of 250 mL of sample has been added to the cell (approximatley 4 additional days). When the cell is again at about 25 mL the amperage is reduced to 0.3 amps and the cell is run until the volume reduced to 12-18 mL (usually about another 5 days).

*In any electrolysis cell, there is always a danger of explosion of the hydrogen-oxygen mixture. Thus electrical connections must be non-sparking, the cells must never be handled with the power on, and electrolysis must be stopped before dryness, or before the liquid level falls below the lower edge of the electrode.*

9. Pull the electrode assembly partially out of the cells to allow sample to drain off of them. Remove the electrodes.  
Set up the electrolysis cell for vacuum distillation with a tared trap to collect the distillate.
10. Cool the trap by placing in a Dewer of liquid nitrogen. The best results are obtained if only the bottom of the trap is immersed in liquid nitrogen. If the trap is immersed too deeply the collection tube may freeze and plug up.
11. Wrap the heating tape around the bottom of the electrolysis cell. Apply vacuum and close off system to maintain vacuum. Turn the heat to 4 on a Minitrol power controller. Distillation will take 2-3 hours.
12. Vacuum may be applied intermittently. The pump does not need to be run continuously but if disconnected it must be run for a short time after reconnecting and reopening the stop-cock. The trap is lowered in the Dewer as needed to keep the bottom immersed.
13. Distillation is complete when the cell appears dry. A coating of NaOH will appear on the sides of the cell. Visual inspection will tell when this is completely dry. The bottom of the cell requires the longest time to dry completely. When the bottom is dry the heating tape is moved up around the top half of the cell for 10-15 minutes to ensure that the entire cell is dry.
14. Disconnect the vacuum and remove the trap. Allow the trap to thaw, dry the outside and weigh.

*The comparison of the initial volume to final volume (weight) will be instrumental in determining the volume reduction factor. The tritium enrichment factor is determined from the standard curve of enrichment factor vs. volume reduction factor.*

15. Transfer sample to a 20mL scintillation vial and allow to come to room temperature (usually overnight). Count 10 mL by normal counting procedures.
16. Final concentrations are computed by multiplying the concentration calculated by the tritium enrichment factor.

#### **APPENDIX B: REQUIRED MATERIALS**

1. Electrolysis cells- **Science Glass Miami.**
2. Vacuum distillation apparatus- **Coors.**
3. Liquid scintillation counter- **Packard Tri-Carb Liquid Scintillation Spectrometer.**
4. Power supply- **Fisher Scientific**
5. Power controller- **Minitrol.**
6. Vacuum pump- **Welch Vacuum Technology.**
7. Heat tape- **Glas-Col.**
8. Liquid scintillation vials-
9. Scintillation cocktail- **Pico-Fluoro (Packard)**
10. NaOH pellets- **Fischer Scientific.**

## APPENDIX C: TRITIUM ENRICHMENT FACTOR

The degree of H-3 enrichment is proportional to the volume, but not equal to it. Thus, the enrichment factor must be determined as a function of the volume reduction. This is best done with standard samples of moderate activity.

Prepare a series of electrolysis cells with aliquot of a known standard and electrolyze to a range of final volumes covering those expected in sample analyses. Carry these through the complete analysis described in appendix A.

The volume reduction factor is,

$$X = V_i/V_f$$

where  $V_i$  and  $V_f$  are the initial and final volumes, the enrichment factor is,

$$Y = C_f/C_i$$

where  $C_f$  and  $C_i$  are the final and initial H-3 concentrations. The values  $X$  and  $Y$ , determined from the standards, are plotted and a straight line relationship should be obtained. The enrichment factor for a sample may then be determined from this plot for the measured volume reduction factor.

### LOWER LIMIT OF DETECTION(LLD)

---

Counter Efficiency	(%)	19.7
Counter Background	(cps)	26.7
LLD (200 min)	(pCi/L)	20

---

The image consists of three separate, vertically aligned abstract graphic elements. The top element is a horizontal rectangle divided into four equal quadrants by a vertical and a horizontal line, with the central area being white. The middle element is a trapezoid pointing downwards, filled with black on its left side and white on its right side. The bottom element is a large, thick, black, semi-circular shape pointing upwards, containing a smaller, solid white semi-circle at its center.

hb / 94  
May / 2011

**DATA**

