From: "Hood, Floyd" <FHood@entergy.com>
To: "'James Kottan'" <JJK@nrc.gov>
Date: 2/2/06 9:10PM
Subject: RE: Tritium separation method

Jim,
Thank you for the information on the micro dist. I've contacted the vendor and submitted a quote to try and get one here to see if we can integrate it into our tritium program here. I have included its use in the current revision of the tritium procedure along with your suggestion on clarifying the use of the Toray filter. Here is a copy of 0-CY-3230 if you wish to add it to the procedures you have reviewed.

-----Original Message-----
From: James Kottan [mailto:JJK@nrc.gov]
Sent: Wednesday, February 01, 2006 11:05 AM
To: Hood, Floyd
Subject: Tritium separation method

Floyd,

Here's the web address for the method I was talking about.http://www.lachatinstruments.com/products/microdist/brochure.asp

CC: "'jdn@nrc.gov'" <jdn@nrc.gov>, "Sandike, Steven" <SSandik@entergy.com>, "Wilson, Daniel" <DWilson@entergy.com>

A146

Procedure Use Is:

☐ Continuous

☐ Reference

☑ Information

Control Copy:_____

Effective Date:_____

NON-QUALITY RELATED

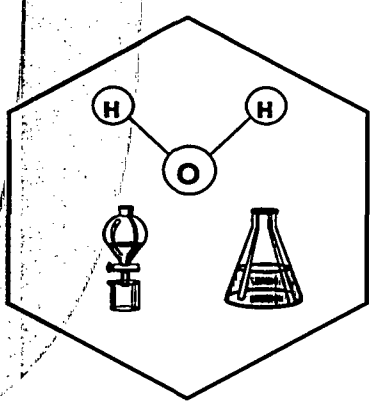
0-CY-3230 Revision 3

TRITIUM ANALYSIS BY LIQUID SCINTILLATION

Note: 0-CY-3230 has been programmatically excluded from the ENN-LI-100 Process Applicability Determination Process.

Chemistry
Indian Point

APPROVED BY:



Floyd Hocd February 2, 2006

Procedure Writer / Date

Chemistry

Procedure Owner / Date

PARTIAL REVISION

REVISION SUMMARY

1.0 REASON FOR REVISION

1.1 Incorporate user comments.

2.0 SUMMARY OF CHANGES

2.1 Added Step 4.3.4 for distillation instruction using a micro dist distillation setup.

2.2 Added Step 4.3.6 to clarify the use of the Toray ion-exchange filter.

TABLE OF CONTENTS

Attachments

1.0 PURPOSE

1.1 This procedure establishes instructions for the determination of tritium in aqueous solutions by liquid scintillation.

1.2 This procedure applies to the use of the Packard TriCarb 2900TR Liquid Scintillation System AND the use of the Beckman LS6500 Scintillation Counting System.

2.0 PRECAUTIONS AND LIMITATIONS

2.1 Precautions and Limitations

2.1.1 The Following samples shall be distilled prior to analysis, unless specifically exempted by Chemistry Management:

- Liquid Waste (LW)
- Reactor Coolant System (RCS)
- Residual Heat Removal (RHR)
- Refueling Water Storage Tank (RWST)
- Spent Fuel Pools (SFP)

2.1.2 Other samples with gamma activities known to be greater than 1E-4 uCi/ml shall also be distilled prior to analysis **{Reference 5.1.1}**.

2.1.3 Storm Drains, Manholes, Monitor Wells, and other samples as deemed necessary by chemistry management, should be filtered in accordance with Step 4.3.4.

2.1.4 The lower limit of detection (LLD) for these instruments are approximately 7.0E-7 uCi/ml based on the following typical operating values:

Counting Efficiency	=	45 %
Sample volume	=	2.5 mls
Scintillator volume	=	18 mls
Background count rate	=	10 cpm
Standard deviation	=	0.3 cpm
Counting time	=	100 minutes

2.1.5 After a power fail, program parameters should be checked from the lab notebook OR tech aids prior to running the instrument.

2.1.6 Due to potentially high levels of Tritium in RCS, secondary plant samples awaiting analysis and suspected of having little or no Tritium should be stored separately to preclude Tritium migration through the plastic vials.

2.1.7 Latex gloves SHALL NOT be used with plastic vials as they can cause severe static problems.

2.1.8 The maximum number of racks per analysis run should not exceed 2 (24 vials including blanks and Quality Assurance samples.

2.1.9 It is NOT recommended to add additional racks OR samples to the machine once a sample run has begun.

3.0 PREREQUISITES

NONE

4.0 PROCEDURE

4.1 Apparatus

- Liquid scintillation counting system
- Automatic-pipette
- Disposable pipettes
- Polyethylene Liquid Scintillation Counting Vials (LSCV)

4.2 Reagents

4.2.1 Refer to 0-CY-1230, Reagent and Chemical Preparation, for preparation and information of silver nitrate and potassium iodide reagents.

4.2.2 The following reagents and chemicals may be used in this analysis:

- Scintillation solution
- Tritiated Water Standard, Approximately 1E-3 uCi/ml
- Tritium control Standard
- Reagent grade water
- Silver nitrate, concentration of 0.1 to 0.2 M.
- Potassium iodide, concentration of .05 to 0.1 M.

4.3 Sample Preparation

NOTE

A separate distillation apparatus should be used for each sample type:

- RCS and Fuel pools(High Level Gamma Activity)
- Liquid Waste Streams(Mid Level Gamma Activity)
- Other (Low Level Gamma Activity).

4.3.1 Turbid samples should be filtered prior to analysis. IF a sample is discolored or turbid, THEN contact Chemistry Management for guidance on sample preparation.

4.3.2 Due to the high potential of sediment contamination, the following samples will be filtered prior to analysis:

- Monitoring wells.
- Storm drains.
- Man-hole samples.

4.3.3 IF a sample is to be distilled with a standard distillation rig, THEN perform the following:

4.3.3.1 Place 50-100 mls of sample in the appropriate boiling flask, if possible. IF < 50 mls of sample is used, THEN note this fact on the final analysis report data sheet.

4.3.3.2 Add 8 drops of silver nitrate to appropriate boiling flask.

4.3.3.3 Add 4 drops of potassium iodide to the appropriate boiling flask.

4.3.3.4 50% to 75% of the sample should be distilled. Do NOT evaporate the sample in the boiling flask to dryness. This prevents fractionalization and unwanted carry over in the distillate.

4.3.4 IF a sample is to be distilled with a Micro Dist distillation unit, perform the following:

4.3.4.1 Place 6.0 mls of sample into the sample tube.

4.3.4.2 Attach the sample tube to the collector tube.

4.3.4.3 Place the tube assembly into the heating block and heat the samples for approximately 30 minutes.

4.3.4.4 Remove each tube from the block and disconnect the sample tube from the collector tube.

4.3.4.5 Snap the collector tube in half.

4.3.5 IF a sample is to be filtered for turbidity, THEN, using a syringe, pass approximately 5.0 mls of sample through a 0.45 um Hydrophlic PVDF Membrane or equivalent filter.

4.3.6 IF a sample is to be filtered for suspected interference from gamma emitting isotopes, THEN pass approximately 20.0 mls of sample through a Toray ion-exchange filter or equivalent filter.

4.3.7 IF noble gas carryover into the sample during distillation in a standard distillation rig is suspected of causing interference, THEN the distillate can be brought to a boil momentarily to drive off any gases in the sample. This practice is not normally needed.

4.3.8 Record a description of each sample per one of the following methods:

- Use a blank Attachment 1, Tritium Counting Cover Sheet or equivalent , OR
- Record the sample description in the Worklist tab of the QuantaSmart Software (for the TRICARB 2900) Assay Definition (per the laboratory notebook), OR
- Record the sample description in the appropriate Excel spreadsheet.

NOTE

Counting vials should be clean on the outside. Descriptive markings should only be placed on the vial cap.

4.3.9 Mark the caps of the vials with the appropriate sample number.

4.3.10 Prepare the standard, sample, and blank vials as necessary, as follows:

4.3.10.1 For Reactor coolant , liquid waste samples, samples suspected of have tritium activity of greater than .1 uCi//ml , or as directed by chemistry management:

a) Gravimetrically prepare sample of .5 mls for each vial.

b) Transfer 2.0 ml of reagent grade water to each vial.

c) Transfer 18.0 mls of scintillator into the individual vials corresponding to the number of samples and standards to be counted.

4.3.10.2 For tritium calibration and control standards and all other samples :

a) Gravimetrically prepare standards and samples of 2.50 mls of sample for each vial.

b) Transfer 18.0 mls of scintillator into the individual vials corresponding to the number of samples and standards to be counted.

4.3.11 For samples where available sample quantity is LESS THAN that specified in step 4.3.8, then perform the following:

a) Measure the available sample THEN add the sample to the scintillation vial.

b) Add deionized water to bring the sample volume to 2.50 mls in the scintillation vial.

c) Transfer 18.0 mls of scintillator into the individual vials corresponding to the number of samples and standards to be counted.

d) Record the sample dilution on the appropriate coversheet as described in step 4.3.6.

4.3.12 For preparing source leak check samples, perform the following:

a) Transfer 1.0 ml of tritium calibration standard AND a clean swab to a scintillation vial.

b) Transfer 1.0 ml of deionized water AND a clean swab to a second scintillation vial.

c) Transfer 1.0 ml of tritium control standard AND a clean swab to the third scintillation vial.

d) Transfer 1.0 ml of deionized water AND the sample swab used to smear the sources to each scintillation vial.

e) Transfer 18.0 mls of scintillator into the individual vials corresponding to the number of samples and standards to be counted.

4.3.13 Ensure the sample, standard, and blank scintillation cocktail is thoroughly mixed.

4.4 Using the TriCarb 2900TR

4.4.1 Calibration and Normalization of the TriCarb 2900TR

4.4.1.1 Reset the "SNC" **Flag** on the cassette by moving the plastic arm all the way to the left.

4.4.1.2 Load the cassette as defined in the laboratory notebook (normally only C-14, but may include other standards or blanks).

4.4.1.3 Place the cassette on the right side of the sample changer deck so that "SNC" on the **Flag** is facing front.

4.4.1.4 Verify the correct parameters for Calibration, Normalization, and IPA procedures per the laboratory notebook.

4.4.1.5 Ensure the printer is available per the laboratory notebook.

4.4.1.6 Begin counting by pressing the green flag **Start Button** on the tool bar in the upper left-hand corner of the window.

4.4.1.7 Ensure the Calibration and/or Normalization was successful. Evaluate any errors or warnings on the printout. Inform Chemistry Management as necessary.

4.4.2 Routine Analyses

4.4.2.1 Ensure Calibration and Normalization has been satisfactorily performed per Section 4.4.1.

NOTE

The Assay "**Routine**" can be used for routine Tritium analysis.

4.4.2.2 Match the **Protocol Flag** number associated with appropriate **Assay** on the QuantaSmart software with the **Flag** number on the cassette.

4.4.2.3 Reset the **Flag** on the cassette by moving the plastic arm all the way to the left.

4.4.2.4 Load vials into the first cassettes as follows:

First position	=	a blank
Second position	=	a Tritium calibration standard
Third position	=	a Tritium control standard
Other positions	=	unknowns

4.4.2.5 IF a second cassettes is required (maximum of two racks per run), THEN ensure a blank and control standard are inserted into positions one and two.

4.4.2.6 Do not use a Protocol Flag on additional cassettes of the same run.

4.4.2.7 Place the cassettes on the right side of the sample changer deck so that the **Protocol** number on the **Flag** is facing front AND the cassette ID number is to the right.

4.4.2.8 Verify the correct **Assay** parameters using QuantaSmart software by performing the following:

a) Select the **Protocol** associated with the **Assay** to be used by double clicking with the left mouse button.

b) IF using the 'Worklist' tab, THEN click the tab and verify that sufficient data has been properly entered to define each vial, ensuring the correct cassette number is used.

c) Verify the BKGD subtract option is set to First Vial.

d) Ensure other counting parameters on the various tabs are as prescribed in the instruction in the laboratory notebook.

e) IF changes are to be saved, THEN click Apply and **Ok.**

f) IF changes are NOT to be saved, THEN close the window.

4.4.2.9 Ensure the printer is aligned and available per the laboratory notebook.

4.4.2.10 Dark adapt for at least twelve hours, or as directed by Chemistry Management.

4.4.2.11 Begin counting by pressing the **Green Flag** start button on the tool bar in the upper left-hand corner of the window.

4.5 Use of the Beckman LS6500

4.5.1 Set up the tritium analysis racks as follows:

4.5.1.1 Select the "USER #" card based on the type of samples being analyzed and place it in the left slot of the first rack of samples. Optionally, a "RACK #" card can be placed in the right slot of each rack. The following user programs are available:

- User 1 – Normal sample count time of 100 minutes and utilizing a 2 sigma count reject.
- User 2 – Specialized counting for gross beta activity. Sample time of 10 minutes. Source leak check swabs are an example of samples using this program.
- User 3 – Specialized counting of standard sample for calculating the chi square test.

4.5.1.2 Place the "HALT" card in the left slot of the red rack.

4.5.1.3 Load vials into the first cassettes as follows:

First position	=	a blank
Second position	=	empty (no vial)
Third position	=	a Tritium calibration standard
Forth position	=	a Tritium control standard
Other positions	=	unknowns

4.5.1.4 Place the "User #" card in the first rack of the set. Only the first rack needs to have a "user #" card.

4.5.2 Sample analysis

4.5.2.1 Log the samples out of the RCA.

4.5.2.2 Place the sample Rack(s) containing the sources and samples into the LS6500 followed by the "RED HALT" rack.

4.5.2.3 Close the Plexiglas lid.

4.5.2.4 Ensure the printer is on AND the "READY" light is illuminated.

4.5.2.5 Ensure the "PAUSE" light is off.

4.5.2.6 Dark adapt the samples for a MINIMUM of 12 hours UNLESS otherwise directed by Chemistry Management.

4.5.2.7 IF not on the main menu display, THEN press the "main menu" key on the keypad to display the upper level menu.

4.5.2.8 Ensure that the automatic sample counting option is highlighted. Move the curser up OR down to select this option if it is not selected.

4.5.2.9 Press the "start" key to begin sample counting.

4.5.2.10 Ensure sample counting begins and basic header information is printed to the printer.

4.5.2.11 To stop the analysis at ANY time PRIOR to completion, depress BOTH the "RESET" buttons on the LS6500 keypad simultaneously.

4.5.2.12 After the completion of the analysis, return AND log tritium samples back into the RCA.

4.5.2.13 Discard samples down the drain in the radio-chemistry lab AND discard the used vials.

4.6 Calculations

4.6.1 Computer Method for TriCarb 2900TR

4.6.1.1 The data will be processed by Microsoft Excel spreadsheets.

4.6.1.2 IF the data does not automatically print out, THEN

- perform manual data reduction (per Step 4.6.2), OR
- Contact Chemistry Management and troubleshoot per the laboratory notebook as directed.

4.6.1.3 Review the data for accuracy. Sign and deliver to Chemistry Management for review. Store the record with other effluent records per Chemistry Management.

4.6.2 Manual Data Reduction for either liquid scintillation counter.

4.6.2.1 Record the count rate for each blank, standard, and sample on Attachment 1 or equivalent.

NOTE

Tritium is quantified from the first channel (0-19 kev). The first vial is normally selected as a blank such that its cpm can be automatically subtracted from subsequent counts.

4.6.2.2 Calculate the counting efficiency from the Tritium standard in each sample set as follows:

$$EFF = \frac{\text{NET CPM}_{\text{Standard}}}{\text{DPM/ ML}_{\text{Standard}} * \text{Sample Volume}}$$

4.6.2.3 Record the efficiency of the standard on the cover sheet (Attachment 1) OR equivalent form. The decay corrected dpm/ml of the standard is obtained from the source files, as follows:

$$\text{dpm/ml} = \mu\text{Ci/ml} * 2.22\text{E} + 6\ \text{dpm}/\mu\text{Ci}$$

4.6.2.4 Calculate the Tritium activity of each sample in the set as follows:

$$\text{H-3 } \mu\text{ci/ml} = \frac{\text{NET CPM}_{\text{Sample}}}{\text{Eff} * \text{SampleVolume} * 2.22\text{E6 dpm}/\mu\text{Ci}}$$

4.6.2.5 IF the net counts per minute are less than the critical level, THEN record the value as less than minimum detectable.

4.6.2.6 Reference 0-CY-1420 for guidance on calculating critical level if needed.

4.6.2.7 Review the data for accuracy. Sign and deliver to Chemistry Management for review. Store the record with other effluent records per Chemistry Management.

NOTE

Program editing is not routinely required and shall only be initiated as directed by Chemistry Management.

4.7 Program Editing for TriCarb 2900TR

4.7.1 Use the laboratory notebook for instruction regarding periodic updates to the parameters included in the QuantaSmart software.

4.7.2 Any changes to the parameters for counting shall be logged in the lab notebook and verified by Chemistry Management.

4.8 Data transfer to Disk for the Beckman LS6500

4.8.1 Place a formatted diskette in the data drive.

4.8.2 Select "Data Management" from the main menu.

4.8.3 Select "Access Data Buffer/Disk" from the Data Management menu.

4.8.4 Select "Move Files to Disk" from the Disk sub-menu.

4.8.5 Select user number to transfer (typically user #1).

4.8.6 Press "select to begin transferring the data files for the user number that the samples were processed with.

4.8.7 A sub-directory on the floppy disk will be created for each user group transferred.

4.8.8 When completed, removed the diskette from the data drive.

4.8.9 Press "Main Menu" to return to the main menu.

4.8.10 This disk can now be used to process the sample results utilizing the excel spreadsheet for tritium calculations.

4.9 Program Editing for the Beckman LS6500

4.9.1 Use the settings listed on the tech aids in the system notebook to re-enter any user program setting needed.

4.9.2 Any changes to the parameters for counting shall be logged in the System notebook and verified by Chemistry Management

4.10 Chi Square Test for the Tricarb 2900TR

4.10.1 At least quarterly, place a prepared standard in the appropriate labeled position in the SNC rack. (Normally H-3 is placed in the second slot but a C-14 standard may be placed in the first slot.) Ensure the lever is to the left.

4.10.2 Insert the rack, close the lid AND dark-adapt for at least 12 hours.

4.10.3 Click the IPA definition menu on the top bar and select "IPA definition".

4.10.4 In the upper right, check the box for Chi Square (C-14 OR H-3, depending on standard used), then OK.

4.10.5 After dark adapting, click the green start flag for the SNC Protocol.

4.10.6 The instrument collects 20 observations and calculates Chi Square as follows:

$$X^2 = \frac{\sum_{i=1}^{n}(X_i - \overline{X})^2}{\overline{X}}$$

Where:

X_i = counts of one measurement
$\overline{X}$ = mean counts of all measurements (20)

NOTE

The printout includes data from many potential diagnostic tests. Disregard all but the Chi Square results for the source used, approximately seven lines down from the top of the report.

4.10.7 Review the results. For twenty observations, the satisfactory Chi Square value should fall between 7.63 and 36.19.

4.10.8 Deliver the Chi Square value to Chemistry Management.

4.11 Chi Square test for the Beckman LS6500

4.11.1 At least quarterly, place a prepared standard in the first position of the rack using user card #3.

4.11.2 Perform normal sample counting as directed in step 4.5.2.

4.11.3 User program #3 will perform 20 counts on the sample for the chi squared calculation.

4.11.4 Perform the follow calculation on the counts produced from the sarnple:

$$X^2 = \frac{\sum_{i=1}^{n}(X_i - \overline{X})^2}{\overline{X}}$$

Where:

$\underline{X}_i$ = counts of one measurement
$\overline{X}$ = mean counts of all measurements (20)

4.11.5 Review the results. For twenty observations, the satisfactory Chi Square value should fall between 7.63 and 36.19.

4.11.6 Deliver the Chi Square value to Chemistry Management.

5.0 REFERENCES

5.1 Commitment Documents

5.1.1 IP3-WAJ-036Z, Response to Inspection No. 50-286/86-09

5.2 Development Documents

5.2.1 ASTM, Part 31, Method D4107-91, Standard Tritium Test Method

5.2.2 CRC Handbook of Tables for Probability and Statistics, 2nd Edition

5.2.3 Packard 2900TR Service Manual

5.2.4 QuantaSmart™ -TriCarb® Liquid Scint Analyzer - Reference Manual

5.2.5 QuantaSmart™ - TriCarb® Liquid Scintillation Analyzer -Getting Started

5.2.6 Beckman LS6500 Liquid Scintillation counter reference manual

5.3 Interface Documents

5.3.1 0-CY-1230, Reagent and Chemical Preparation

5.3.2 0-CY-1420, Radiological Quality Assurance Program

6.0 RECORDS AND DOCUMENTATION

6.1 Records

The following required records are generated by this procedure and SHALL be maintained in accordance with IPEC Records Retention Schedule.

6.1.1 Tritium Counting Cover Sheet, Attachment 1 (or equivalent)

6.1.2 Tritium Calculation spreadsheet, Attachment 2 (or equivalent).

6.2 Documentation

NONE

ATTACHMENT 1 Page 1 of 1

TRITIUM COUNTING COVER SHEET

Sample Set No._____ Run Date ___/___/___

Smp No.	Sample Size, mls	Unit #	Sample Date	Description	CPM	Activity
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
Cal Std # _____ Date_____ Activity _____						

Prepared by _____ Control Chart Plotted _____

Init

ATTACHMENT 2 Page 1 of 1

TRITIUM CALCULATION SHEET

Tritium Data Reduction

Data Processed: 4/20/2005 11:39 AM

SIN	Volume	Unit #	SAMPLE INFORMATION Sample ID	uCi/ml	CPM	ANALYSIS DATA Notes
			Blank			
			Calibration Standard			
			Control Standard			

SOURCE DATA			
Date of Source:	09/25/01	5.12E-02 uCi/ml	Cnt Level = 1.53E+00 cpm
Date & Time Sample Counted:		N/A uCi/ml	Efficiency= 0.00% cpm/dpm
			Background= 0.00 cpm

(NOTE: Background is automatically subtracted from sample counts)

Performed By:

Control Chart Updated: (initial)

Reviewed By:

SCINTILATOR USED:
Beckman / Tricarb 2900