Measurement of Tritium (^3H) in Natural Water Samples

1.0 Introduction

Environmental Tritium is a powerful tool for quantitative groundwater research, because it is a useful tracer for groundwater movement. However, it is not possible to determine the correct age of groundwater by measuring the tritium concentration alone, but one should have other information about the aquifer in question and the flux of water. Tritium concentration in precipitation varied quite a lot during the last forty years due to atmospheric nuclear tests. Usually ground-water will be a mixture of different water inputs at different times and so the tritium concentration will be a "mixture" of many years' input of tritium concentrations. If the tritium concentration is zero, then we can say that the water is old and has been cut off from the atmosphere for more than 50 years.

The tritium distribution in the groundwater is determined by a) the input function for the tritium concentration in recharge water and b) the movement and mixing of water within the saturated zone. Both the above factors have to be addressed when using the tritium concentration to estimate the age of water.

Tritium analysis may be used to estimate the time since recharge to the groundwater system occurred and the susceptibility of the groundwater system to contamination. Groundwater systems with recharge occurring prior to the 1950s will have a tritium level decreased by radioactive decay to below 1 TU.

Detection of tritium takes advantage of the small amounts of radioactivity it emits. Tritium, being a radioisotope, and as it loses half of its radioactivity every 12.34 years, hydrogeologists use tritium to estimate how long water has

been underground. One may also trace the groundwater flow path and mean transport velocity. Hydrologists also use tritium to study the surface water and groundwater interaction in streams / lakes. It can also be used to identify the groundwater recharge zones for deeper aquifers along with many other associated information regarding aquifer dynamics.

2.0 Sampling

Sampling for environmental tritium is simple, since there are very few geochemical processes in nature that alter its concentration. However, excessive exposure of the sample to the atmosphere might alter the tritium concentration and therefore must be avoided.

The quantity of natural water sample for tritium analysis in the laboratory is collected as per the expected level of tritium. Typically, for environmental tritium analysis an aliquot of one litre is sufficient. The sample is collected as raw unfiltered water with no preservatives and is stored either in a glass or HDPE (high density polyethylene) bottle with air-tight caps. Samples are given a unique sequential number and their description (i.e., sample, date of collection, source type, location etc.) is logged into a record book for reference. Samples are then submitted to the Laboratory along with the details duly filled in a form (FORM-A) for analysis. (Note: All FORMS are annexed at the end of this Manual).

3.0 Pretreatment of Samples

The samples are distilled (called primary distillation) in the laboratory to remove all dissolved salts. This is a pre-requirement before further processing. The various ions that are naturally found in water (Cl^-, SO_4^{--}, CO_3^{--}, Mg^{++}, Na^+, K^+, etc) could interfere with the electrolysis process (i.e. produces gases at either the anode or cathode other than oxygen or hydrogen) and also corrode the mild steel electrodes. It is important to note that not all salts are removed through

primary distillation. If volatile salts or soluble gases are present they could distill over with the water. The distilled samples can be kept at the appropriate places and the information can be recorded in FORM-B for the identification of location.

Procedure for distillation of samples using distillation assembly (Fig. 1):

1. Clean the distillation flask, condenser, and receiving flask with 1:1 HCl, HNO_3 and rinse with distilled water. Dry the glassware in oven.
2. Install the distillation assembly as per the details shown in fig. 2.
3. Pour about 600 ml of sample into a distillation flask and then turn on the heating unit.
4. Frequently check distillation process, adjusting cooling-water flow rate as necessary to prevent steam from entering receiving flask.
5. When sample in distillation flask is nearly or completely distilled to dryness, turn off the heating unit check the conductivity of the distilled water sample. If it is upto 10 μ S/cm then place the distilled samples in a tightly sealed container. In case of saline samples, the conductivity of the distilled sample may be more than 10 μS/cm. In such cases water samples should be distilled again.
6. Clean and dry all distillation apparatus as given above (Point no. 1).

4.0 Enrichment of Samples

After primary distillation, samples are enriched by electrolytic process. The electrolytic reduction is done to concentrate the tritium. The samples contain mainly HHO and HTO molecules. By passing electric current through a conducting water solution, the bonds of the water molecules are broken with evolution of hydrogen and oxygen. The temprature of the sample is maintained between 0°C to 5°C in order to achieve the maximum fractination or enrichment of HTO. The enrichment unit (Figure 2) is used for the enrichment of samples.

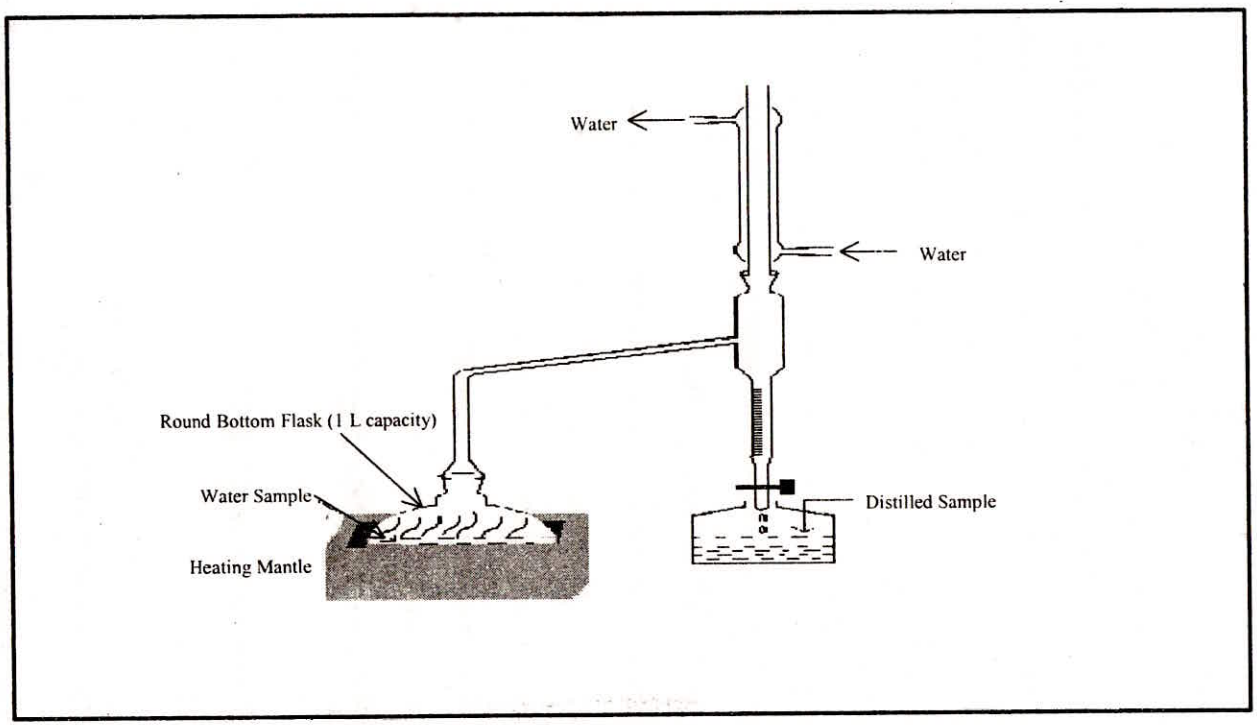


Figure 1. Set up of primary distillation unit

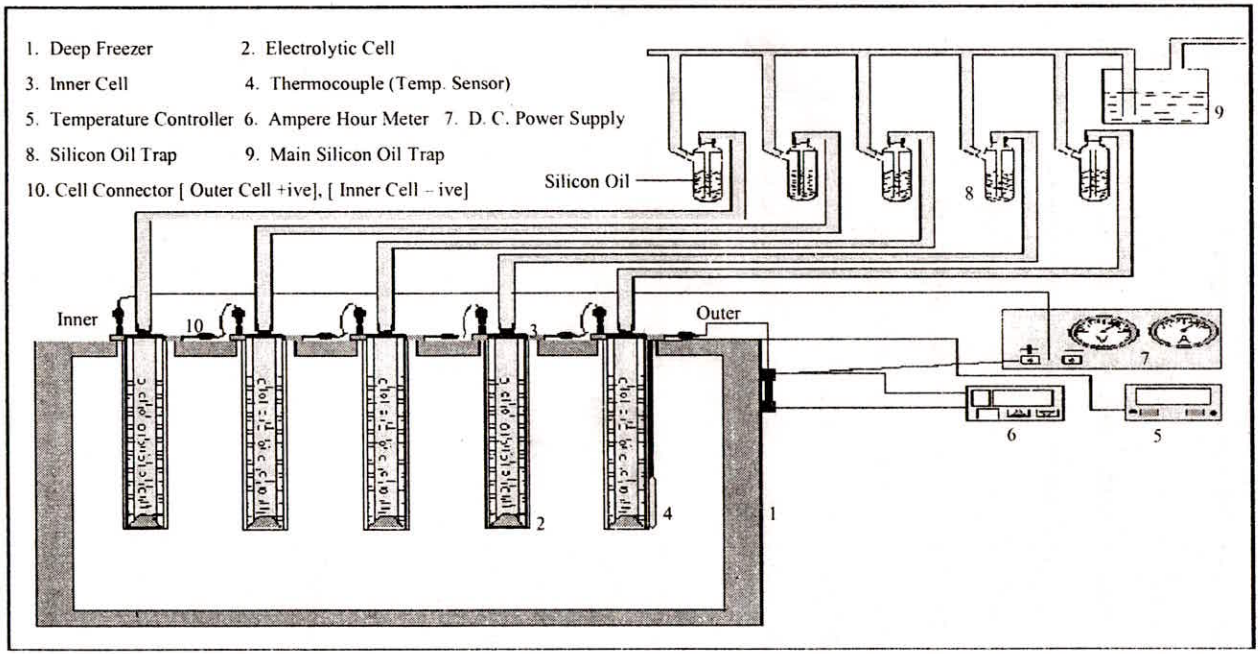


Figure 2. Set up of Tritium Enrichment Unit

The following procedure is to be followed along with the associated precautions.

1. Ensure enrichment cells are clean and dry.
2. Enrichment cells are cleaned by rinsing with tap water to get a clean appearance (scrub with soap if all residue is not removed, the outer electrodes are additionally rinsed with one molar HCl acid). Rinse the cells again with de-ionised water or distilled water. Check the pH with indicator paper and make sure the pH is about 7. Dry the outer cells in oven and the inner cells with hot-air blower.
3. Weigh 1 gm aliquots of sodium peroxide (Na_2O_2) into clean dry 20 ml glass scintillation vials. Precautions should be taken in using Na_2O_2 as it is inflammable when in contact with moist air.
4. Weigh the empty enrichment cells and record it on the tritium enrichment data form (FORM-C). Make sure the numbers on the outer and inner cells (anode and cathode) match.
5. Gently pour approximately 500 ml of a known standard solution (Std-C)* in 4 cells, distilled NIH water in one cell, and distilled samples in the remiaining.

** Preparation of standard solution (STD-C):*

- *Take about 2000 ml of Tritium Free Water and required amount (nearly 30ml) of ISD-EIL-Standard-B (25100 TU) and mix to get 2030 ml of 332 TU (Standard C). ISD-EIL-Standard-B is prepared from ISD-EIL-Standard-A (150591 TU) that in turn has been prepared from NIST standard 4926C (Date: 01.07.1991).*
- The prepared solution is sufficient for loading in 4 cells of 500ml each, and counting in Quantulus through 2 vials of 10ml each.

6. Add 1.0 gm sodium peroxide to each cell and check the conductivity. Reweigh all the cells and record the weight in FORM - C.

7. Place all the enrichment cells in the freezer of the Enrichment Unit as per their positions in the logbook. Connect all the cells in series to pass a D.C. current through them. Attach gas ventilation tubes to each cell.
8. Connect the cells in series ie., outer cell to the positive and inner cell to the negative points of the power supply, as shown in Fig. 2.
9. Turn on main power for electrodes, freezer and temperature controller. Turn on the freezer and D.C. power supply, set the current limit to about 4 Amperes and the Temperature Controller to 2°C. Make sure that the voltage drop (potential difference) is less than 3 volts for each cell i.e. if 20 cells are connected in series, then the total voltage applied to the cells (at 4 to 6 amperes) should not be more than 60 volts.
10. Verify that the electrolysis is occurring in each cell by observing the bubbles in the silicon oil traps, which indicate the production of gases within the cells.
11. Enrichment from 500 ml to 20 ml will take about 12 days. Determine the total time required for the electrolysis process with the following equation:

$$\text{Time (Hrs)} = [(W_o - W_f) \times 2.97545]/I$$

Where: W_o = Initial weight of the cell with sample

W_f = desired weight of the cell after electrolysis

2.97545 = ampere-hours required to dissociate 1 gm of H_2O

I = constant current of power supply i.e. 4 amps at 47 V.

13. Determine the Q value for the run. Normally it is about 1450 Ampere Hours.

$$Q \text{ (Amp-hours)} = \text{Time (Hours)} \times I$$

14. Set the Ampere-Hour meter to the determined Q value. Monitor the power supply current setting and adjust as necessary.
15. Check cells occasionally to see that they are functioning and venting correctly. Intermittently, at least once in two days, weigh any cell that is randomly chosen and record the weight of remaining sample in the logbook.
16. When electrolysis is complete, de-assemble the unit.
17. Weigh all the cells to know the final weight (W_f) and record in the logbook (FORM C).
18. Transfer each electrolyzed sample into different glass bottles with screw caps, which are labeled with the corresponding cell and run numbers. The enriched samples are stored in the refrigerator until they are taken up for Secondary distillation.

5.0 Distillation of Enriched Samples (Secondary-distillation)

1. Transfer the enriched samples in to 50 ml round bottom flasks.
2. Add 4 gm of $PbCl_2$ in each flask, if 1 gm Na_2O_2 was added and 8 gm if 2 gm Na_2O_2 was added to the water sample.
3. Place the round bottom flask in the secondary-distillation unit and make all connections according to Figure 3.
4. Switch on the unit and set the temperature variac as follows:

   15% for the first hour

   20% for the next 1½ hours

   30% up to completion (No sample should remain in the distillation flask except the salts).
5. Remove the collector flasks from the distillation assembly and transfer the contents into 20ml glass vials.
6. Rinse all glassware of the secondary distillation assembly with HNO_3 and de-ionized water several times and place in the drying oven.

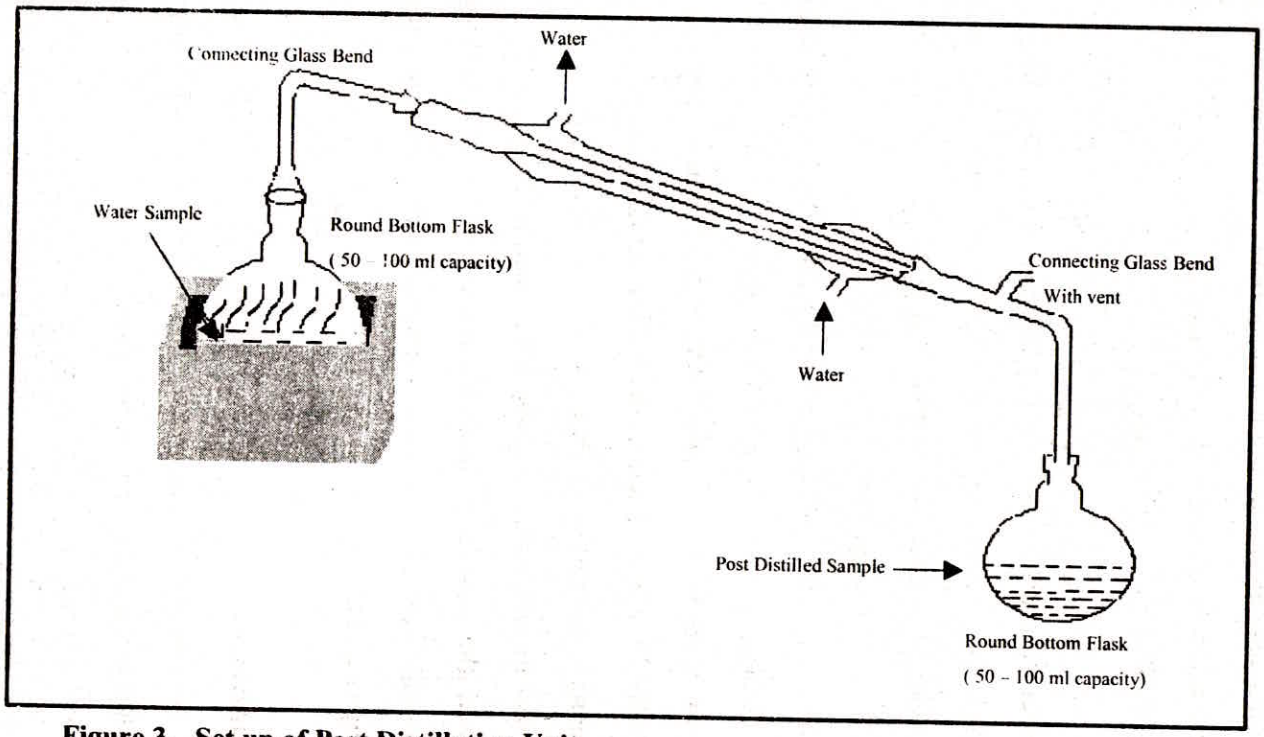


Figure 3. Set up of Post Distillation Unit

6.0 Preparation for counting

Sample prepared for counting contains the standards STD-B and STD-C (2 vials each), three vials of tritium free water and all the enriched samples. Canberra-Packard Pico-flour LLT (Low Level Tritium) cocktail is used. Enter the order and position number of each vial along with the ID in the Quantulus logbook (FORM E).

1. Number the caps of a set of new polyethylene scintillation vials in which the samples and cocktails are to be filled in the following format **Cell # /Run #** for enriched samples and standard **B, C or TF** (for tritium free) as the case may be.
2. Measure 13 g of Pico-flour LLT in the polyethylene scintillation vials with the help of clean pipette using suitable transfer device. Transfer 8 g of sample in the vial with MERCK make 1000 µl transferpette using separate tips. USE SEPARATE TIP FOR DIFFERENT SAMPLE.
3. Close the vial tightly and shake well.
4. Transfer the standard in the last with separate tip.
5. Keep all the samples at a dark place overnight in an inverted position.
6. Rinse all Micro-set tips with de-ionised water and place them on the top of drying oven until dry.

7.0 Counting

Place the vials in counter trays in the pre-planned positions corresponding to the plan previously entered in the Quantulus logbook.

1	2	3	4	5
6	7	8	9	10
11	12	13	14	15
16	17	18	19	20

21	22	23	24	25
26	27	28	29	30
31	32	33	34	35
36	37	38	39	40

41	42	43	44	45
46	47	48	49	50
51	52	53	54	55
56	57	58	59	60

The standards and T-Free vials are placed in a spatially distributed manner. The whole counting is done in 10 cycles. Each vial is counted for 40 minutes in each cycle thus each sample is counted for a total time of about 400 minutes. The cycling helps in averaging any change that may occur such as loss of sample/cocktail weight, change in the counting characteristics of the scintillator, change in counter stability etc., which may affect the sample count rate. This also helps in discarding any particular data, which is not statistically acceptable.

Allow samples to remain in the counter for 24 hrs prior to the counting in order to adjust to counter temperature. The Quantulus machine is operated through the Queue Manager (QM) software. The QM software is a user-friendly one that is menu driven. The main-menu and the sub-menu are shown in Figures 4 to 10. The description of each menu is given below.

- **Figure 4** - The main screen display is divided into three columns viz., Queue, User and Protocol. Toggle from one column to other by using TAB key. First Choose the User column and select an existing NAME or enter a new NAME. Currently 'SYSTEM' is being used. Protocol name: Any name, Preferably 'TEU' (Select by return key and go to Figure 5 – The Protocol window).
- **Figure 5**
  - You may edit the following parameters: Saving path: C:\DIRECTORY_NAME where directory name is restricted to five characters only. The remaining three is appended by the QM program as 0,1,2…..
  - Protocol Name: Give a new name or an existing one. For tritium TEU is being currently used.
  - Number of cycles: 10 (preferably)
  - Parameter Listing: YES

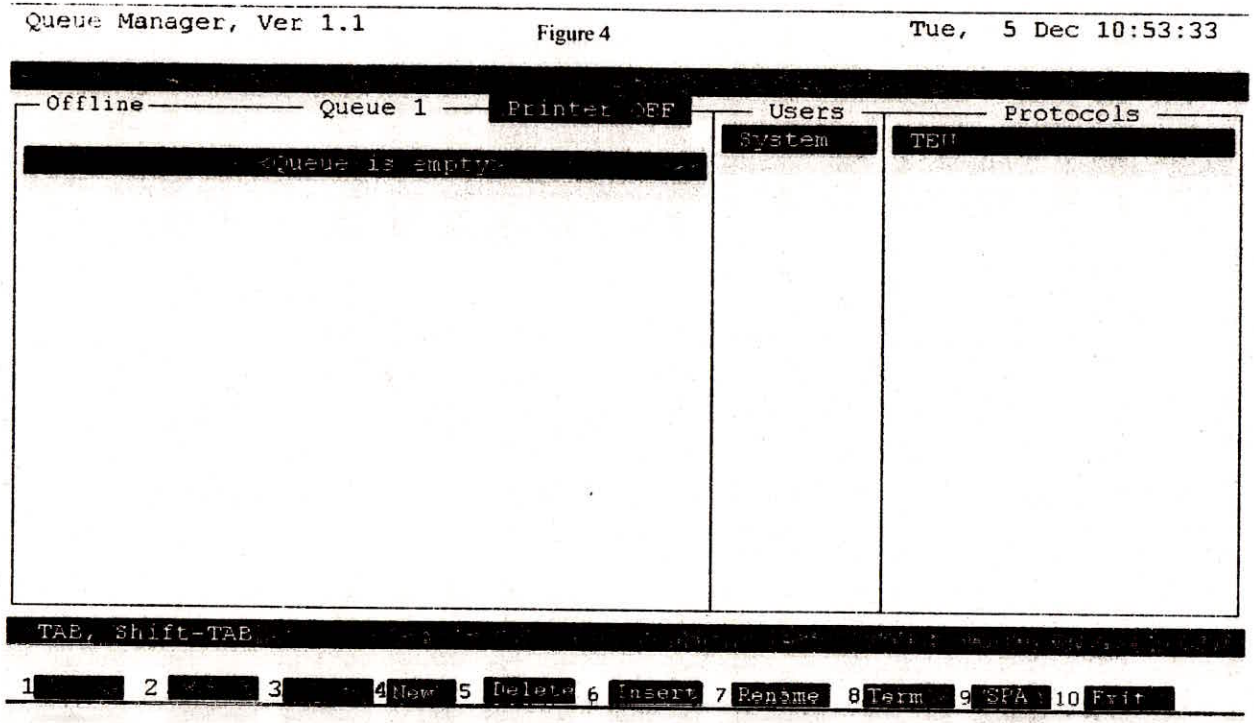

Queue Manager, Ver 1.1
Tue, 5 Dec 10:53:33
Offline
Queue 1
Printer OFF
Users
Protocols
System
TEU
<Queue is empty>
TAB, Shift-TAB
1
2
3
4New
5Delete
6Insert
7Rename
8Term
9SPA
10Exit

Figure 4

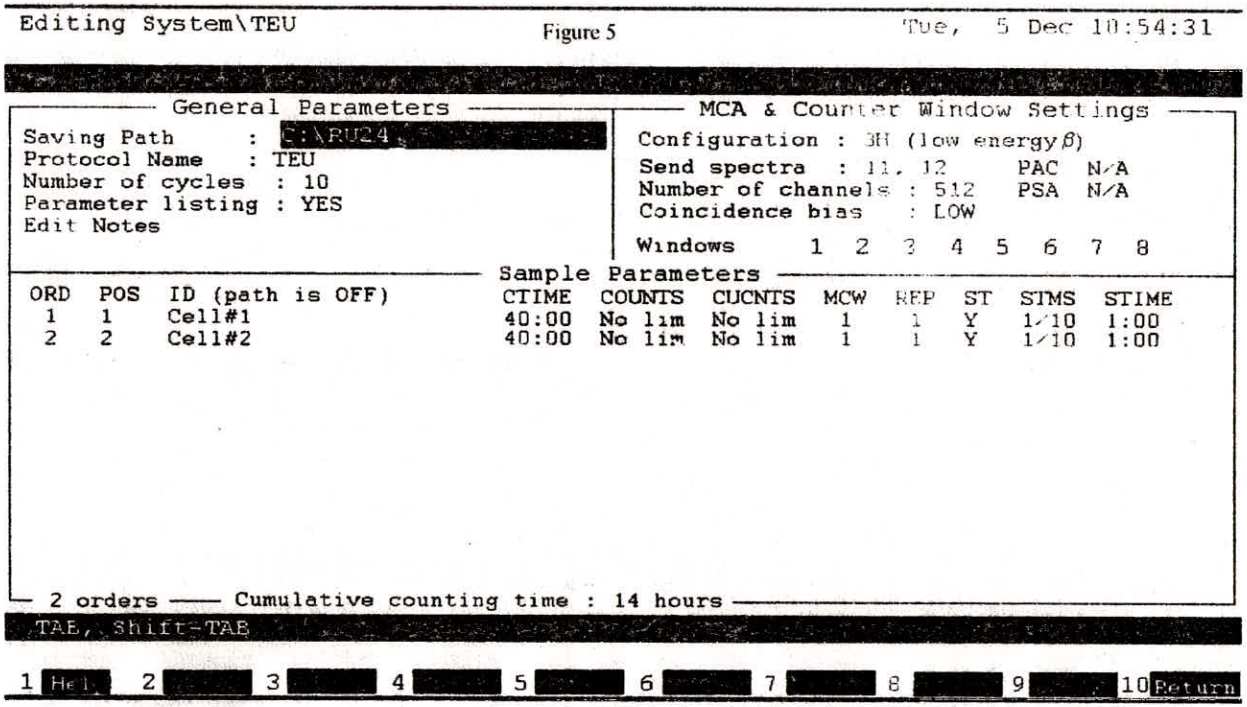

Editing System\TEU
Tue, 5 Dec 10:54:31
General Parameters
Saving Path : C:\RU24
Protocol Name : TEU
Number of cycles : 10
Parameter listing : YES
Edit Notes
MCA & Counter Window Settings
Configuration : 3H (low energy β)
Send spectra : 11, 12 PAC N/A
Number of channels : 512 PSA N/A
Coincidence bias : LOW
Windows 1 2 3 4 5 6 7 8
Sample Parameters
ORD POS ID (path is OFF) CTIME COUNTS CUCNTS MCW REP ST STMS STIME
1 1 Cell#1 40:00 No lim No lim 1 1 Y 1/10 1:00
2 2 Cell#2 40:00 No lim No lim 1 1 Y 1/10 1:00
2 orders — Cumulative counting time : 14 hours
TAB, Shift-TAB
1 Help 2 3 4 5 6 7 8 9 10 Return

Figure 5

- **Figure 6**
  - Edit Notes: Comments about the run and counting etceteras are given in this window (See Figure 6). Press ESC key to move back to the previous menu.
- **Figure 7:**

This window is related to the configuration of the counter. This has to be selected carefully, as variations in the combinations will result in different sets of MCA being used for counting. However, in Quantulus there are in-built configurations that are suitable for radiocarbon, tritium, alpha/beta or special set-up. If you prefer your own combinations you must choose special set-up. It is recommended that for tritium one choose "3H (low energy beta)" set-up. As soon as one chooses any particular set-up the send spectra, coincidence bias, windows, PAC or PSA commands also automatically change in correspondence with the configuration chosen. However, one may alter or modify these commands also.

- **Figure 8:**

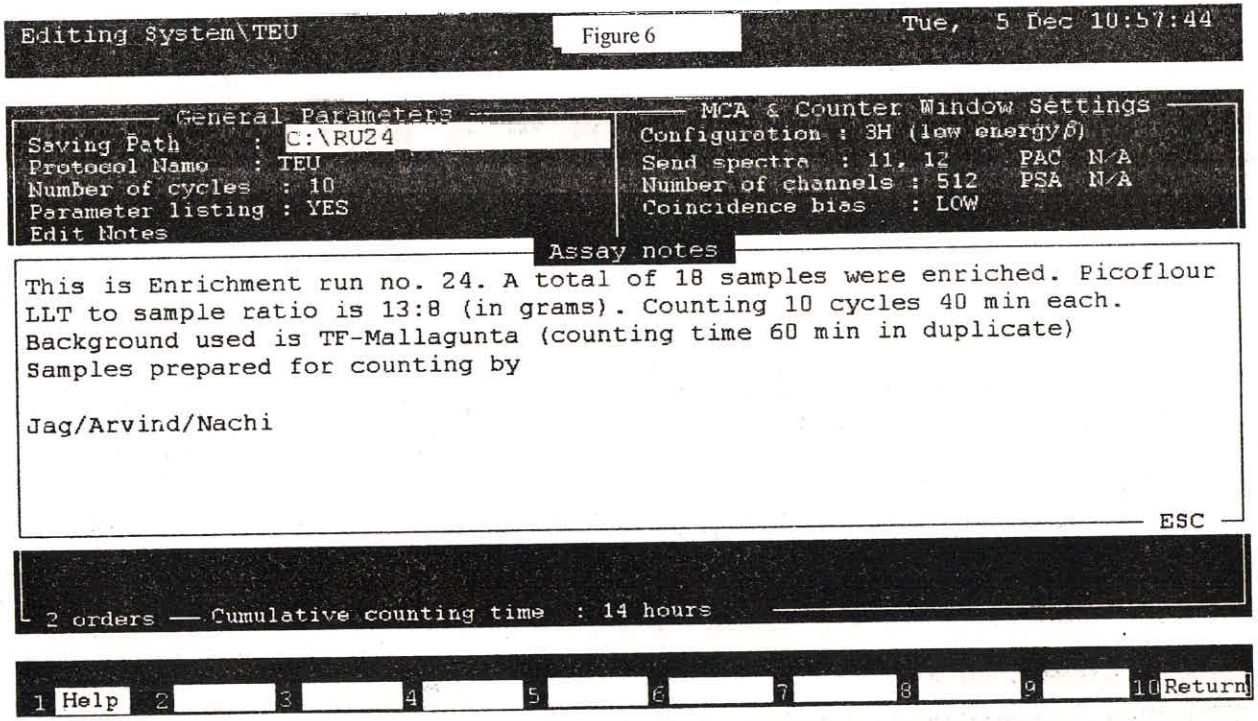
This figure shows the window corresponding to the channel range corresponding to the counting windows. There are 8 windows. The default values are loaded once a particular MCA configuration is chosen. However, according to ones experience one may alter these window ranges. For example, due to quenching in samples prepared at laboratory, the windows for low energy tritium may be moved towards the lower end in comparison to the unquenched standards. If one prefers to view the statistics in the registry file directly, then it is better one alter the window ranges at this stage.

- **Figure 9:**

This figure shows the Coincidence Bias window. One may choose either Low or High Coincidence bias. For Tritium it is normally set to Low.

- **Figure 10:**

This figure shows the send spectra window. To save the computer disk space, for normal operations it is preferable to save only the SPECTRA 12 for tritium,


Editing System\TEU
Figure 6
Tue, 5 Dec 10:57:44
General Parameters
Saving Path : C:\RU24
Protocol Name : TEU
Number of cycles : 10
Parameter listing : YES
Edit Notes
MCA & Counter Window Settings
Configuration : 3H (low energy/β)
Send spectra : 11, 12 PAC N/A
Number of channels : 512 PSA N/A
Coincidence bias : LOW
Assay notes
This is Enrichment run no. 24. A total of 18 samples were enriched. Picoflour
LLT to sample ratio is 13:8 (in grams). Counting 10 cycles 40 min each.
Background used is TF-Mallagunta (counting time 60 min in duplicate)
Samples prepared for counting by
Jag/Arvind/Nachi
ESC
2 orders — Cumulative counting time : 14 hours
1 Help 2 3 4 5 6 7 8 9 10 Return

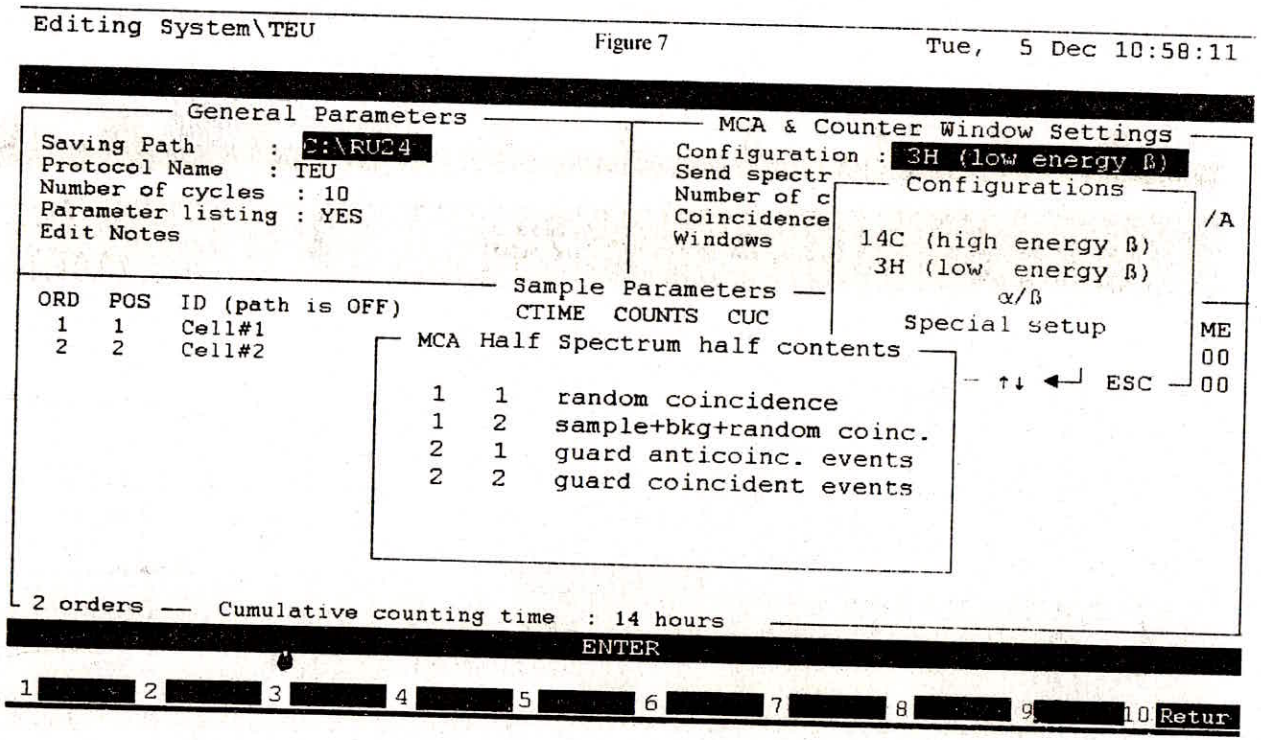
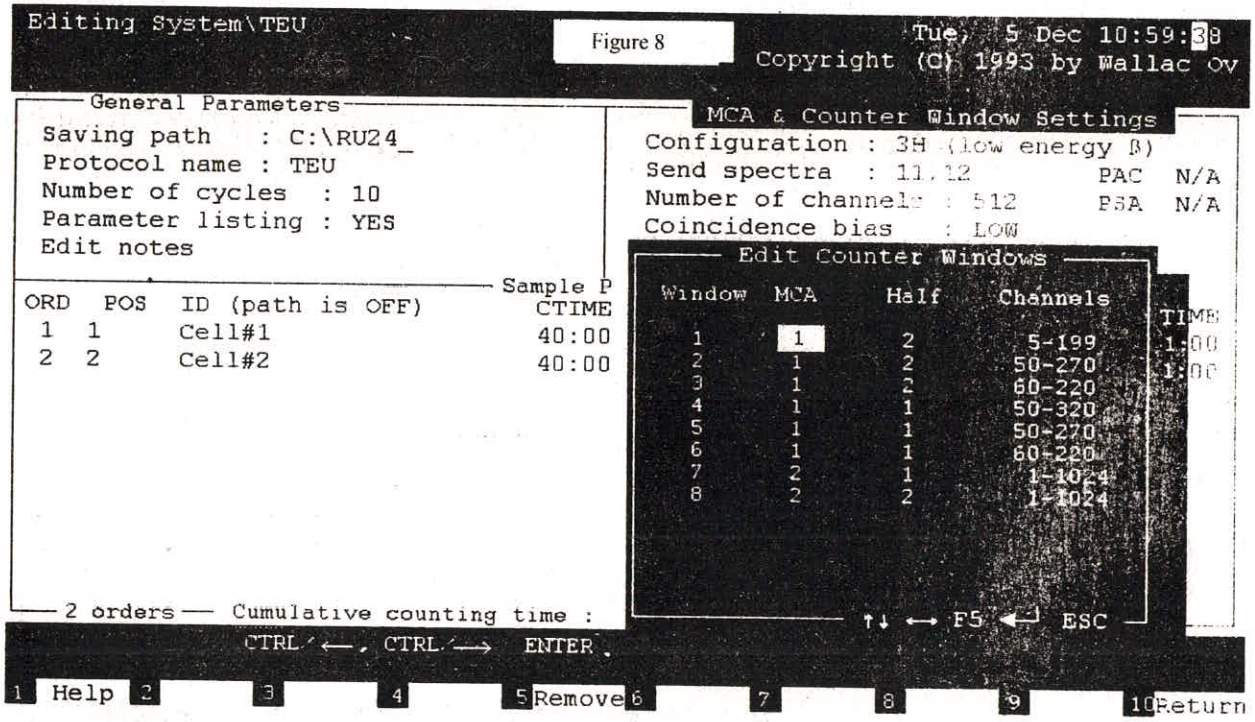

Editing System\TEU
Figure 7
Tue, 5 Dec 10:58:11
General Parameters
Saving Path : C:\RU24
Protocol Name : TEU
Number of cycles : 10
Parameter listing : YES
Edit Notes
MCA & Counter Window Settings
Configuration : 3H (low energy ß)
Send spectr
Number of c
Coincidence
Windows
Configurations
14C (high energy ß)
3H (low energy ß)
α/ß
Special setup
↑↓ ↵ ESC
/A
ME
00
00
Sample Parameters
ORD POS ID (path is OFF) CTIME COUNTS CUC
1 1 Cell#1
2 2 Cell#2
MCA Half Spectrum half contents
1 1 random coincidence
1 2 sample+bkg+random coinc.
2 1 guard anticoinc. events
2 2 guard coincident events
2 orders — Cumulative counting time : 14 hours
ENTER
1 2 3 4 5 6 7 8 9 10 Retur

Figure 8


Editing System\TEU
Tue, 5 Dec 10:59:38
Copyright (C) 1993 by Wallac Oy
General Parameters
Saving path : C:\RU24_
Protocol name : TEU
Number of cycles : 10
Parameter listing : YES
Edit notes
MCA & Counter Window Settings
Configuration : 3H (low energy β)
Send spectra : 11,12
Number of channels : 512
Coincidence bias : LOW
PAC N/A
PSA N/A
Edit Counter Windows
Window MCA Half Channels
1 1 2 5-199
2 1 2 50-270
3 1 2 60-220
4 1 1 50-320
5 1 1 50-270
6 1 1 60-220
7 2 1 1-1024
8 2 2 1-1024
Sample P
ORD POS ID (path is OFF) CTIME
1 1 Cell#1 40:00
2 2 Cell#2 40:00
TIME
1:00
1:00
2 orders — Cumulative counting time :
CTRL ←, CTRL →, ENTER
↑↓ ↔ F5 ↵ ESC
1 Help 2 3 4 5 Remove 6 7 8 9 10 Return

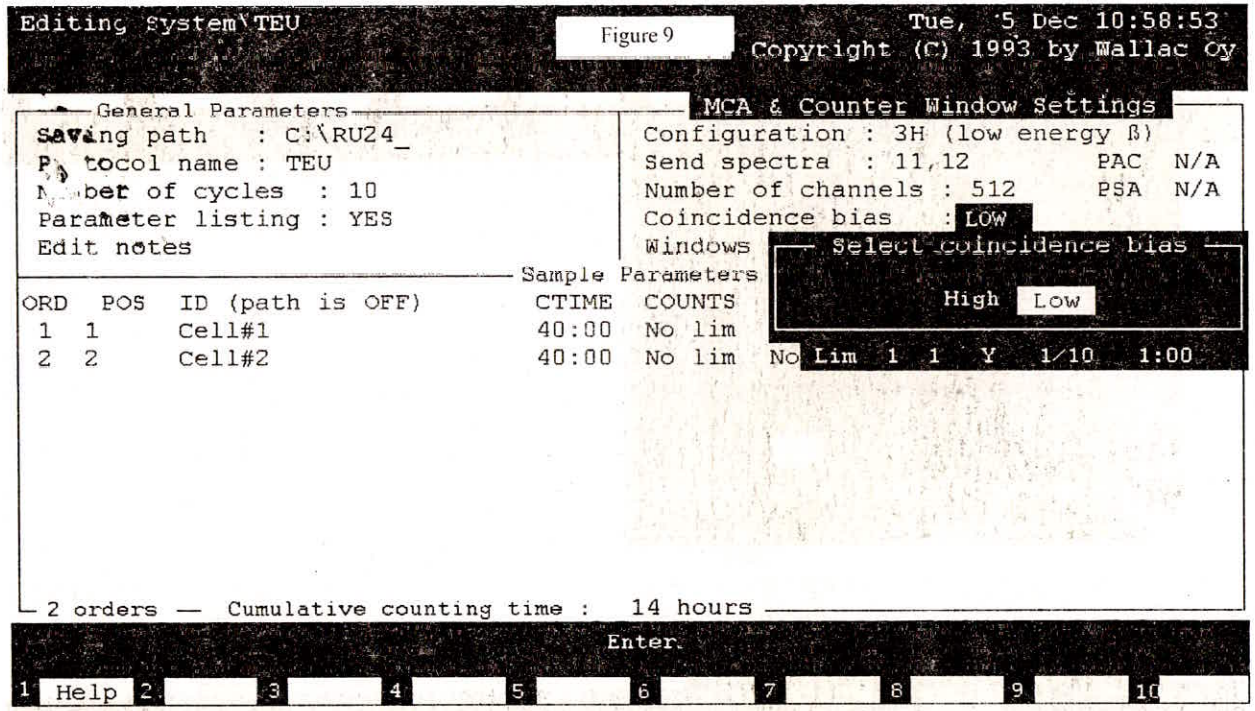
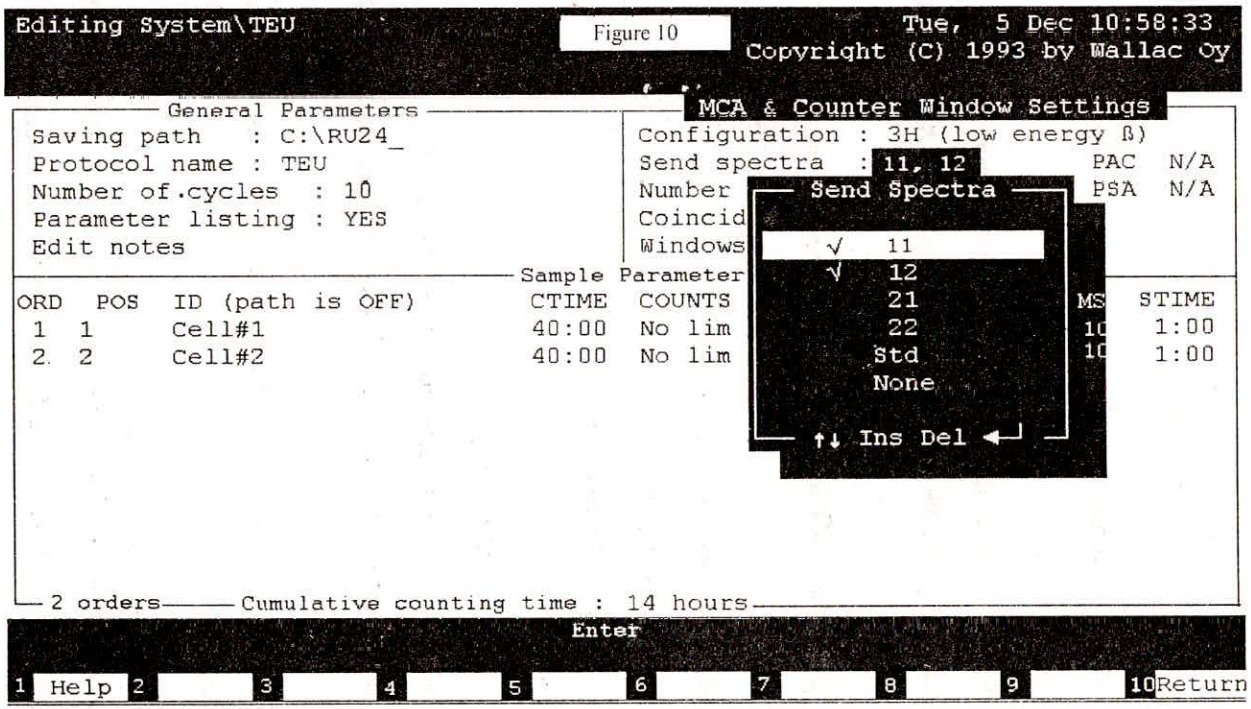

Editing System\TEU
Tue, 5 Dec 10:58:53
Copyright (C) 1993 by Wallac Oy
General Parameters
Saving path : C:\RU24_
Protocol name : TEU
Number of cycles : 10
Parameter listing : YES
Edit notes
MCA & Counter Window Settings
Configuration : 3H (low energy ß)
Send spectra : 11,12
PAC N/A
Number of channels : 512
PSA N/A
Coincidence bias : LOW
Windows
Select coincidence bias
High
Low
Sample Parameters
ORD POS ID (path is OFF) CTIME COUNTS
1 1 Cell#1 40:00 No lim
2 2 Cell#2 40:00 No lim
No Lim 1 1 Y 1/10 1:00
2 orders — Cumulative counting time : 14 hours
Enter
1 Help 2 3 4 5 6 7 8 9 10

Figure 9


Editing System\TEU
Figure 10
Tue, 5 Dec 10:58:33
Copyright (C) 1993 by Wallac Oy
General Parameters
Saving path : C:\RU24_
Protocol name : TEU
Number of cycles : 10
Parameter listing : YES
Edit notes
MCA & Counter Window Settings
Configuration : 3H (low energy ß)
Send spectra : 11, 12
Number
Coincid
Windows
PAC N/A
PSA N/A
Send Spectra
√ 11
√ 12
21
22
Std
None
↑↓ Ins Del ↵
Sample Parameter
ORD POS ID (path is OFF) CTIME COUNTS MS STIME
1 1 Cell#1 40:00 No lim 1(1:00
2 2 Cell#2 40:00 No lim 1(1:00
2 orders
Cumulative counting time : 14 hours
Enter
1 Help 2 3 4 5 6 7 8 9 10 Return

SPECTRA 11 for radiocarbon etc. The SPECTRA 21 and 22 are useful for analysing the background radiation checks.

Following these, enter the details of the samples to be counted in the Quantulus in the lower Window as shown in Figure 5.

- Insert the sample parameters as shown in Figure 5. A maximum number of 24 orders can be given.
- For every order one has to input the following parameters

✓ POS: Position no. given to the individual samples as they are placed in the tray.

✓ ID – Enter the Sample ID such as "cell number/run number", STD-C of Run Number, etc.

✓ CTIME – Counting Time. Usually 40.00

✓ COUNTS – Set to No limits

✓ CUCNTS – Cumulative counts. Set to No lim

✓ MCW – Set to 1

✓ REP – Replicate counting. Set to 1

✓ ST – External standard for quench correction. Set to "Y"

✓ STMS – Number of times the external standard has to be counted per cycle. Usually set to 1/10.

✓ STIME – Length of time the external standard has to be counted (in min:sec). Usually set to 00.15.

The latest statistics of the counting can be viewed from the file REGISTRY.TXT by pressing F3 (SAMPLE VIEW OF FILE REGISTRY.TXT enclosed).

➢ After editing the protocol move to the 'Queue' column and press F6 Key to insert the selected protocol. Press F4 key to Run the Protocol.

Out of the maximum sixty samples that can be accommodated in the counter chamber in three trays (20 each), any sample can be selectively counted by indicating the position. Each sample is counted in the full spectrum channel (1-1024) automatically and any sample's beta - spectrum can be compared with that of the standard and background samples. Thus three spectra (of sample, background & standard) can be plotted simultaneously on the computer screen. This enables one to choose the best figure of merit (E^2/B) by adjusting the left and right cursor lines and get the tritium content of the samples under investigation in TU or dpm with the associated errors (see figures 11 and 12). In these figures, the X-axis shows the channel no. (1-1024) and Y-axis the sample count rate in cpm. In figure 11, curve A is the β - spectrum of the tritium standard sample and B is the β - spectrum of the background sample. By adjusting the cursor lines, one can get the best figure of merit (In the figure shown here, the best F.M. is 888 and counting efficiency is 28.06%).

The channel width represented by the space between the left and right cursor lines i.e. 27-181 is best suited for tritium counting. The figure 12 is similar to the figure 11 but the curve C represents the β - spectrum of that of the sample under investigation. The standard sample count rate is given as 254.47 cpm, the background sample count rate is 0.887 cpm and the unknown sample count rate is 3.199 cpm. The tritium content of the sample under investigation can be determined and 141.4 ± 4.7 T.U. At the top of the figures, the sequences against A, B and C are scale of the curve in cpm/ch, the total time of counting in minutes and the sample identify respectively.

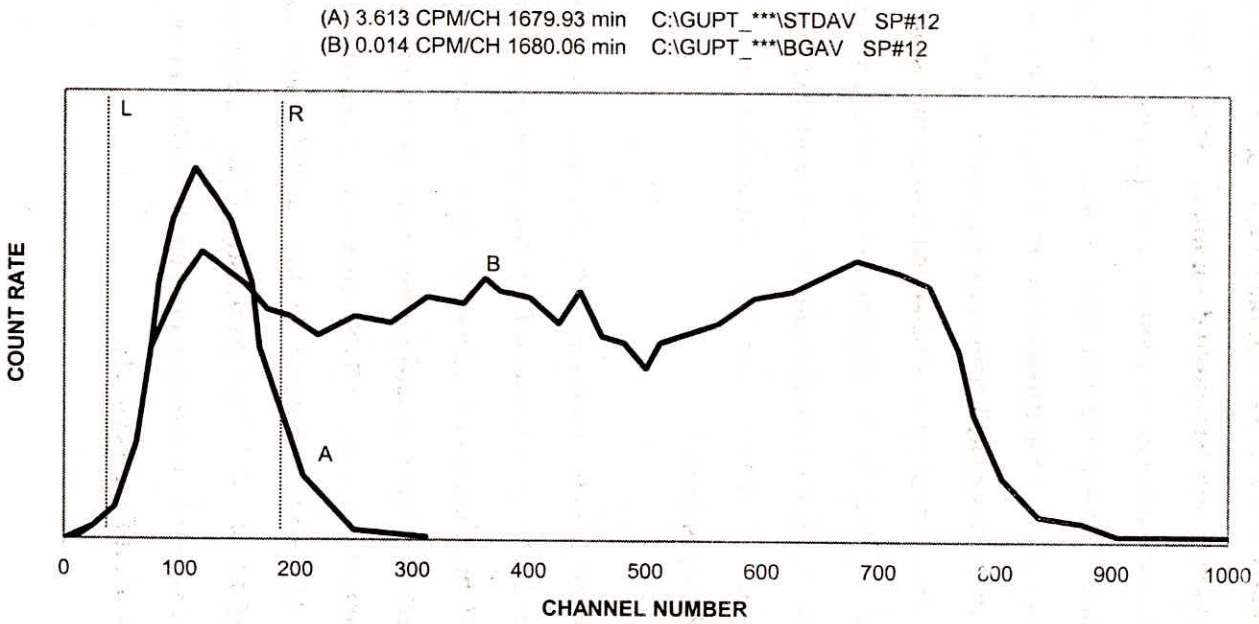


Figure 11 Beta spectrum of standard A and background B

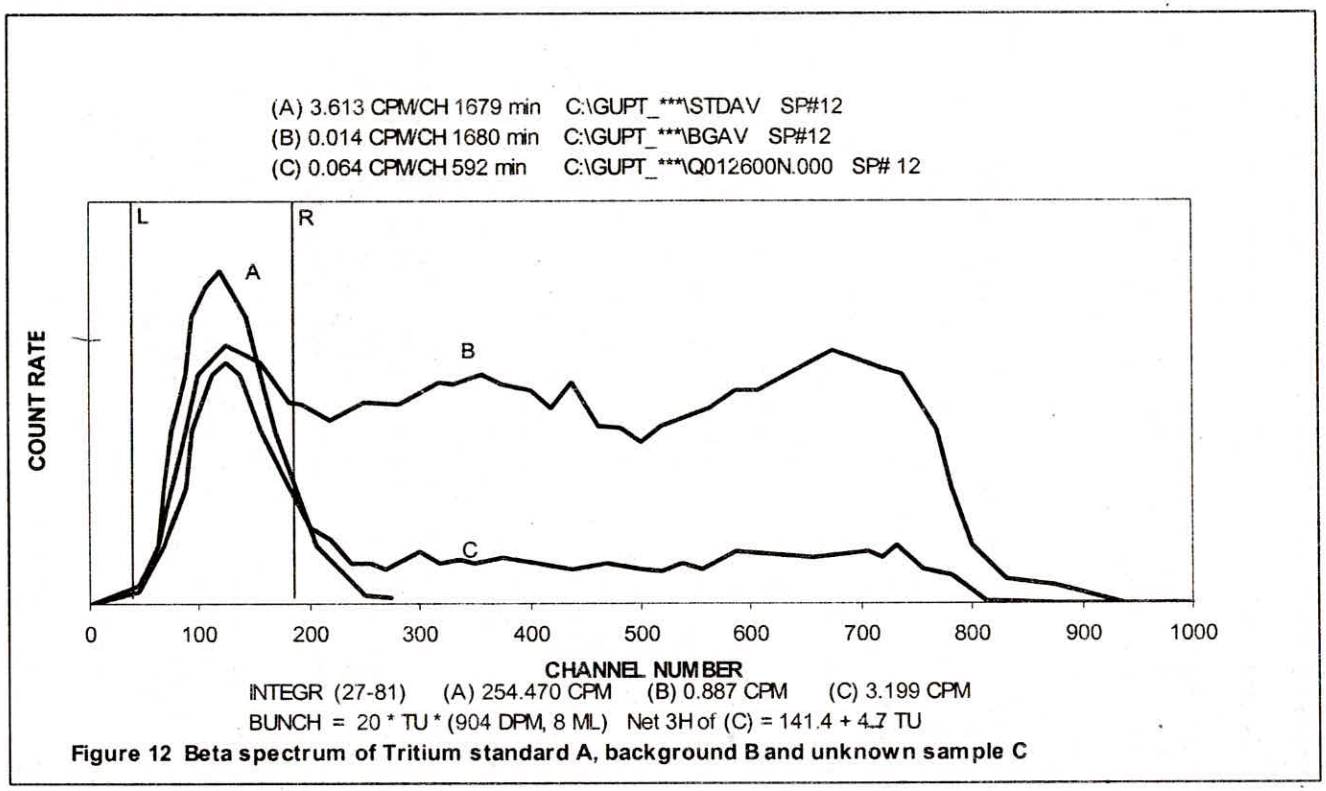


Figure 12 Beta spectrum of Tritium standard A, background B and unknown sample C

SAMPLE VIEW OF FILE REGISTRY.TXT

Efficiency testing done by the service engineer from m/s Pharmacia Biotech Delhi, on 01.11.2000.

MON 30 OCT 2000 14:43

*** DIRECTORY PATH :C:\GUPT_***
PARAMETER GROUP: 8
ID: EFF
00A PROGRAM MODE 6 ->

ORDER	POS	ID	CTIME	COUNTS	CUCNTS	MCW	REP	STD	STMS	STIME
1	2	WALLAC-T	3:00	NO LIM	NO LIM	1	1	Y	1/1	1:00
2	4	WALLAC-BLANK	3:00	NO LIM	NO LIM	1	1	Y	1/1	1:00

NUMBER OF CYCLES 1
COINCIDENCE BIAS (L/H) L

MCA	INPUT	TRIGG.	INHIBIT	MEMORY SPLIT
1	LRSUM		L*R	PAC+G
2	GSUM		G	L*R

PULSE COMPARATOR LEVEL 1

WINDOW	CHANNELS	MCA	HALF
1	5- 320	1	1
2	5- 650	1	1
3	300- 640	1	1
4	50- 650	1	2
5	70- 500	1	2
6	300- 640	1	2
7	1- 1024	2	1
8	1- 1024	2	2

SEND SPECTRA 11,12,21,22,S
RESOLUTION OF SPECTRA 1024
LISTING Y
INSTRUMENT NUMBER 1

CYC	POS	REP	CTIME	DTIME1	DTIME2	CUCNTS	SQP	SQP%	STIME
	ID	CPM1	COUNTS1	CPM1%	CPM2	COUNTS2	CPM2%		
		CPM3	COUNTS3	CPM3%	CPM4	COUNTS4	CPM4%		
		CPM5	COUNTS5	CPM5%	CPM6	COUNTS6	CPM6%		
		CPM7	COUNTS7	CPM7%	CPM8	COUNTS8	CPM8%		

Q010201S.001 30 OCT 2000 14:46
Q010201N.001 30 OCT 2000 14:49

1	2	1	3:00.769	4.014	2.342	198628	952.80	.04	1:01
WALLAC-T			67424.92	198628	.22	68282.38	201154	.22	
			2154.17	6346	1.26	8.48	25	20.00	
			8.48	25	20.00	.00	0	.00	
			8.74	26	19.61	.00	0	.00	

Q030401S.001 30 OCT 2000 14:58
Q030401N.001 30 OCT 2000 15:01

1	4	1	3:01.765	2.390	2.388	30	954.08	.04	1:01
WALLAC-BLANK			10.03	30	18.26	17.72	53	13.74	
			9.03	27	19.25	.00	0	.00	
			.00	0	.00	.00	0	.00	
			2.67	8	35.36	.00	0	.00	

7.1 Minimum Detectable Concentration of Tritium

In an ideal counting experiment, Poisson statistics govern the error, which can be minimized by increasing the counting time and decreasing the background count rate. The fractional standard error σ(N)/N of a net sample count rate N may be expressed as,

$$\sigma(N)/N = \frac{1}{N}\sqrt{\frac{N+B}{T_S}+\frac{B}{T_B}} \qquad (1)$$

Where B is the background count rate and T_S and T_B are the counting times for sample and background respectively.

The minimum detectable concentration C_{min} may be defined as the smallest concentration, which can be distinguished from the background sample at the required confidence level.

$$C_{min} = \sigma(C_{min}) = F\sqrt{[\sigma(N)]^2+[\sigma(B)]^2} \qquad (2)$$

$$= F\sqrt{2\sigma(B)^2} \quad \text{Since} \quad N = B \qquad (3)$$

$$= F\sqrt{2B/T} \quad \text{for } 1\sigma \text{ or } p = 68\ \% \qquad (4)$$

where F is the calibration factor (TU/CPM i.e. Tritium activity of the standard/its net cpm), N and B are the sample count rate and background count rate respectively, p the confidence level and T, the counting time.

$$C_{min} = F\sqrt{2B/T} \quad (\text{for } 2\ \sigma \text{ or } p=95\%) \qquad (5)$$

As per the above equation, the minimum concentration of tritium that can be measured without enrichment using the Quantulus counter is about 21 TU for 400 minutes counting.

7.2 Estimation of Tritium Concentration

Estimation by Spiking the Samples with Tritium

Out of all electrolytic cells, any three cells are used for enriching tap water samples spiked with known tritium activity and another three for blank tap water samples. The spiked samples are meant for determining their tritium enrichment factor 'Z' (final tritium concentration/initial tritium concentration). C. B. Taylor, I.A.E.A. has developed the following equations for the estimation of tritium enrichment factor of unknown samples.

$$In\ Z/r_a\ ln\ N = (1\text{-}1/\beta) + r_c/r_a \times (1\text{-}d) \qquad (6)$$

where r_a = rate of electrolysis/total loss rate of hydrogen from cell

$N = W_O/W_f$ (Initial wt. of the sample/Final weight of the sample).

β = instantaneous electrolytic separation factor for tritium

r_c = rate of hydrogen loss as water vapour/total loss rate of hydrogen from cell

and d = fractionation factor for loss of tritium by evaporation.

On the right hand side of equation 6, the second term is of order of 0.5% of the first term and its variation from cell to cell is negligible if a similar set is operated under the same conditions. Equation 6 therefore suggests that a set of cells with uniform separation factor β, when run simultaneously, should show uniformity of the parameter $ln\ Z/r_a\ ln\ N$. This parameter, which is assigned the symbol E, is the parameter which should be used to evaluate enrichment factors, and to monitor the performance of a set of batch electrolysis cells.

With slight modification of 6, the enrichment parameter E may be represented by:

$$E = [(W_o-W_f)/W_e] \times \ln Z/\ln N = (1-1/\beta) + (r_c/r_a) \times (1-d) \quad (7)$$

where (W_O-W_f) is the total weight loss of the sample due to electrolysis, evaporation and spray losses and 'W_e' is the weight of electrolyzed water. If 'W_e' can not be measured accurately in the absence of an accurate ampere hour meter, then it can be made constant for all cells by passing series current for the same time. Because the second term on the right hand side of equation 7 is so small, the separation factor β is the parameter which mostly affects the magnitude and variability of the enrichment parameter E. In the case of spike samples, Z is measured and applied to determine E; the mean value 'E_m' of E of the three samples, is then used to calculate Z for the unknown samples.

If the total charge passes is Q ampere - hours, then

$$W_e = Q/2.97545$$

Since the same amount of current is passed through all cells in series for the same length of time, the modified enrichment parameter, W_eE is used for the calculation of Z of an unknown sample.

$$W_eE = [(W_o-W_f)] \times \ln Z/\ln N \quad (8)$$

Therefore,

$$\ln Z = [(W_eE_m \times \ln N] \times (W_o-W_f) \quad (9)$$

where, W_eE_m is the mean enrichment parameter of the three spiked cells, and N, Z and (W_O-W_f) are the mass reduction factor, tritium enrichment factor and total weight loss of the unknown sample (due to electrolysis, evaporation and spray

losses) respectively. The separation factor β for a spiked cell can be calculated using the equation,

$$\beta_{eff} = ln(W_f/W_o)/ln(Z \times W_f/W_o) \qquad (10)$$

The tap water samples are enriched mainly to determine the background countrate of the spiked samples. This has become necessary as large quantity of tritium - free water is always not readily available to prepare the spike samples.

As the three spike cells are changed in rotation one after another in each run, one gets the enrichment parameter values of every cell which are found to be uniform if the cathode surfaces are well developed and unaffected by corrosion, chemical damage, mechanical damage etc.

The tritium concentration of a sample on counting date is calculated as

$$C_s = C_{st} \times (N_s/N_{st}) \times 1/Z \qquad (11)$$

where, C_s = the tritium concentration in TU of the sample.

C_{st} = the tritium concentration in TU of the standard, N_s = the net count rate of the sample.

N_{st} = the net count rate of the standard.

7.3 Determination of Error in Tritium Measurement

The main error in the measurement of tritium is the counting error.

The counting error, $\sigma C = \pm\sqrt{C}$ (12)

where C is the total number of counts obtained after counting a sample for a time T. The error in count rate R can be calculated as follows.

$$R = C / T \quad \textbf{(13)}$$

$$\sigma \text{ R (error in R)} = \sigma \text{ (C/T)} \quad \textbf{(14)}$$

$$= \sqrt{C}/T = \sqrt{R/T} \quad \textbf{(15)}$$

When the background count rate is subtracted from the gross count rate of a sample, the error in the net count rate is calculated using the formula,

$$\sigma(C_n) = \sqrt{\sigma^2 C_g + \sigma^2 B} \quad \textbf{(16)}$$

where, $\sigma (C_n)$, $\sigma (C_g)$ and σ (B) are the errors in net count rate, gross count rate and background count rate respectively.

The error in enrichment,

$$\sigma (Z) = \sigma E \times \ln Z \quad \textbf{(17)}$$

where σ E is the error in enrichment parameter, estimated after a large number of enrichment runs (over a period of time) for a set of cells, and often found to be below 1%.

The combined error,

$$\sigma(C_s) = \sqrt{\sigma^2 N_s + \sigma^2 N_{st} + \sigma^2 Z + \sigma^2 C_p} \qquad (18)$$

where $\sigma(N_s)$ = error in sample countrate, $\sigma(N_{st})$ = error in standard countrate

$\sigma(Z)$ = error in enrichment, $\sigma(C_p)$ = error in weighing, pipetting etc.

$\sigma(N_{st})$ is negligible and $\sigma(C_p)$ normally does not exceed 1% by experience. Normally, all the errors are expressed in percentage so that the combined error is expressed in percentage so that the combined error is expressed in terms of percentage error of the net count rate of the sample. An example of the calculation for tritium concentration in TU of a sample under investigation and the error in estimation is shown below.

Let the net tritium count rate in cpm of a sample be 1.69 ± 0.13

Tritium activity (TU) of the sample

$$= 1.69 \times (\text{TU/cpm})/Z \qquad (19)$$

where, TU/cpm is the sensitivity factor (calibration factor) of the counter i.e. (C_{st}/N_{st}) in equation 11. Equation 18 can be modified as follows by rejecting the negligible terms.

$$\sigma(C_s) = \sqrt{\sigma^2 N_s + \sigma^2 Z + \sigma^2 C_p} \qquad (20)$$

$$\sigma(C_s) = \sqrt{\sigma^2 N_s + \sigma E \times \ln Z + \sigma^2 C_p} \qquad (21)$$

$$\sigma(C_s) = \sqrt{\left(\frac{0.13}{1.69} \times 100\right) + (0.72 \times 2.72)^2 + (0.15)^2} = 7.94\%$$

Therefore 1σ error in the estimation of the tritium concentration of the above sample is (1.69 * 7.94/100) cpm which when converted into TU, gives

$$\left[\frac{0.13\times 7.94\times TU\,/\,cpm}{100\times Z}\right]TU$$

Fig. 13 shows the relationship between tritium concentration and the error in measuring it after enrichment. It shows that the error in estimating the tritium concentration of a sample of 2 TU is as high as 19% whereas error in the case of a sample of tritium concentration of about 10 TU is less than 5%.

7.4 Drawbacks in the Estimation of Tritium by Spiking Method

As discussed earlier, the enrichment factor of an unknown sample is determined by the equation.

$$\ln Z = (W_e E_m \times \ln N) / (W_O - W_f).$$

However, if one determines Z using the above equation without considering the cathode surface conditions, this could lead to large errors. The above equation is derived assuming that $\ln Z / r_a \ln N$ is uniform in every cell, But, $\ln Z/r_a \ln N$ need not be uniform in the case of every cell as per experience gathered during the last few years.

The value of N does not depend solely on electrolytic reduction of weight of the sample. It has been observed that the cell temperature varies from 1°C to about 8°C, depending on the position of the cell in the refrigerator and the stage of electrolysis. Therefore, factors such as evaporation loss and spray loss can vary largely from one cell to another. These factors result in the non-uniformity of $\ln Z/r_a \ln N$ value from one cell to another. Therefore, there will be large errors than anticipated while estimating the tritium enrichment factors of samples in the various cells using the mass reduction factors.

Though the samples are electrolyzed after distillation and sometimes even after double distillation to make sure that the conductivity of the sample is less

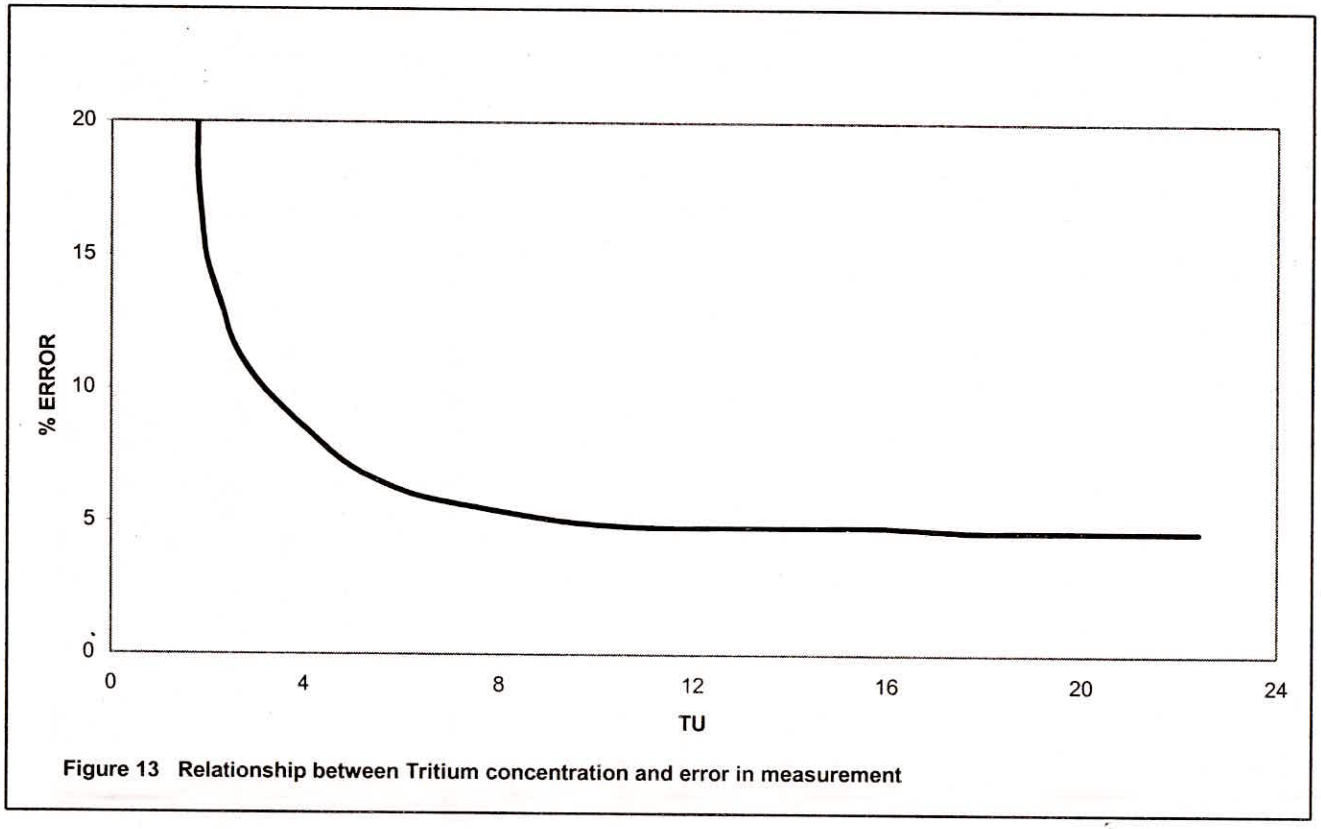


Figure 13 Relationship between Tritium concentration and error in measurement

than 10 μs cm^{-1}, there could still be organic impurities such as alcohol, which can corrode the cells during electrolysis. These organic impurities often go unnoticed. A corroded cathode requires mechanical treatment such as brushing and chemical treatment such as dipping in dilute hydrochloric acid to remove the corroded mass. This results in the deterioration of its enrichment characteristics. It has been seen that a cathode surface which used to exhibit tritium recovery factor (ratio of the product of the final tritium content and final mass of the sample to the product of its initial tritium content and initial mass i.e. $T_f \times W_f / T_O \times W_O$ of about 0.9 has deteriorated after corrosion to exhibit a value of about 0.7 due to the above treatment. In order to bring the cell back to normal operation by developing the surface of the cathode, one has to pass about twenty thousand ampere hours of current by electrolyzing distilled water. Till then it can neither be used as a spiked cell nor as a cell with an unknown sample, as the enrichment parameter of such a cell varies largely from that of other cells.

Another drawback in this technique is the use of tritium standard for spiking the cells. The level of tritium activity used for spiking the cells in this laboratory is about 3 orders of magnitude higher than that of the samples under investigation. Therefore, extreme care is to be given during preparation, electrolysis, distillation and counting of the spiked samples. The materials used for processing the spiked samples are normally not used to process other samples, as they can be potential sources of contamination. With all these meticulous procedures, there have been instances of contamination of the samples. After each run of electrolysis, the spiked cells are rinsed with hot running water, along with other cells to get rid of any tritium in the form of NaOH. But one is not sure of the decontamination, until the results of the next run are known. One approximate way of checking the decontamination is testing for any traces of alkali (NaOH), present in the final washings of the spiked cell using a pH paper. One has to continue the rinsing till it is free of any alkali.

Isotope Hydrology Laboratory, National Institute of Hydrology
FORM A: Investigator's Request for Analysis of Environmental Tritium

Submitter
Name:_____
Full Official
Address:_____
Phone, Fax and E-mail:_____
Project Title / reference:_____
Number of total samples submitted:_____Date of Submission:_____

1	2	3	4	5	6	7
Sample #	Date of collection	Source Type	Location / Site	E.C..	Remarks	Lab. ID #

Note: Column 3 - River / Lake / Rainwater / Snow / Glacier / Groundwater (depth)
Column 4 - Use additional sheet if required.
Column 5 - Field E.C in micro-mhos
Column 6 - If special attention to a specific sample is required
Column 7 - To be filled by the Lab. Manager

Investigator's Signature

Lab. Manager's recommendation:
Priority: High / Medium / Low
Signature of Lab. Manager

Isotope Hydrology Laboratory, National Institute of Hydrology
FORM B: Pre-distillation of ET samples

Technician:_____

1	2	3	1	2	3
Laboratory ID #	Date of distillation	Shelf # / Row #	Laboratory ID #	Date of distillation	Shelf # / Row #

NOTE: In column # 3 please enter the Storage shelf number and Row number for locating the samples.

Technician's Signature

Isotope Hydrology Laboratory, National Institute of Hydrology
FORM C: ET Enrichment Data (TE Unit)

Run No._____Technician:_____
Date of start:__/__/__ Date of completion:__/__/__ Elapsed Time _____Hrs.
Temp. ___°C Temp. Cell #_____Initial current:__Amps. Final current:___Amps.
Sample weight___gm. Na_2O_2 __gm. Spike ID_____ DPM____ Q_____Amp-Hr

Sl. No.	1	2	3	4	5	6	7
	Cell #	Sample ID #	Dry cell Weight (g)	Cell + Sample + Na_2O_2 Weight (g)	Post-electrolysis Weight (g)	Yield (4-5) (g)	Remark
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							

Comments:

Technician's Signature

Isotope Hydrology Laboratory, National Institute of Hydrology

FORM D: Post-Enrichment distillation of ET samples

Technician:_____

1	2	3	1	2	3
Laboratory ID #	Date of distillation	Remarks	Laboratory ID #	Date of distillation	Remarks

NOTE: In column # 3 please enter the Storage shelf number and Row number for locating the samples.

Technician's Signature

Isotope Hydrology Laboratory, National Institute of Hydrology
FORM E: Counting of Enriched ET samples in Quantulus

Run No._____Date of start:_____ Date of Completion:_____
Sample:Cocktail_____Data Storage Directory:_____
Counting time:_____ FM_____ Eff:_____Window selected_____

Sample ID#	Cell #	Count Position	# of cycles	SUM File Name	CPM	Sigma

Remarks:

Technician's Signature

Isotope Hydrology Laboratory, National Institute of Hydrology
FORM A1: Lab Manager's Key Form

1	2	3	4	5	6	7
Lab. ID #	Investigator	Sample #	Date of Receipt	Date of Completion	Result (TU)	Data File ref.

Remarks: (Letter number etc. communicating the results to the investigators)