2.1 Introduction

In spite of the increase in tritium content in natural samples due to thermonuclear explosions its level is so low that all natural samples need enrichment in their tritium content, before estimation. As the large mass differences among the various isotopes of hydrogen produce greater differences in physical properties of the isotopes rather than their chemical properties, a number of physical methods have been developed for the enrichment of tritium. Some of the techniques for tritium enrichment are described below:

2.2 Tritium Enrichment Techniques

2.2.1 Thermal Diffusion:

The partial demixing of gases due to a temperature gradient is called thermal diffusion: the heavier isotope moves towards the cooler region. The existence of thermal diffusion was first suggested by W. Fedderson in 1873, but its theoretical derivation was independently developed by Enskog\textsuperscript{114} and by Chapman\textsuperscript{115}. First experimental verification was done by Chapman and Dootson\textsuperscript{41,114-116}. In this method the degree of
separation that can be obtained is not very large. The same was improved upon by using multi stages\textsuperscript{118}. Though this method has the advantage of good reproducibility and high yield\textsuperscript{39,118,119}, it is expensive and complicated.

2.2.2 Fractional Distillation:

In 1919 F.A.Lindman presented theoretical arguments indicating that isotopes could be enriched by distillation since the rate of escape of atoms or molecules from a liquid surface are generally inversely proportional to the square root of their masses\textsuperscript{41}. Using this technique, preliminary concentration of heavy water has been made\textsuperscript{41,120}. As the separation factor in this method is very small, multistage distillation techniques are necessary for any significant enrichment. The disadvantages of this method are long times required\textsuperscript{39,118}, poor reproducibility\textsuperscript{122} and small enrichment factors attained\textsuperscript{118,122}. Following concentration by distillation, further reconcentration would be required for estimating low-activity samples\textsuperscript{122}.

Thermodynamically hydrogen gas distillation is more attractive than water distillation\textsuperscript{120,123}. The separation factors are considerably greater, but the low boiling point of liquid hydrogen requires use of special
techniques for handling $^{120}$.

2.2.3 Electrolysis:

Electrolysis causes decomposition of molecules and the rate of dissociation of heavy isotope molecules is less as compared to that of the lighter isotope, with the result the electrolyte gets enriched in heavier isotope. Electrolysis was first suggested as means of isotope separation by Kendall and Crittenden in 1923 and was first confirmed by Washburn and Urey in 1932 by enrichment of deuterium during electrolysis of water. Faltings and Harteck $^{37}$, Oestlund and Weiner $^{124}$, Brown and Grummit $^{27}$ and Libby $^{125}$ were among the first few to use electrolysis for tritium enrichment. As the difference in rates of dissociation of lighter and heavier isotopes decreases with temperature, the enrichment is more effective at lower temperatures. Electrolysis is a relatively simple technique and gives consistent and reliable results.

2.2.4 Other Methods:

Gas chromatography $^{126}$, adsorption and desorption on palladium $^{127-130}$ and molecular sieves $^{131,132}$, gaseous diffusion process $^{133,134}$ etc are some of the other methods feasible for enrichment of tritiated samples. But these methods are rarely used since they are time consuming, expensive and require large quantities of
reactants. Chemical exchange processes generally used for heavy water production can be applied in the enrichment of tritium as well\textsuperscript{120, 135, 136}. However this method is not well established for regular processing of the environmental tritiated water samples.

2.3 Enrichment by Electrolysis

2.3.1 Details of the Electrolytic Method

Of all the methods considered electrolysis is relatively simple and most widely used for tritium enrichment of water at the laboratory scale\textsuperscript{39}. In order to improve the electrical conductivity of the water sample, an acid or an alkali is normally added as an electrolyte. The electrolysis is accompanied by heat generation due to resistive dissipation of the energy and this heat needs to be removed. Further, cooling the electrolyte solution to fairly low temperatures is essential to avoid evaporation losses and to make enrichment more effective. It is also necessary to control the rate of electrolysis since at faster rates, water is likely to be lost from electrolysis cell by entrainment\textsuperscript{137}. Single stage electrolysis results in about 5 to 15 fold enrichment\textsuperscript{124} and for higher enrichments, electrolysis has to be carried out in several stages\textsuperscript{27, 138-140}. To obtain consistent and reliable results in multi-stage electrolysis, attention must be paid to the electrolyte temperature, current
density and electrolyte concentration\textsuperscript{27,39,138-140}.

2.3.2 Theory of Electrolytic Enrichment Process\textsuperscript{141}

Due to the difference in the rate of dissociation of protium, deuterium and tritium, the hydrogen gas produced during electrolysis contains less percentage of deuterium and tritium and the electrolyte gets enriched in them. At low current densities the isotopic shift is mainly due to chemical exchange; but at high current densities, the kinetic effects may contribute to relatively high separation factors of deuterium and tritium. If \((dH/H)\), \((dD/D)\) and \((dT/T)\) are the fractions of protium, deuterium and tritium produced in a small period of electrolysis, then

\[
\frac{dH}{H} = \alpha \cdot \frac{dD}{D} \quad \text{-- (2.1)}
\]
\[
\frac{dH}{H} = \beta \cdot \frac{dT}{T} \quad \text{-- (2.2)}
\]
\[
\frac{dD}{D} = \gamma \cdot \frac{dT}{T} \quad \text{-- (2.3)}
\]

where \(\alpha\), \(\beta\) and \(\gamma\) are electrolytic separation factors of deuterium and protium and tritium and protium.

i.e.

\[
\frac{D_0}{D} = \left(\frac{H_0}{H}\right)^{1/\alpha} \quad \text{-- (2.4)}
\]
\[
\frac{T_0}{T} = \left(\frac{H_0}{H}\right)^{1/\beta} \quad \text{-- (2.5)}
\]
\[
\frac{T_0}{T} = \left(\frac{D_0}{D}\right)^{1/\gamma} \quad \text{-- (2.6)}
\]

where \(H_0\), \(D_0\), and \(T_0\) are the initial concentrations and \(H, D\) and \(T\) are the final concentrations of protium, deuterium and tritium in the electrolytic solution. The values of \(\alpha\), \(\beta\) and \(\gamma\) depend on a number of factors of
electrolysis, but most of the observed values of $\alpha$ lie in the range of 4 to 6, those of $\beta$ in the range 8 to 12 and $\gamma$ the ratio of $\beta$ to $\alpha$ is close to 2.

Bigeleisen$^{142}$ showed theoretically, that the logarithmic ratio of tritium separation factor $\beta$ to deuterium separation factor $\alpha$ should be 1.4±0.01, which is in good agreement with experimentally obtained value of 1.4±0.09 obtained by Kaufman and Libby$^{23}$. Foster, Purcell and Wheat$^{24}$, using nickel electrodes and Na$_2$CO$_3$ electrolyte, got average values of $\alpha = 5.6$, $\beta = 10.4$ and $\gamma = \beta/\alpha = 1.9$.

If the volume of water sample is reduced from $V_0$ to $V$, we have

\[
\frac{(D_0/V_0)/(D/V)}{(T_0/V_0)/(T/V)} = \left\{\frac{(H_0/V_0)/(H/V)}{(H/V)}\right\}^{1/\beta} \cdot \left\{\frac{(V/V_0)}{(V/V)}\right\}^{1-(1/\alpha)} \tag{2.7}
\]

\[
\frac{(T_0/V_0)/(T/V)}{(D_0/V_0)/(D/V)} = \left\{\frac{(H_0/V_0)/(H/V)}{(H/V)}\right\}^{1/\gamma} \cdot \left\{\frac{(V/V_0)}{(V/V)}\right\}^{1-(1/\gamma)} \tag{2.8}
\]

and

\[
\frac{(T_0/V_0)/(T/V)}{(D_0/V_0)/(D/V)} = \left\{\frac{(H_0/V_0)/(H/V)}{(H/V)}\right\}^{1/\gamma} \cdot \left\{\frac{(V/V_0)}{(V/V)}\right\}^{1-(1/\gamma)} \tag{2.9}
\]

On simplification,

\[
\{\alpha/(\alpha-1)\} \cdot \log (CD/CD_0) = \log (V_0/V) \tag{2.10}
\]

\[
\{\beta/(\beta-1)\} \cdot \log (CT/CT_0) = \log (V_0/V) \tag{2.11}
\]

\[
\{\gamma/(\gamma-1)\} \cdot \log (CT/CT_0) + 1/(\gamma-1) \log (CD_0/CD) = \log (V_0/V) \tag{2.12}
\]

where $CH_0$, $CD_0$ and $CT_0$ and $CH_0$, $CD$ and $CT$ stand for the initial and final concentrations of protium, deuterium and tritium respectively. Here it is assumed that the
original deuterium and tritium concentrations are extremely small as compared to concentration of protium.

In case of heavy water, when concentration of tritium is relatively small, the second term on the left side of equation (2.12) becomes negligible and it assumes approximation relation

\[
\left\{ \frac{v^*}{(\beta-1)} \right\} \times \log \left( \frac{CT}{CT_0} \right) = \log \left( \frac{V_0}{V} \right) \quad -- (2.12)
\]

In equation 2.11, the factor \((\beta-1)/\beta\) \((= n)\) is referred to as enrichment factor. The quantity of tritium obtained in the sample after electrolysis, expressed as percentage of quantity of tritium present in the original sample, is referred to as tritium recovery.

For multistage electrolysis, where final volume and concentration of the sample of a particular stage are the initial volume and concentration for the next stage, one can use the above equations successively. Thus for a three stage electrolytic process, the equations are:

\[
\begin{align*}
\log \left( \frac{T_1}{T_0} \right) &= \frac{\beta-1}{\beta} \times \log \left( \frac{V_0}{V_1} \right) \quad -- (2.13) \\
\log \left( \frac{T_2}{T_1} \right) &= \frac{\beta-1}{\beta} \times \log \left( \frac{V_1}{V_2} \right) \quad -- (2.14) \\
\log \left( \frac{T_3}{T_2} \right) &= \frac{\beta-1}{\beta} \times \log \left( \frac{V_2}{V_3} \right) \quad -- (2.15)
\end{align*}
\]

where \(T_0\), \(T_1\), \(T_2\) and \(T_3\) refer to tritium concentrations in the initial, after the first, after the second and after the third stage of electrolysis respectively. The
equations (2.13) to (2.15) can be combined to obtain:

$$\log \left( \frac{T_3}{T_0} \right) = \left( \frac{\beta - 1}{\beta} \right) \log \left( \frac{V_o}{V_3} \right) \quad --(2.16)$$

Ideally one could use this equation, but since in multi stage electrolysis there is a possibility of loosing some sample during transfer and distillation after each stage. Hence equations 2.13 to 2.15 are used instead of equation 2.16.

2.4 Standardisation of the Electrolysis Set-up

2.4.1 Single stage Electrolysis

In the developmental stages, different materials, geometries and sample holding capacities of electrolytic cells were used. In most of the cases, pyrex glass cells and nickel(Ni) and stainless steel(SS) electrodes were used. In one of the trial runs, SS cell was used which served as cathode also. Since this did not give satisfactory results, use of glass cell was continued. A rubber cork was used for isolating the electrolysis sample from surroundings to avoid molecular exchange. The electrodes were held parallel to each other with teflon spacers.

To increase the conductivity, water could be made either acidic or alkaline. Apart from corrosion of electrodes that could be caused by adding acid to the medium, it necessarily results in the addition of external hydrogen thereby changing T/H ratio of the
original sample. This could be avoided by using Na₂O to make the sample alkaline. However, Na₂O₂ was preferred since its oxidising property removes any organic matter present in the sample by oxidation. Hence, in the present study, the sample to be electrolysed was made alkaline by adding Na₂O₂ (1% W/V).

For the trial runs a spiked low active water sample of known activity was used and the electrolysis was carried out with a current in the range of 3 to 5 amp. For removal of heat generated during electrolysis, initial runs were made with the cells kept in a water bath through which tap water or chilled water was circulated. The results, as summarised in Table 2.1, are not satisfactory with respect to reproducibility, enrichment and recovery of tritium which could mainly be attributed to insufficient cooling.

From the Table 2.1 it can be seen that enrichment factors obtained were in the range 0.24 to 0.41 and tritium recovery was also quite poor besides having large variation. To improve the recovery as well as reproducibility of enrichment a deep-freeze set up was used for cooling. The deep freeze temperature was maintained at about 0°C. To maintain the constant temperature of the electrolyte, the cell was kept in a constant temperature bath within the deep-freeze. As
Table 2.1

Trial experiments prior to standardisation of cells

<table>
<thead>
<tr>
<th>Remarks</th>
<th>Volume(ml)</th>
<th>Con(cpm/ml)</th>
<th>Enrichment</th>
<th>n</th>
<th>$\beta^{3}H$ rec.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Through const. temp. bath,</td>
<td>150</td>
<td>20</td>
<td>135.4</td>
<td>222</td>
<td>7.5</td>
</tr>
<tr>
<td>water at R.T.</td>
<td>150</td>
<td>17</td>
<td>104.7</td>
<td>246.3</td>
<td>8.82</td>
</tr>
<tr>
<td>was circulated</td>
<td>150</td>
<td>28</td>
<td>98.4</td>
<td>187.2</td>
<td>5.36</td>
</tr>
<tr>
<td>Ice used as cooling agent,</td>
<td>150</td>
<td>18</td>
<td>94.3</td>
<td>225.9</td>
<td>8.3</td>
</tr>
<tr>
<td>when const. temp. bath was</td>
<td>150</td>
<td>35</td>
<td>126.2</td>
<td>227.2</td>
<td>4.29</td>
</tr>
<tr>
<td>15°C &amp; initial cell temp. was</td>
<td>20°C</td>
<td>15°C</td>
<td>4°C-6°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

electrolysis proceeded, the constant temperature bath attained a temperature of $4^\circC-6^\circC$. The electrolysis was carried out at a constant current of 3 amp. For standardisation, a cylindrical glass cell with an initial sample volume of 500 ml was used with the electrodes held parallel to each other 2 cm. apart. Fig 2.1 gives sketch of the cell used.

A number of runs were made with standard spiked samples containing tritium activity in the range of 20-50 dpm/ml (333.3 - 833.3 Bq/l). The recovery and enrichment factors obtained for different volume
FIG. 2.1, SKETCH OF ELECTROLYSIS CELL USED FOR 1st AND 2nd STAGE.
Table 2.2

Standardisation of large cell to be used for 1st & 2nd stage

<table>
<thead>
<tr>
<th>Volume(ml)</th>
<th>Con(dpm/ml)</th>
<th>Enrichment</th>
<th>( ^3 \text{H} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vo V Co C</td>
<td>(Vo/V) (C/Co) %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
<td>------------</td>
<td>----------------</td>
</tr>
<tr>
<td>500</td>
<td>79</td>
<td>24.15</td>
<td>110.38 6.33 4.57 0.82 5.66 72.2</td>
</tr>
<tr>
<td>500</td>
<td>62</td>
<td>24.15</td>
<td>135.49 8.06 5.61 0.83 5.76 69.6</td>
</tr>
<tr>
<td>500</td>
<td>105</td>
<td>46.91</td>
<td>169.77 4.76 3.62 0.82 5.69 76</td>
</tr>
<tr>
<td>500</td>
<td>103</td>
<td>46.91</td>
<td>175.86 4.85 3.76 0.84 6.13 77.2</td>
</tr>
<tr>
<td>200</td>
<td>11</td>
<td>47.29</td>
<td>531 18.18 11.23 0.83 5.88 61.8</td>
</tr>
<tr>
<td>200</td>
<td>40</td>
<td>47.29</td>
<td>173.78 5 3.67 0.81 5.26 73.5</td>
</tr>
<tr>
<td>200</td>
<td>8</td>
<td>47.29</td>
<td>658.5 25 13.92 0.82 5.56 55.7</td>
</tr>
<tr>
<td>200</td>
<td>40</td>
<td>47.29</td>
<td>182.3 5 3.86 0.84 6.25 77.1</td>
</tr>
</tbody>
</table>

reductions are given in Table 2.2. Using method of regression, the average value of electrolysis enrichment factor obtained was 0.83. In Fig 2.2 is given the variation of \( (C/C_0) \) for different \( (V_0/V) \) ratio and compared with computed values using exponent \( n=0.83 \). Thus in a single stage electrolysis, a volume reduction by a factor 5 results in tritium recovery of about 75% and enrichment by a factor of about 3.6 as indicated in Figs 2.2 and 2.3.

For small volume samples a cell of different geometry to accommodate an initial volume of 100 ml was
Fig 2.2 Vari. of H3 con. wit vol.

For 1st & 2nd stage (n=0.83)
Fig 2.3 Vari. of H3 rec. v th vol.
For 1st & 2nd stage (n=0.83)
FIG. 2.4, SKETCH OF ELECTROLYSIS CELL USED FOR 3\textsuperscript{rd} STAGE.
used. The sketch of the cell is given in Fig 2.4. As in the case of larger volume cells, the cell was standardised and the results obtained are given in Table 2.3. In order to maintain approximately the same current density as in the previous case, the electrolysis was carried out using a current of 2 amp. Using the method of regression the average value of enrichment factor works out to be 0.67. Fig 2.5 gives variation of \( \frac{C}{C_0} \) for different \( \frac{V_0}{V} \) ratio and compared with computed values using \( n=0.67 \). Fig 2.6 gives the variation of recovery with volume reduction and compared with the computed values for \( n=0.67 \). As can be seen, the volume reduction by a factor of 4 results in a recovery of about 62% and enrichment by a factor of about 2.6.

2.4.2 Multi stage Electrolysis:

Whenever single stage enrichment was found to be inadequate to bring the environmental samples within the range of reliable measurement levels, recourse had to betaken to three stage process. In first and second stages, larger cells were used and in each stage a volume reduction of 5 was obtained at a current of 3 amp. In the final stage the smaller cell was used and volume reduction of 4 was obtained employing a current of 2 amp.

The enrichment factor for the 3rd stage is
Table 2.3

Standardisation of small cell to be used for 3rd stage

<table>
<thead>
<tr>
<th>Volume(ml)</th>
<th></th>
<th>Con.(dpm/ml)</th>
<th></th>
<th>Enrichment</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ini</td>
<td>Fin</td>
<td>Ini</td>
<td>Fin</td>
<td>Vol.</td>
<td>Co</td>
</tr>
<tr>
<td>Vo</td>
<td>V</td>
<td>Co</td>
<td>C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>10</td>
<td>7</td>
<td>29.2</td>
<td>8.0</td>
<td>4.17</td>
<td>0.69</td>
</tr>
<tr>
<td>100</td>
<td>7.5</td>
<td>7</td>
<td>40.24</td>
<td>13.33</td>
<td>5.75</td>
<td>0.68</td>
</tr>
<tr>
<td>100</td>
<td>9</td>
<td>7</td>
<td>34.08</td>
<td>11.11</td>
<td>4.87</td>
<td>0.66</td>
</tr>
<tr>
<td>80</td>
<td>8.6</td>
<td>6.67</td>
<td>28.94</td>
<td>9.3</td>
<td>4.34</td>
<td>0.66</td>
</tr>
<tr>
<td>100</td>
<td>7.8</td>
<td>6.67</td>
<td>38.78</td>
<td>12.82</td>
<td>5.81</td>
<td>0.69</td>
</tr>
<tr>
<td>100</td>
<td>7.0</td>
<td>6.67</td>
<td>36.52</td>
<td>14.29</td>
<td>5.48</td>
<td>0.64</td>
</tr>
<tr>
<td>40</td>
<td>9.2</td>
<td>12.86</td>
<td>34.76</td>
<td>4.35</td>
<td>2.7</td>
<td>0.68</td>
</tr>
<tr>
<td>40</td>
<td>11.0</td>
<td>12.86</td>
<td>30.65</td>
<td>3.64</td>
<td>2.38</td>
<td>0.67</td>
</tr>
<tr>
<td>100</td>
<td>11.0</td>
<td>12.86</td>
<td>57.76</td>
<td>9.09</td>
<td>4.49</td>
<td>0.68</td>
</tr>
</tbody>
</table>

different from that for the 1st and 2nd stages. Apart from difference in the cell geometry, current density etc., towards final stages because of small amount of sample left in the cell, temperature of electrolyte will increase resulting in volume reduction due to excess evaporation without contributing to enrichment.

In this case due to possible loss of sample due to transfer, and distillation etc at each stage, one has to use equations 2.13 to 2.15 successively and not single equation 2.16.
Fig 2.5 Vari. of H3 con. with vol.

For 3rd stage (n=0.67)
Fig 2.6 Vari. of H3 rec. with vol.
For 3rd stage (n=0.87)

Recovery %

vo/v

+ Expt
2.5 Sample Processing

Before starting electrolysis, the fresh water sample is filtered and the sea/spring water sample is distilled to remove suspended materials and dissolved salts. For each environment sample a volume of one litre is taken. The first stage of enrichment is carried out in two separate large cells containing 500 ml of sample each and made to 1% W/V solution with Na$_2$O$_2$. The first stage is discontinued when volume of electrolyte in each cell reduces by a factor of 5 (i.e. to 100 ml). The two 1st stage aliquots are pooled together, final volume of electrolyte obtained is noted and distilled to the last drop. The volume of the distillate so obtained is also noted, again made to 1% W/V electrolyte solution and 2nd stage electrolysis is carried out in a single large cell till the volume is reduced by a factor of 5 (i.e. to about 40 ml). The electrolyte volume obtained at the end of 2nd stage is noted, electrolyte distilled to the last drop and volume of distillate noted. The distillate obtained is made to 1% W/V solution of Na$_2$O$_2$ and put for third stage electrolysis in a smaller cell. When the electrolyte volume is decreased by a factor of 4 (i.e. to about 10 ml), the electrolysis is discontinued and the volume of the electrolyte leftover is noted and distilled to the last drop. The volume of distillate so obtained is noted. A fixed volume of this is used for
tritium counting and computation of the tritium content of the original sample.

As the electrolysis proceeds, its rate reduces due to polarisation effect. This could be mitigated by intermittent stoppage of electrolysis. One single run from initial filtration or distillation of the samples to counting, takes about 1000 working hours. The timings required for 1st, 2nd and 3rd stages of electrolysis are about 500, 350 and 150 hours respectively.

In view of the inordinately long duration of processing, five samples are taken as a single set. The required cells are connected in parallel. Fig. 2.7 gives the schematic of sequential processing procedure.

2.6 Safety Precautions

As the electrolysis proceeds, the liberated hydrogen, if not removed to outside atmosphere, is likely to reach its explosive threshold of 4% in the freezer chamber. This necessitates its removal to ensure safety.

Initially, an outlet from the rubber cork leading to outside atmosphere was provided. However there existed a possibility of leakage through the holes provided for electrodes. In order to ascertain the
5 Samples each of volume 1000 ml

Distil or filter
Add Na₂O₂ to make 1% W/V solution

Divide in 10 cells each containing 500 ml sample. Electrolyse till volume of each cell decreases to ~ 100 ml

Pool two cells containing same sample. Distil
Add Na₂O₂ to make 1% W/V solution

5 samples of ~ 200 ml each. Electrolyse till volume of each cell decreases to ~ 40 ml.
Distil. Add Na₂O₂ to make 1% W/V solution

5 samples of ~ 40 ml each.
Electrolyse till volume of each cell decreases to ~ 10 ml. Distil

Count each sample for tritium

Fig. 2.7 Schematics of sequential processing procedure
concentration levels, samples were collected from different parts of freeze chamber and analysed for hydrogen content by gas chromatography. Hydrogen was observed to be present in the chamber with a concentration gradient, the highest concentration of about 6% being in the upper part of the chamber. This was decreased to a level below explosive threshold by purging inert nitrogen gas. However as slight variations in purging rate could result in the concentration going above explosive threshold, the following modifications were made:

1) the rubber cork was replaced by ground glass conical joint completely stopping gas leakages

2) the outlet tube of each cell was connected to a gas flow indicator. The reduction in flow was considered as an indication for either a disturbance in the electrolysis or leakage in the freezer' chamber for which immediate corrective steps have to be taken.

2.7 Tritium Counting Methodology

2.7.1 Introduction

After enrichment, the sample is used for estimation of its tritium content. Normally one of the following two methods viz, gas phase counting or liquid scintillation counting is used.
2.7.2 Gas-phase Counting:

In this method before analysis, the sample is chemically treated and converted into an organic gas like acetylene, ethane, methane etc., or hydrogen. The gas that is generated is filled into a pre-calibrated G.M. counter up to the specified pressure and counted using normal electronics. In case of conversion into hydrogen, it is mixed with a quenching gas prior to counting. Conversion into hydrogen does not require large sample volume, but its counting efficiency is low. Conversion into an organic gas needs large volume of sample but has a high counting efficiency. A major problem in this technique is that the pulse height produced by tritium betas is not significantly different from that of electronic noise of the counting set-up making it difficult to distinguish tritium pulse from the noise pulses. Further, in spite of lead shielding, cosmic ray background in G.M. counter is high. This problem is mitigated by surrounding the counter with a ring of counters connected in parallel and obtaining the anti-coincidence counts. This helps in reducing electronic noise as well.

2.7.3 Liquid Scintillation Counting (LSS)\textsuperscript{145-148}:

Scintillation, a process of converting ionising radiation energy into light photons can be accomplished in gas, liquid and solid media. In case of gases (like
xenon), due to their low density, efficiency of photon production is very low and is normally used for special purposes only. In case of solids like plastic scintillators, organic and inorganic scintillators, though density is high, the tritium betas do not penetrate into the bulk of the scintillator. Liquid scintillators provide intimate contact with tritium betas through out the volume and produce scintillations with fairly high efficiency. In view of this, the liquid scintillation counting is widely used for the estimation of tritium.

2.7.3.1 Principle of LSS

Liquid scintillator solution is a many component system consisting of primary solvent, secondary solvent, primary solute and secondary solute and is termed as scintillation "cocktail". For estimation of radioactivity present in the sample, it is mixed with appropriate scintillation cocktail. If A,B,C,D are the primary solvent, secondary solvent, primary solute and secondary solute molecules respectively, * indicates the excited state of the molecule, $\beta$ is the emitted particle and $h\nu'$ is the finally emitted light photon, then the process of absorption of energy emitted by the radiation and re-emitting the same as photon can be schematically represented as:
Depending on the nature of the sample, scintillator cocktails of different compositions are used. Some of the most commonly employed compositions use either dioxane or toluene as primary solvent with diphenyloxazole (PPO) and p-bis-2(5-phenyloxazyl)-benzene (POPOP) as primary and secondary solutes. Water has a poor miscibility with toluene-based cocktails as compared with the dioxane based ones and hence the later is preferred for water samples. However in this case water interferes with the transfer of energy from dioxane to PPO. In order to mitigate this problem, napthalene which competes with water sample in transfer of energy is added to cocktail. While the energy transferred to water molecule is lost for detection that which is transferred to napthalene is further transferred to PPO molecule.

In addition, some commercially available cocktails like instagel, instaflour etc. show wide range of adaptability with different chemical forms of samples.
and also have higher detection efficiency. In the present work all studies were carried out with commercially available cocktail viz. instagel. Liquid scintillation spectrometer Model 4530 manufactured by Packard Instruments Co. was used as the counting system.

2.7.3.2 Instagel

Instagel, a commercially available liquid scintillation cocktail manufactured by M/s Packard Instruments can accept water samples upto 100% of cocktail volume. As the volume of sample added to a fixed volume of the instagel is increased slowly it forms a clear homogenous mixture upto 10% volume of sample added. As the sample content is further increased from 10% to 30%, phase separation takes place and from 30% onwards the mixture results in gel formation. Fig 2.9 gives variation of the efficiency with percentages of water sample added to 10 ml of instagel. The counting efficiency is a little over 50% for water sample of 0.1 ml and drops to less than 20% for 10 ml water sample. Notwithstanding this, the figure of merit (efficiency x % vol.of water sample in the sample-cocktail mixture) increases up to about 40% water volume and decreases thereafter (Fig 2.10 A).
Figure 2.8 Liquid Scintillation Spectrometer (LSS)
Fig 2.9  Instagel calibration curve

Instagel volume 10 ml

- Efficiency (%) vs. Volume of sample (ml)
- Homogeneous mixture
- Phase separation
- Gel

Volume of sample (ml)
Fig 2.10A Characteristic curve - Instagel

- Figure of merit ($\text{Eff} \times \% \text{ water added}$)
- % water added

- Homogeneous mixture
- Phase separation
- Gel formation

- 0
- 10
- 20
- 30
- 40
- 50
- 200
- 400
- 600
- 800
Though the manufacturer defines figure of merit as above, it appears more appropriate to define figure of merit as a product of the volume of sample added to a fixed volume of the cocktail and corresponding counting efficiency. Fig 2.10 B gives characteristics of Instagel when figure of merit is defined in this manner. From this figure it is clear that there is increase in figure of merit of the sample with increased volume of sample added up to about 7 ml and thereafter there is no further significant increase in figure of merit. This gives the maximum volume of sample that can be added to give counting advantage.

2.7.3.3 Quenching and Methods of Quench Correction

Presence of the sample and colour changes of cocktail due to impurities in the sample and the chemicals used result in absorption of a part of the light produced in the scintillator. In the first case a part of the energy deposited by the particle is scavenged by the impurities prior to onward transmission to the solute for photon production. Further, in the presence of colouring impurities, some of the photons are absorbed by the colouring agent resulting in fewer photons for pulse production. The first effect which results in absorption of energy before production of photon is referred as chemical
Fig 2.10B Characteristic curve - 1st stage

[Graph showing the relationship between fig of merit (eff x sample vol added) and sample added (ml)]
quenching and the second type, which results in a part of energy of the photon produced being lost is referred to as colour quenching.

The net effect of quenching is the reduction in the number of photons emitted which leads to reduction in the pulse height. As can be seen from Fig 2.11, spectrum of the quenched sample will be compressed in comparison with that of the unquenched sample. Because of this general reduction in pulse height, for a given bias setting of the counting set up, a fraction of the events which would have been otherwise recorded can be lost due to quenching. In order to determine the correct amount of activity present in the sample, correction due to quenching has to be determined. Some of the widely used methods for this purpose are:

**Spike method:** After sample counting, a known amount of activity of the same nuclide is added and the counting efficiency is determined from the increase in the counting rate due to addition of known activity. In this method, the amount of standard added should be very small. Further this method has the disadvantage of being destructive in nature since the sample can not be used again for recounting.

**Channel's ratio (C.R)**: In this method, the count spectrum of the nuclide is divided into two parts. The
FIG. 2.11, UNQUENCHED / QUENCHED $\beta$ SPECTRUMS
extent of compression of the spectrum and hence response in the two regions is dependent on the amount of quenching and the ratio of the responses in the two regions is a measure of the quenching factor. Using a set of quenched standards, a calibration curve of C.R vs efficiency is determined and this is used for determining quench correction of the sample being analysed. This method may give some uncertainty in case of heavily quenched samples. Fig 2.12 gives the efficiency curve obtained using this method.

Automatic external standard channels ratio (AES): In the channels ratio (CR) method of determining quench correction, it is the pulse spectrum of the sample which is used. In case the sample does not contain a high activity, statistical variations of the sample counting would seriously affect the satisfactory determination of quench correction factor. In order to overcome this, an external gamma rays source is brought to a fixed geometry with respect to the sample. The compton electrons produced by interaction of gamma behave similar to beta particles emitted by the radionuclide and are used for channel's ratio determination. The sample is counted both in the presence and absence of the source to determine the contribution due to source alone. The ratio of this in the two channels, as in the
Fig 2.12  L.S.S. calibration curve
(sealed tritium standards)
case of C.R. method, is used to determine quenching. As in previous method, a calibration curve is constructed with the help of a set of quenched standards and is then used for determining counting efficiency for sample (Fig 2.13).

In the LSS used for the present studies provision exists for quench corrections by both CR and AES methods. In AES method the gamma source used is a 10 uCi $^{226}$Ra source. The quench correction parameters for both the methods are computed by the spectrometer after scanning the entire spectrum due to sample and are referred to SIS (i.e. spectral index of sample) and SIE (i.e. spectral index of external source) respectively. Tritium calibration curves are given in Figs 2.12 and 2.13. Fig 2.14 gives variation of efficiency with SIE for different volumes of sample added to 10 ml of Instagel. Abrupt variation of efficiency in lower efficiency values could be due to phase separation.

2.7.4 Detection System

The block diagram of the detector assembly is shown in Fig. 2.15. The scintillations produced in the cocktail are viewed by two photomultiplier tubes connected in coincidence. The pulses from the two photomultipliers arriving at coincidence gate within 20 nano seconds are passed as coincidence pulses and are
Fig 2.13  L.S.S. calibration curve

(sealed tritium standards)
Fig 2.14 L.S.S. calibration curve
(Different sample vol in 10ml Instagel)
FIG. 2.15. BLOCK DIAGRAM OF COUNTING SET UP
recorded as detection of a beta particle. For spectral analysis, the coincidence pulses are fed to a summing gate amplifier where the two co-incidence pulses are summed up. Depending on the spatial distribution of scintillations produced, their individual contribution at the two photo cathodes can vary, but their sum is nearly proportional to the energy of the particle responsible for its production. The output of the summing gate amplifier is recorded as in a normal multi channel analyser (Fig 2.16). Some of the characteristics of the LSS used are given in Figs. 2.12, 2.13 and 2.14.

2.7.5 Inter-comparision of IAEA Samples

To establish the reliability of the method for $^{3}$H analysis of low concentration samples an inter-comparision of low level tritium measurement was undertaken by I.A.E.A. under it's "inter-comparision of low level tritium measurement in water-programme 1986". For this IAEA had included 88 institutions from different parts of the world. Each institution was supplied with four samples in the range < 5 TU, 5-20 TU, 20-50 TU and 50-200 TU. After standardisation of the system, the samples were enriched and analysed for their tritium content, and the results were sent to IAEA. Using method of successive iteration IAEA arrived at the average value of the samples within ±2 standard deviation. From the results it is observed that our
FIG. 2.16. SUMMATION CIRCUIT.
results consistently over-estimate the activities by about 30% as compared to IAEA average. This could be due to difference in the primary/secondary standard used by us for calibration, background countrate determination and variation in institutional average which will reflect on the IAEA average value etc. However one should keep in mind that though this overestimate will reflect on individual values but will not reflect on trend of variations.

2.7.6 Determination of True Background

The major contribution to background comes from cosmic rays and a relatively small component is due to electronic noise of LSS and the radioactivity of counting vial material. Electronic noise can be determined by counting without loading the vial. Combined noise and material activity of the vial can be determined by loading an empty vial. Counting with vial containing only liquid scintillation cocktail gives total background due to all the three. But this does not give the true working background for the sample, since the sample addition causes quenching, resulting in decreased counts. Normally true background is determined by counting vial containing scintillation cocktail and same volume of distilled water as that of sample.
For the studies undertaken, the true background was determined using tritium-free spring water received from Hungary (courtesy Ms Fodor P Canyi, Evotvos University, Budapest, Hungary). The sample was distilled and counted both before and after enrichment. As no tritium was present in the sample, both enriched and direct samples gave same count rates.

Determination of background was repeated using distilled tap water, when distillation avoids water contamination due to dissolved salts. The count rate due to this was same as that obtained from tritium-free sample. Table 2.4 gives the counting results of the

Table 2.4

<table>
<thead>
<tr>
<th>Sample</th>
<th>counts/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass distilled water</td>
<td>16.83±0.41</td>
</tr>
<tr>
<td>Glass distilled tritium-free spring water</td>
<td>17.44±0.42</td>
</tr>
<tr>
<td>Enriched tritium-free spring water</td>
<td>17.65±0.42</td>
</tr>
</tbody>
</table>

distilled tap water and the tritium-free spring water. This is obvious as the tritium content of ordinary distilled water is much below the detection limit of the counting set-up. Thereafter distilled tap water was used for background determination.