AP2

DETERMINATION OF TRITIUM

PART A

PRINCIPLE

The tritium in aqueous and solid samples is distilled using an Allihn condenser. For solid samples, an appropriate volume of water is added to facilitate distillation. Certain solid samples may be refluxed to ensure distribution of any tritium that may be in the samples. The samples may be spiked with a standard tritium solution to evaluate quenching and counting efficiency. After the samples have been distilled, an aliquot of the distillates is added to a scintillation cocktail and the samples are counted using a liquid scintillation analyzer.

REFERENCE

1. Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, August 1980.

2. Annual Book of ASTM, Standards Vol. 11.02, pp. 395-397.

Certification Record for

PROCEDURE AP2

DETERMINATION OF TRITIUM

CHECKPOINTS

1. **JOB HAZARD ANALYSIS (JHA)** _____
2. **MSDS/HAZARDS DISCUSSED** _____
3. **DISTILLATION EQUIPMENT SET-UP** _____
4. **END OF DISTILLATION** _____
5. **COCKTAIL-SAMPLE PREP** _____
6. **FINAL CALCULATION(S)** _____

ANALYST SIGNATURE: _____

CERTIFIED BY: _____

DATE: _____

ANALYSIS VALUE: _____

KNOWN VALUE: _____

MEASURED/KNOWN RATIO: _____

COMMENTS: _____
_____
_____
_____
_____

PART B

1.0 PURPOSE AND SCOPE

This procedure provides the methodology for the determination of tritium (H-3) in soil, sediment, animal tissue, vegetation, smears and water samples.

2.0 INTERFERENCES

2.1 Other volatile radionuclides such as iodine and carbon isotopes may interfere and may require that the sample be made alkaline using solid sodium hydroxide before distillation.

2.2 Organic impurities may interfere and may require the addition of an oxidizing agent to the sample as well as spiking the samples with a standard tritium solution. The addition of a standard tritium solution to each sample allows for counting efficiencies to be calculated for each individual sample. This method is called internal efficiency calculation.

3.0 REAGENTS

Scintillation cocktail, Ultima Gold XR, or equivalent

Sodium Hydroxide, NaOH, solid pellets

Tritium, NIST traceable standard

10% Foam Blast

4.0 APPARATUS

Allihn condenser and connecting apparatus
Round bottom flask (appropriate size)
Carborundum or boiling chips
Centrifuge tubes, 50 mL
Class A pipettes or equivalent
Friedricks refluxing condenser
Heating mantle (appropriate size)
Liquid Scintillation Analyzer (LSA)
Scintillation vials (glass)
Stir bar

5.0 PROCEDURE

5.1 General Requirements

Before proceeding, you must be certified as indicated in QCP1 of this manual and Section 3 of the Quality Program Manual. See page two for a copy of the certification record.

An efficiency spike must be run with each batch to determine the counting efficiency (see section 7.0 for calculation). The efficiency spike may be internal or external (section 6.0). This is not a QC sample. Two QC samples must be run with each batch.

5.2 Water Samples

Place an appropriate aliquot (typically 50-250 mL) of sample in an appropriate sized round bottom flask. Go to step 5.3.4. **See step 5.2 of AP2 JHA.**

5.3 Soil, Sediment, and Animal Tissue Samples

5.3.1 All animal tissue samples should be preserved frozen until ready for analysis. Just prior to analysis, the tissue samples should be ground and thawed.

5.3.2 Weigh and record approximately 50 g samples. Place the sample in a 500 mL round bottom flask. **See step 5.3.2 of AP2 JHA**.

5.3.3 Add 50 mL of reagent water, 1 mL of 10% Foam Blast, 1 to 2 pellets of NaOH and swirl to disperse the water throughout the sample. **See step 5.3.3 of AP2 JHA**.

5.3.4 Assemble distillation system using an Allihn condenser, heating manifold, rheostat, and various lengths of tubing. Place a small stir bar or carborundum chip in each round bottom flask to facilitate boiling and begin distillation. **See steps 5.3.4a-5.3.4d of AP2 JHA**.

5.3.5 Collect the first 10 mL in a centrifuge tube and discard in the appropriate waste stream. **See step 5.3.5 of AP2 JHA.**

5.3.6 Continue distillation and collect the next 30 mL in another centrifuge tube. Do not go to dryness. (Some samples will bump and carry over particles. These samples need to be redistilled.) **See step 5.3.6 of AP2 JHA**.

5.3.7 Place an appropriate (usually 10 mL) aliquot from the 30 mL collection in a glass scintillation vial and mix with 10 mL scintillation cocktail. An external counting efficiency standard must be used when internal spiking of samples is not performed. This counting efficiency standard usually contains about

500 pCi diluted to 10 mL with reagent water and 10 mL of scintillation cocktail. Set up a detector blank with 10 mL of reagent water and 10 mL of scintillation cocktail. **See step 5.3.7 of AP2 JHA.**

5.3.8 Submit the samples to the count room. **See step 5.3.8 of AP2 JHA.**

5.4 Vegetation Samples

5.4.1 All vegetation samples should be refrigerated until ready for analysis. Just prior to analysis, the vegetation samples should be ground.

5.4.2 Weigh and record approximately 50 g samples. Place the sample in a 500 mL distillation flask. **See step 5.3.2 of AP2 JHA**.

5.4.3 Add 100 mL of reagent water, 1 mL of 10% Foam Blast, 1 to 2 pellets of NaOH and swirl to disperse the water throughout the sample. The initial distillate that is collected may have to be redistilled in order to remove excess organic material that can distill across. Go to step 5.3.5 **See step 5.3.3 of AP2 JHA.**

5.5 Smear Samples

5.5.1 If smear samples are not already in scintillation vials with water, place smears in glass scintillation vials containing 10 mL of water. Add 10 mL of scintillation cocktail and shake well. **See step 5.5.1 of AP2 JHA.**

5.5.2 Set up a blank smear with 10 mL of water and 10 mL of Ultima Gold XR, or equivalent scintillation cocktail. **See step 5.5.1 of AP2 JHA.**

5.5.3 After all samples have been processed, submit the scintillation vials to the counting room. **See step 5.5.3 of AP2 JHA.**

5.5.4 After the first sample count, add a known amount of H-3 standard to each smear sample and shake well. **See step 5.5.4 of AP2 JHA.**

5.5.5 Submit samples to the count room. **See step 5.3.8 of AP2 JHA.**

6.0 CALIBRATION

6.1 Tritium in water, External Efficiency

6.1.1 Add approximately 500 pCi of an appropriate tritium standard to 5 to 7 mL of reagent water and mix. Dilute to 10 mL with reagent water and then mixed with 10 mL of scintillation cocktail. This spiked water is used to calculate counting efficiency. Prepare a detector blank with 10 mL of reagent water and 10 mL of scintillation cocktail to measure the detector

background. **See step 5.3.7 of AP2 JHA.**

6.1.2 Submit the tritium standard to the count room. The counting statistics for this standard should be 1 percent or less. **See step 5.3.8 of AP2 JHA.**

NOTE: A review of the quench indicator parameters must be performed to ensure that the efficiency and sample values agree within 20% for the batch analysis. For DOE work, the values must agree within 5%.

6.2 Tritium on Smears, External Efficiency

6.2.1 Spike a blank smear in 10 mL reagent water with approximately 500 pCi of an appropriate tritium standard and then mixed with 10 mL of scintillation cocktail. This spiked smear is used to calculate counting efficiency. Set up a blank smear with 10 mL of reagent water and 10 mL of scintillation cocktail for the detector background. **See step 5.3.7 of AP2 JHA.**

6.2.2 Submit the tritium smear standard to the count room. The counting statistics for this standard should be 1 percent or less. **See step 5.3.8 of AP2 JHA.**

6.3 Tritium in Water, Internal Efficiency

6.3.1 Add 5 mL of each sample to a glass scintillation vial and mix with 10 mL of scintillation cocktail by shaking. Prepare a reagent water blank with 5 mL of reagent water and 10 mL of scintillation cocktail for the detector background. **See step 5.3.7 of AP2 JHA.**

6.3.2 Submit samples to the count room. **See step 5.3.8 of AP2 JHA.**

6.3.3 After the first sample count, add a known amount of tritium standard to each water sample and shake well. **See step 5.3.7 of AP2 JHA.**

6.3.4 Submit samples to the count room. **See step 5.3.8 of AP2 JHA.**

6.4 Tritium on Smears, Internal Efficiency

6.4.1 Place each smear in a glass scintillation vial containing 10 mL of reagent water and mix with 10 mL of scintillation cocktail. Set up a blank smear with 10 mL of reagent water and 10 mL of scintillation cocktail for the detector background. **See step 5.3.7 of AP2 JHA.**

6.4.2 Submit smears to the count room. **See step 5.3.8 of AP2 JHA.**

6.4.3 After the first sample count, add a known amount of tritium standard to each smear sample and shake well. **See step 5.3.7 of AP2 JHA.**

6.4.4 Submit smears to the count room. **See step 5.3.8 of AP2 JHA.**

7.0 CALCULATIONS

Critical data values will be documented on approved assignment and calculation forms referenced to the current procedure and revision. See pages 10-12 of this procedure for approved forms. Critical records are maintained as hardcopy in the archived site file or electronically in the IEAV database. The following equations define the critical data values. All data will be recorded and reduced according to these calculations.

Tritium activity for samples analyzed by internal spiking is calculated as follows:

$$Concentration = \frac{G-B}{Q} \cdot \frac{P}{S-G} = pCi/unit$$

$$2\sigma\ Error = \frac{1.96\sqrt{(G+B)\cdot T}}{Q \cdot T} \cdot \frac{P}{S-G} = pCi/unit$$

$$2\sigma\ TPU = C \cdot 1.96\sqrt{\frac{(G+B)\cdot T}{((G-B)\cdot T)^2} + \frac{(S+B)\cdot T}{((S-B)\cdot T^2} + RP^2 + RE^2 + RQ^2} = pCi/unit$$

$$MDC = \frac{3+4.65\sqrt{B \cdot T}}{Q \cdot T} \cdot \frac{P}{S-G} = pCi/unit$$

Where:

B	=	background counts/minute
C	=	concentration in pCi/unit
G	=	sample gross counts/minute
MDC	=	minimum detectable concentration
P	=	activity added to spiked sample, pCi
Q	=	sample quantity
RP	=	1σ relative uncertainty of the pCi added
RE	=	1σ relative uncertainty of the efficiency
RQ	=	1σ relative uncertainty of the quantity
S	=	spiked sample gross counts/minute
T	=	count time in minutes
TPU	=	total propagated uncertainty

Tritium activity for samples analyzed by external counting efficiency is calculated as follows:

$$Concentration = \frac{G - B}{E \cdot Q} = pCi / unit$$

$$2\sigma\ Error = \frac{1.96\sqrt{(G + B) \cdot T}}{E \cdot Q \cdot T} = pCi / unit$$

$$2\sigma\ TPU = C \cdot 1.96\sqrt{\frac{(G + B) \cdot T}{((G - B) \cdot T)^2} + RE^2 + RQ^2} = pCi / unit$$

$$MDC = \frac{3 + 4.65\sqrt{B \cdot T}}{E \cdot Q \cdot T}$$

$$E = \frac{G_E - B}{E_{ACT}} = cpm / pCi$$

Where:

B	=	background counts/minute
C	=	concentration in pCi/unit
E	=	tritium counting efficiency (cpm/pCi)
E_{ACT}	=	pCi of tritium added to efficiency standard
G_E	=	efficiency standard gross cpm
G	=	sample gross counts/minute
MDC	=	minimum detectable concentration
Q	=	sample quantity
RE	=	1σ uncertainty of the efficiency
RQ	=	1σ uncertainty of the quantity
T	=	count time in minutes
TPU	=	total propagated uncertainty

8.0 RECORDS

8.1 Reference QA Manual for general record requirements.

8.2 The raw count data are saved during the weekly backup of the Liquid Scintillation Analyzer to the ORISE network disks. A disk image backup is performed once a month.

8.3 Hard copies of the assignment and calculation sheets are maintained in the archived site file. Electronic copies of assignment and calculation sheets are saved during the daily incremental backup of the network system. The following data

sheets show the required data and information. These forms or the equivalent should be completed and retained:

- Tritium Analysis Assignment Form
- Tritium Lab Data Sheet
- Tritium Concentration and Uncertainty Report (This report may be generated using approved Excel spreadsheets or from the database, if available.)

AP2(Rev 16) - TRITIUM ANALYSIS ASSIGNMENT FORM

Assigned To: _____ **Date:** _____ **Batch:** _____

Task #: _____ **LWR #:** _____ **Activity Level*:** _____

Sample #s: _____

_____

_____

Analysis Required:

Distillation ☐

Dir. Scintillation ☐

Eff. Spike ☐ **H-3 STD #** _____ **Quantity:** _____
(see Special Instructions, if any) **Units:** _____

☐ **External (EFF SPK per Batch)**

☐ **Internal (EFF SPK per Sample)**

QC Required:

Blank ☐ **Initials**

LCS ☐ **H-3 STD #** _____ **Quantity:** _____ ☐
Units: _____

Pipette # _____ Volume (mL) _____ Weight (g) _____

Replicate ☐ **Sample #** _____ **# Replicates:** _____

Matrix Spike ☐ **Sample #** _____ **Initials**

H-3 STD # _____ **Quantity:** _____ ☐
Units: _____

SPECIAL INSTRUCTIONS: _____

_____

_____

_____

* If Activity Level is indicated as Moderate or High, perform area survey

COMMENTS: _____

_____

_____

_____

AP2(Rev 16) - TRITIUM LAB DATA SHEET

SAMPLE #							
Smpl. Quantity							
Unit of Measure							
Total Vol Distilled, L							
Water Vol. Distilled, L							
Sample Vol. Counted, L							

SAMPLE #							
Smpl. Quantity							
Unit of Measure							
Total Vol Distilled, L							
Water Vol. Distilled, L							
Sample Vol. Counted, L							

SAMPLE #							
Smpl. Quantity							
Unit of Measure							
Total Vol Distilled, L							
Water Vol. Distilled, L							
Sample Vol. Counted, L							

SAMPLE #			
Smpl. Quantity			
Unit of Measure			
Total Vol Distilled, L			
Water Vol. Distilled, L			
Sample Vol. Counted, L			

AP2(Rev 16) - Tritium by Distillation Concentration and Uncertainty Report

INPUT BY:

DATE:

TASK#

BATCH#

Efficiency (Eff) Calculation	
Eff spike cpm	
Background cpm	
pCi added	
pCi added error	
Eff (cpm/pCi)	
Eff Error (cpm/pCi)	
Eff Relative Error	
Counting time for efficiency calculations (min)	

Position #	SAMPLE ID	GROSS cpm	QUANTITY	QUANTITY ERROR	UNITS	TIME (min)	CONCENTRATION	TPU	4.65 sigma MDC
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									

H-3 Known	**Unc.**	**Meas/ Known**	**Unc**

BLANK CORRECT? YES[ ] NO[ ] INIT_____

LCS CORRECT? YES[ ] NO[ ] INIT_____

BATCH YIELD CORRECT? YES[ ] NO[ ] INIT_____

IF NO, SPECIFY REASON:

ANALYST REVIEW: _____ DATE: _____

REVIEWED BY: _____ DATE: _____

GIVEN TO: _____ DATE: _____

QC ENTERED BY: _____ DATE: _____