AP9

DETERMINATION OF CARBON-14 IN WATER AND SMEARS

PART A

PRINCIPLE

Water samples are treated with sulfuric acid and potassium permanganate. The sample is heated to release carbon as carbon dioxide. The carbon dioxide is purged through the system with an inert gas and bubbled through an absorbing material. Water vapor is removed by a cold trap. A batch yield is used to determine the chemical yield. The carbon-14 (C-14) is counted on a liquid scintillation analyzer.

Smear samples are placed into scintillation cocktail without sample preparation and counted in a liquid scintillation analyzer. This option is viable if tritium is the only other possible contaminant.

REFERENCE

Krieger, H. L., Gold, S., Procedures for Radiochemical Analysis of Nuclear Reactor Aqueous Solutions, U. S. EPA Publ., EPA-R4-73-014, 1973.

CERTIFICATION RECORD FOR

AP9

DETERMINATION OF CARBON-14 IN WATER AND SMEARS

CHECKPOINTS

1. **JOB HAZARD ANALYSIS (JHA)** _____
2. **MSDS/HAZARDS DISCUSSED** _____
3. **SET OF APPARATUS** _____
4. **SAMPLE ADDITION** _____
5. **ADDITION OF OXIDIZERS** _____
6. **COLLECTION OF SAMPLE** _____
7. **FINAL CALCULATIONS** _____

ANALYST SIGNATURE: _____

CERTIFIED BY: _____

DATE: _____

ANALYSIS VALUE: _____

KNOWN VALUE: _____

MEASURED/KNOWN RATIO: _____

COMMENTS:_____
_____
_____
_____

PART B

1.0 PURPOSE AND SCOPE

This procedure provides a method for determination of C-14 in water and smears.

2.0 INTERFERENCES

2.1 Excessive carbon in the samples may overload the absorption capacity of the carbon trapping cocktail. This may be countered by running a matrix spike to determine sample specific recovery.

2.2 Materials that will not be oxidized to carbon dioxide in the presence of sulfuric acid and $KMnO_4$, such as heavier organic material, will not be quantified.

3.0 REAGENTS

All chemicals are hazardous. See MSDS for specific precautions. **See step 3.0 of AP9 JHA.** Unless otherwise indicated, all references to water should be understood to mean reagent grade water.

C-14, NIST traceable standardized solution.

C-14 trapping cocktail (RJ Harvey supplied or equivalent).

Inert purge gas (He or N_2).

Potassium permanganate, $KMnO_4$: ACS reagent.

Potassium permanganate solution: Dissolve 0.5 g of $KMnO_4$ in 25 mL of water. Make fresh daily.

Sulfuric acid, H_2SO_4, 18 M: concentrated reagent.

4.0 APPARATUS

Cold finger trap
Flask, (large enough to hold sample and reagents)
Hot plate
Liquid scintillation analyzer
Pasteur pipettes
Teflon and Tygon tubing
Scintillation vials, low potassium glass

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 2 for a copy of the certification record.

A batch yield sample must be run with each batch to determine chemical recovery for the batch (see calculations). This is not a QC sample; two QC samples must be run with each batch.

5.2 Water Samples

5.2.1 Assemble the oxidation/trapping apparatus (see figure 1). Position the cold finger trap in ice bath. **See step 5.2.1 of AP9 JHA.**

5.2.2 Set the nitrogen gas regulator to 1 to 2 psi. Open the regulator value and check the gas flow through the scintillation vial containing water. There should be 3 to 5 bubbles per second through the solution. **See step 5.2.2 of AP9 JHA.**

5.2.3 Place a clean scintillation vial containing 15 mL of trapping cocktail under the Pasteur pipette holder. Position the Pasteur pipette well below the surface of the trapping cocktail. **See step 5.2.3 of AP9 JHA.**

5.2.4 Place the required sample into an appropriate flask. Add approximately 25 mg of manitol to each sample. Connect apparatus to flask and ensure all flask openings are completely sealed and ensure all openings are completely sealed and that the gas is still bubbling through the scintillation cocktail. Place the flask on a heating device. For batch yield and Laboratory Control Standard (LCS), add 100-500 pCi of C-14 and reseal the flask to make sure the gas is still flowing properly. **See step 5.2.4 of AP9 JHA.**

5.2.5 Add 1 mL of the $KMnO_4$ solution and 5 mL 18 $\underline{M}$ H_2SO_4 to the delivery flask. Slowly bring the sample to a boil. Continue heating and purging until ~2 to 3 mL of condensate forms in the cold trap. This should be completed in less than 15 minutes. **(DO NOT ALLOW SAMPLE TO GO TO DRYNESS.) See step 5.2.5 of AP9 JHA.**

5.2.6 Remove scintillation vial from trapping system and cap. **See step 5.2.6 of AP9 JHA.**

5.2.7 After all samples have been processed, submit the scintillation vials to the counting room. **See step 5.2.7 of AP9 JHA.**

5.3 Smear Samples

5.3.1 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 5.3.1 of AP9 JHA.**

5.3.2 Set up a blank smear with 10 mL of water and 10 mL of Ultima Gold XR, or equivalent scintillation cocktail. **See step 5.3.1 of AP9 JHA.**

5.3.3 After all samples have been processed, submit the scintillation vials to the counting room. **See step 5.2.7 of AP9 JHA.**

5.3.4 After the first sample count, add a known amount of C-14 standard to each smear sample and shake well. **See step 5.2.3 of AP2 JHA.**

5.3.5 Submit samples to the count room. **See step 5.2.7 of AP9 JHA.**

6.0 CALIBRATIONS

6.1 Water Samples

6.1.1 Add ~500 pCi of C-14 to 15 mL of the trapping scintillation cocktail to determine counting efficiency for the batch. **See step 5.2.3 of AP9 JHA.**

6.1.2 Submit the water standard to the counting room. The counting statistics for this standard should be less than 1 percent. **See step 5.2.7 of AP9 JHA.**

6.1.3 The Laboratory Manager or designee must review and approve the counting efficiency.

6.2 Smear Samples

6.2.1 A blank smear in 10 mL of water is spiked with ~500 pCi of an appropriate C-14 standard and then mixed with 10 mL of Ultima Gold XR, or equivalent scintillation cocktail. **See step 5.2.3 of AP9 JHA.**

6.2.2 Submit the smear standard to the counting room. The counting statistics for this standard should be less than 1 percent. **See step 5.2.7 of AP9 JHA.**

6.2.3 The Laboratory Manager or designee must review and approve the counting efficiency.

7.0 CALCULATIONS

Critical data values will be documented on standard forms maintained as critical records. The following equations define the critical data values. All data will be recorded and reduced

according to these calculations.

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

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

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

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

To calculate efficiency:

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

To calculate chemical yield:

$$Y = \frac{G_Y - G}{E \cdot pCi} = no\ units$$

where:	B	=	background cpm
	C	=	concentration to pCi/unit
	E	=	counting efficiency (cpm/pCi)
	G	=	sample gross counts per minute (cpm)
	G_E	=	efficiency sample gross counts per minute (cpm)
	G_Y	=	batch yield sample gross counts per minute (cpm)
	MDC	=	minimum detectable concentration
	Q	=	sample quantity
	RE	=	1σ relative uncertainty of the efficiency
	RQ	=	1σ relative uncertainty of the quantity
	RY	=	1σ relative uncertainty of the yield
	T	=	sample count time (minutes)
	TPU	=	total propagated uncertainty
	Y	=	batch chemical recovery (Yield will be 1.0 for smears.)

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.

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:

- C-14 Analysis Assignment form
- C-14 Lab Data Sheet
- C-14 Concentration and Uncertainty Report (This report may be generated using approved Excel spreadsheets or from the database, if available.)

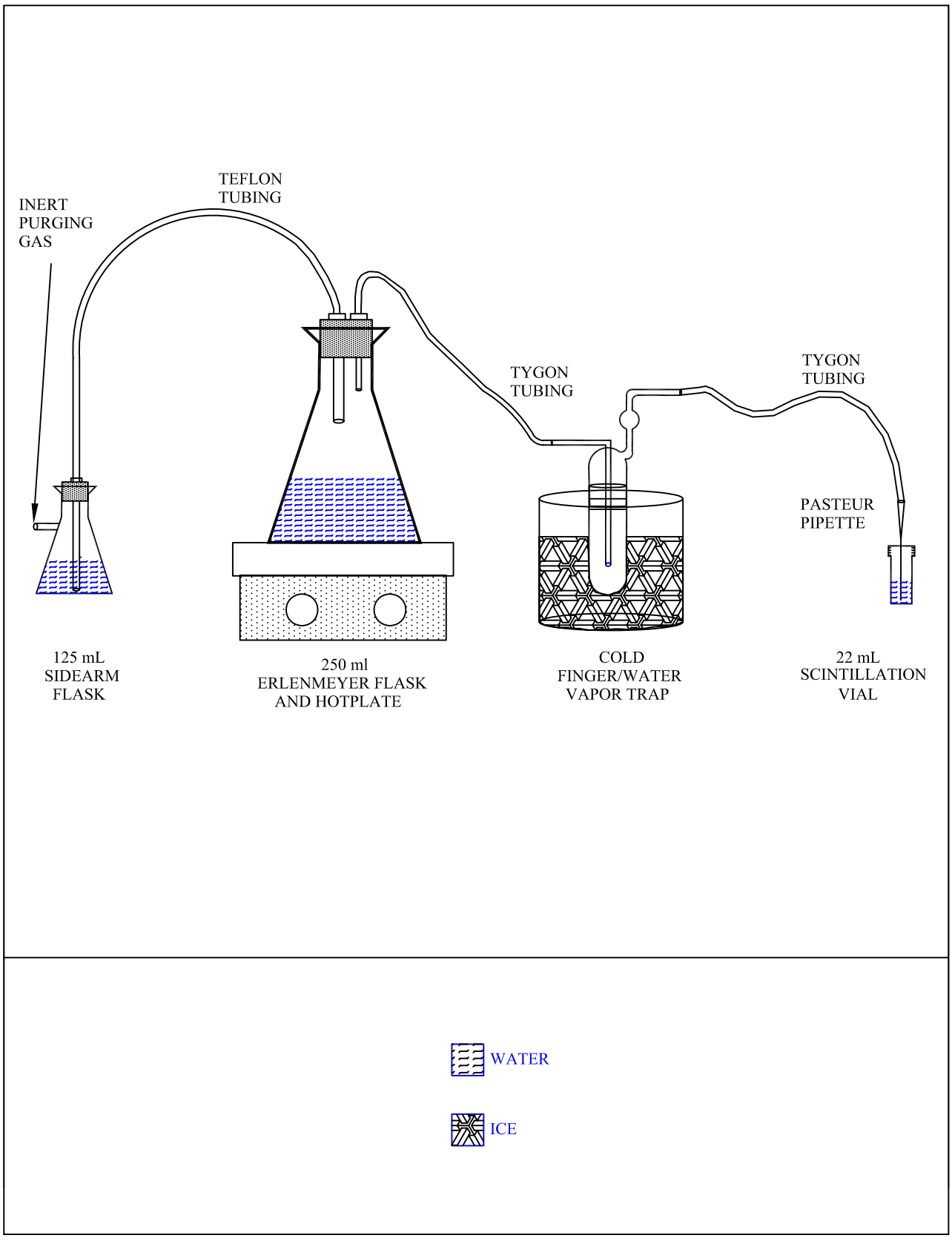

FIGURE 1: Carbon -14 Oxidation and Trapping System

AP9(Rev 4) - C-14 BY DISTILLATION ASSIGNMENT FORM

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

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

Sample #s: _____

_____

_____

Analysis Required:

Batch Yield ☐
Initial below sample
Sample # _____
C-14 STD # _____ **Quantity:** _____
Units: _____

Eff. Spike ☐
C-14 STD # _____ **Quantity:** _____
(see Special Instructions, if any) **Units:** _____

QC Required:

Blank ☐

LCS ☐ **C-14 STD #** _____ **Quantity:** _____ **Initials** ☐
Units: _____

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

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

Matrix Spike ☐ **Sample #** _____ **Initials** ☐
C-14 STD # _____ **Quantity:** _____
Units: _____

SPECIAL INSTRUCTIONS: _____

_____

_____

_____

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

COMMENTS: _____

_____

_____

AP9(Rev 4) - C-14 BY DISTILLATION
LAB DATA SHEET

			BATCH YIELD	SAMPLE			
Sample #							
Quantity							
Units							

Sample #							
Quantity							
Units							

Sample #							
Quantity							
Units							

Sample #			
Quantity			
Units			

AP9 (Rev 4) - Carbon-14 by Distillation Concentration and Uncertainty Report

INPUT BY:

DATE:

TASK#

BATCH#

Batch Yield (BY) Calculation	
BY sample cpm	
BY sample quantity	
BY sample quantity error	
Sample cpm	
Sample quantity	
Sample quantity error	
BY pCi added	
BY pCi added error	
BY	
BY Error	
BY Relative Error	

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 and yield calculations (min)	

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

C-14 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: _____