IMPROVEMENT OF TRITIUM ENRICHMENT ELECTROLYSIS CELL FOR ENVIRONMENTAL MONITORING

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INTRODUCTION

The measurement of Tritium in environmental water sample has being carried out for the monitoring of the contaminated level by effluent from the atomic institution and the investigation in geochemistry, e.g. streams of water under ground. These measurements have need of the pre-concentration of HTO by any method. In recent years, some methods have been discussed for these purposes, e.g. electrolysis and thermal diffusion. In these methods, the electrolysis has been employed generally, because of compact apparatus, easy handling and possibility of certaion results.

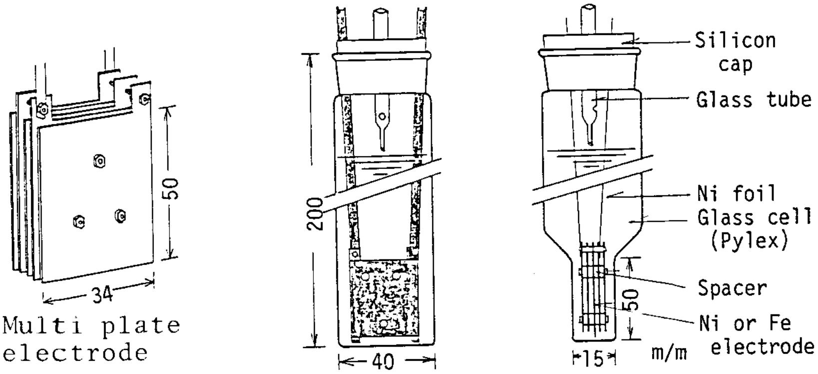
Where, on the pre-concentration, more correct data of Tritium activities can be gotten by using large volume of water sample. But, it requires a long time and large electric energy. Up to this time, one pair of slender electrodes made of materials of nickel or iron has been employed. However, for such electrodes, the re-adjustment of electric current should be made to make itself agreeable to change of the electrode surface area in sample water, because of decrease of effective surface area of electrode, as reduces gradually by electrolysis.

In this study, the electrolysis glass cell of its volume 100 ml inserted multi plate electrode was designed and produced, and, its characteristics for concentration of HTO and conditions of procedure e.g. required electric current density and time for electrolysis, were clarified.

EXPERIMENTAL

1. Apparatus and procedure for pre-concentration

As illustrated in Fig. 1, as for the electrolysis cell, the bottom of cylindrical hard glass vessel which was dismeter of 40 mm and length of 200 mm was formed into rectangular shape (size ; 50 mmH x 40 mmW x 15 mmD). And the multi plate electrode consisting of five plates (size ; 50 mmH x 35 mmW, thickness; 1.0 mm, combination of nickel and iron) were set in the part. The effective total area of the electrode was about 60∿62 cm^2.



Multi plate electrode

Electrolysis glass cell

Fig. 1 Diagram of electrode and electrolysis cell

The experiments were carried out setting five cells connected in the electric circuit into the controlled low temperature water bath (2∿5°C). The individual cell held the sample water of 100 ml. The sample water in each cell decreased to about 15 ml by electrolysis of current density between 50∿280 mA/cm^2.

2. Measurement of Tritium and calculation of recovery rate

The experiments on pre-concentration efficiency were carried out using slightly activity Tritium solution (3 x 10^{-3}μCi/ml). Samples of 8.0 ml before and after electrolysis were pipetted out and infused into 20 ml vials with liquid scintillator Triton-100X (Packard Co., Ltd.)12 ml. Radioactivities of each vial were counted using low back ground liquid scintillation counter TRI-CARB 3255 type (back ground; 10 cpm, counting efficiency; 25%). Recovery percent (R) of HTO are calculated with next formula.

$$R\ (\%) = (Cf \times Vf) \times 100 \,/\, (Ci \times Vi) \qquad (1)$$

where, Ci and Cf ; radioactivities of Tritium before anf after electrolysis, Vi and Vf ; volume of sample water before and after electrolysis.

RESULT AND DISCUSSION

1. Decreasing rate of sample water by electrolysis

If electro-chemical change of electro-materials is disregarded, decreasing rate of sample water by electrolysis are calculated from total electric current used with Faraday's constant.

The solid lines in Fig. 2 show the decreasing rate in the range of 80∿280 mA/cm^2 in current density. When water volume decrease to 26 ml, the top of electrode appears on the surface of sample water. Therefore, the electric current must be re-adjusted in a few hours to responded value according to electrode surface area under water. Therefore, decreasing rates of sample water is slightly late.

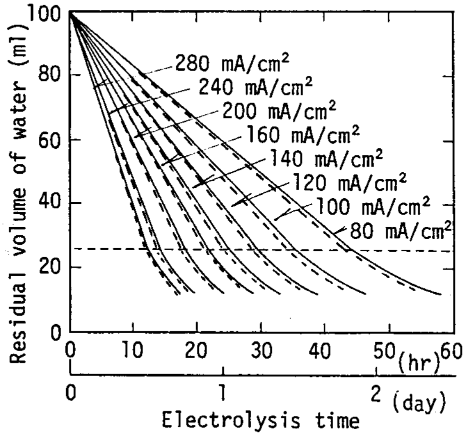


Fig. 2 Decreasing of sample water by electrolysis

The required time to decrease the sample water from 100 ml to 15 ml by electrolysis is 16∿57 hours with above current density range. Under the higher current density, the required time is shorter. But, as show in the next clause, the higher current density, being the more loss of HTO. Then, for the purpose of measurement with a high accuracy, it needs the definite knowledge to divide the time to pre-concentrate HTO and to count the Tritium activities。

While, broken lines shown in Fig. 2 are decreasing rates of sample water obtained experimentally. These rates are more rapid than that obtained by calculation, because of loss of sample water yield in electrolysis by volatilization.

2. Correlation of Tritium recovery and current density

It has been reported that the optimum current density on the electrolysis concentration was 100 mA/cm^2. The value was determined by experimental results using one pair electrode cell of cathode and anode。

Then, correlations of recovery rate of Tritium and current density used multi plate electrode cell are different with a kind of electrode materials as shown in Fig。3. The recovery rate is higher in range 60 100 mA/cm^2 used Ni-Ni electrode. But, the range is wider of 60∿140 mA/cm^2 used Fe-Fe electrode. Still, in the range of current density over 100 mA/cm^2, the rate using of Ni-Ni is lower. The other hand, the rate using Fe-Fe is not down.

Turning the attention only to recovery rate of HTO, employing Fe-Fe electrode leads to more effective than Ni-Ni. But, if employ iron plate as anode, its defect is more corrosionable. Using nickel plate as cathode and iron plate as anode, the level of HTO recovery is intermediate of those values of Ni-Ni and Fe-Fe.

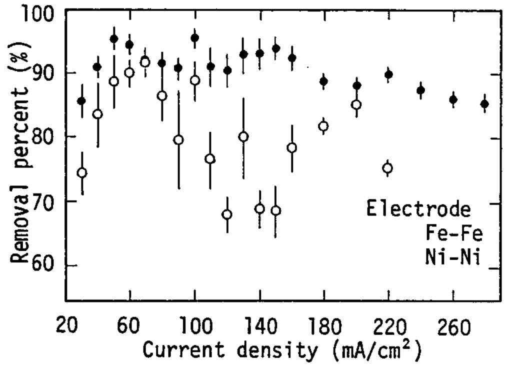


Fig. 3 Removal rate of HTO

While, as comparison of a kind of materials, the recovery percentages at the next conditions, current density ; 180 mA/cm^2, low temperature water bath ; 2 °C, shown in Table 1 .

Table 1 Tritium recovery rate by electrode of Fe-Fe, Fe-Ni, Ni-Ni

	Electrode Fe-Fe	Fe-Ni	Ni-Ni
Tritium recovery (%)	90	85	75

3. Required time for Tritium measurement

On the measurement of Tritium activities, required total time is consistent for 1) Pre-treatment (e.g. oxidation of organic substance in sample and evaporation etc.), 2) Pre-concentration of HTO, 3) Counting of Tritium activity.

In above three terms, 1) is same in any sample and measurement condition. 2) and 3) are different with following conditions, that activity level of sample, counting conditions (e.g. counting efficiency and back ground level etc.), pre-concentration effect (recovery and concentration rates of HTO etc.), and expected level of precision of data. Therefore, at the conditions of measurement that expected precision levels as expressed in fomula (2) are ±10% or ±20%, Tritium concentration levels about 10, 20, 50 and 100 pCi/l in samples and using liquid scintillation counter mentioned at experimental term, the required total time to pre-concentrate and count of the sample were calculated as shown in Fig. 4 .

$$\{(Ns/t)+(Nb/t')\}^{1/2} \times 100 \Big/ [\{(Ns \pm \sqrt{Ns})/t\} - \{(Nb \pm \sqrt{Nb})/t'\}] = 10 \text{ or } 20 \qquad (2)$$

where, Ns and Nb ; counts of sample and back ground, t and t' ; counting time of those.

Solid lines shown in Fig. 4 are required time for pre-concentration of HTO.

As a result, for the sample of higher Tritium level and the higher permissible level of statiatial error, it needs longer time to pre-concentrate than that to count. As a concrete example, setting up the current density of 180 mA/cm^2 and expected precision level of ±10% for Tritium level in the low sample of 10 pCi/l , it needs for 20 and 10 hours to pre-concentrate and count.

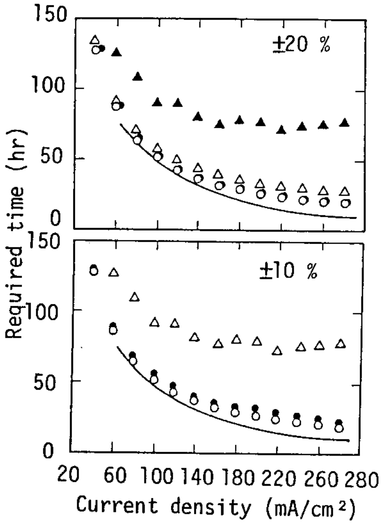


Fig. 4 Required time to pre-concentrate and count

Tritium activity level(pCi/l)
▲ 10, △ 20, • 50, ○ 100

CONCLUSION

On HTO pre-concentration, following results were obtained using multi plate electrode with effective surface area 60~62 cm^2 and sample capacity 100 ml cell. 1) At the condition of current density 60~140 mA/cm^2, recovery rates were more than 90% using Fe-Fe electrode, 2) Fe-Ni electrode are more corrosion-resistant, but HTO recovery rates are lower, 3) In the following conditions of the measurement with precision level of ±10% for low level Tritium sample as 10 pCi/l and current density of 180 mA/cm^2 , the required time to pre-concentrate and to count are 20 and 10 hours.