6. COMMENTS ON METHODOLOGY OF EXCESS TRITIUM DETERMINATION

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ABSTRACT

Three methods of tritium data analysis are considered—comparison between experimental and theoretical data, total mass balance and curve-fitting.

1.0 INTRODUCTION

The evidence for tritium production in electrochemical cells, with few exceptions (Will *et al, 1992)*, is based on measurements of tritium increase in the electrolyte phase in excess of that predicted from the isotopic separation factor. Often, this enrichment was con1puted under conditions of constant electrolyte volume which, in turn, implies continuous additions and withdrawals, a somewhat unrealistic undertaking. In those instances where the total tritium content at the end of an experiment was ten times or more greater than what was present in the beginning, it cannot be disputed that generation of tritium occurred. However, for low levels of tritium production, care must be taken in the analysis, especially if open cells are used. In this communication, we comment on the methodologies of analysis used and point out their advantages and disadvantages.

2.0 USE OF SIMULATED DATA TO EVALUATE METHODS OF TRITIUM ANALYSIS

To evaluate the methods of analyzing tritium, we needed data that would show various degrees of tritium production and include measurements of both the electrolyte and gaseous phases over a fairly long period of time. In addition there could be no question of contamination of tritium from the cell, cell components or outside environment or of erroneous tritium measurements resulting from chemical reactions in the scintillator fluid. To meet all of these requirements, it was deemed necessary to use simulated data.

2.1 Development of Model

In an open cell, a volume of electrolyte, *V*, is electrolyzed. Throughout the experiment, electrolyte is being wit hdrawn for tritium analysis and is being replaced. Assuming sampling is instantaneous. for any given time the rate of change of tritium in the electrolyte, $\frac{dT_L}{dt}$; on the recombining electrode, $\frac{dT_R}{dt}$ and in the gas phase, $\frac{dT_G}{dt}$, are given by:

$$\frac{dT_L}{dt} = -\zeta(f_L m_L)\phi - \alpha(f_L m_L) + C \tag{1}$$

$$\frac{dT_R}{dt} = \zeta(f_L m_L)\phi - \alpha(f_R m_R) - \zeta_R(f_R m_R) \tag{2}$$

$$\frac{dT_G}{dt} = \zeta_R(f_R m_R) - \alpha(f_R m_R) \tag{3}$$

where ξ and ξ_R are the isotopic enrichment factor for tritium during electrolysis and on the recombining electrode. respectively; α and C are the radioactive decay rate and generation rate of tritium. respectively. both are in *atoms sec*[-1]; f_L and f_R are the mass fraction of tritium in the electrolyte and on the recombiner, respectively; and $\phi = \dfrac{ieM_{D_2O}}{2F}$ where MD_2O is the molecular weight of D_2O *and ε* is the Faradaic efficiency. In this model the amount of D/T absorbed/desorbed by the *Pd*-electrode and losses due to evaporation are not considered. Using these differential equations. simulated data for tritium in the gas and liquid phases were calculated under conditions of no production, low continuous production. continuous production near the end of an experiment. and pulse production. In constructing these data sets, the total volume was fixed at 50 ml; $\xi = 1.8$: $\xi_R = 1.0$, which corresponds to 100% efficiency of the recombiner; $\alpha = 250$ *atoms sec*[-1]; and Gaussian noise, with a. 1% standard deviation, was superimposed on the calculated values. The simulated data for zero and pulse production are shown in Figure 1.
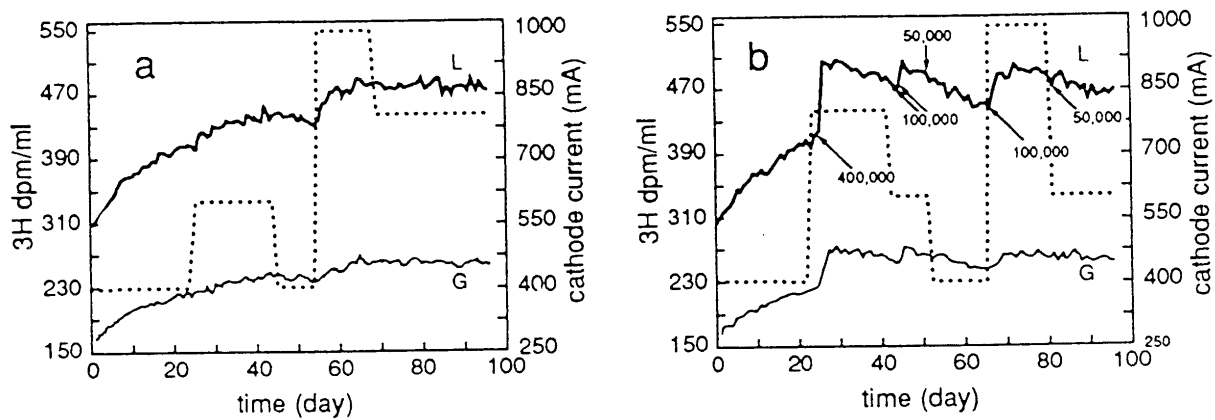
Figure 1. Simulated data for (a) zero tritium production and (b) pulse tritium production. Solid lines are the liquid, L, and gas, G, phase tritium measurements and dotted lines represent the cathodic current profile. Tritium production bursts, in atmos sec-1, are indicated.

3.0   EXPERIMENTAL METHODS OF ANALYSIS

The methods of analysis fall into three general categories. In one method, samples of the gas and liquid are taken, the tritium content is measured and compared with the theoretical value. The second method is one of total mass balance. The third method utilizes curve-fitting.

3.1   Method 1: Comparison of Experimental and Theoretical Values

Usually theoretical values for the liquid and gas phases are calculated using the expression derived by Bockris et *al.* (*Lin et al*, 1990):

$$\frac{a(t)}{a(0)} = \zeta - (\zeta - 1)\exp\left(\frac{-ti}{2F\zeta nV}\right) \qquad (4)$$

where $a(0)$ and $a(t)$ *are* the activity of tritium initially and at time t, respectively, and n is the concentration of D_2O. Equation (4) assumes a constant current, i, and that the number of deuterium atoms far exceeds the number of tritium atoms. It also assumes a constant volume, V; *i.e.*, after electrolysis for a given time period, D_2O is added to restore the volume prior to sampling. The differential equations (1)–(3) were solved for this experimental procedure to yield data sets under the conditions of no tritium production, $i = 0.4A$, $\xi = 1.8$, $V = 50ml$, $a(0) = 300$ *dpm ml*[-1] and no Gaussian noise on the data.

These data sets were compared to the *a(t)* values calculated using Eqn. (4). Without correcting for sampling, the data agree well with one another for about one week. Afterwards, the values calculated using Eqn. (4) are much higher. When sampling is included, there is good agreement up to the one month period at which time the values calculated using Eqn. (4) were again larger.

3.2   Method 2: Total Mass Balance

In this approach, for a given time interval, the total amount of tritium in the beginning is compared to the total amount in the liquid and gas phases at the end. For the zero production case, the difference between the amount of tritium at the end and the beginning of a time interval (Δ), followed a Gaussian distribution with Δ's evenly divided between positive and negative σ's. In the cases of tritium production, *i.e.*, low continuous production, pulse production and production at the end, the overall distribution of Δ's was not Gaussian and was skewed towards more positive σ's. This skewing towards more positive 's clearly indicates that tritium was produced.

3.3   Method 3: Curve-fitting

If the initial mass of deuterium and tritium, $m(0)$, is electrolyzed at a constant cell current, i, for a specified period of time, τ, at which time a sample is withdrawn and analyzed for tritium and D_2O is added to restore the initial volume. The tritium mass fraction in the electrolyte, fL(t), is given by:

$$f_L(t) = [m(0) - \tau(i)t]^{\xi-1}\left[\frac{f_L(0)}{m(0)^{\xi-1}} + \int_{t=0}^{\tau}\frac{Cdt}{[m(0) - \tau(i)t]^{\xi}}\right] \qquad (5)$$

where $\tau(i)$ is the rate of removal due to electrolysis. Equation (5) is a general solution of the differential equations (1)-(3) and neglects the radioactive decay and loss by evaporation. As written, Eqn. (5) has two adjustable parameters which will be strongly coupled to one another—the isotopic separation factor, ξ, and the tritium generation rate, C. The simulated data for all four cases were computer analyzed using Eqn. (5). In the zero tritium and low continuous production cases, there was excellent agreement between the data and the computer analyzed curves. However, the computer analyzed curves did not agree with the remaining two cases especially in the regions where the tritium production occurred.

4.0   CONCLUSIONS

All three methods discussed for analyzing tritium data require 100% efficiency of the recombining electrode. Efficiencies less than 100% result in a preferential loss of *DT* over D_2 in the gas phase. The technique advocated by Bockris and others, that of comparing the measured tritium values with those calculated using Eqn. (4), is valid for short term experiments. This approach requires that the isotopic separation factor, ξ be known. For the *Pd/D* system, ξ's ranging from 2 to 10 have been reported. Furthermore, it is assumed that ξ remains constant throughout the course of the experiment. This assumption may not be valid since ξ depends upon the kinetics of the system as well as the current density. With the technique of total mass balance, ξ need not be known nor is it required to remain constant. Likewise with curve-fitting, one does not need to know the value of ξ, but ξ is assumed to be constant. Therefore, when the experimental and computer analyzed curves don't agree, it is not known if ξ was affected or if tritium production occurred. However, curve-fitting does indicate that something happened during the course of the experiment. The total mass balance and curve-fitting approaches require long term experiments in order to achieve a statistically significant analysis. Of the three techniques, curve-fitting is the least sensitive to detecting burst production of tritium.

5.0   References

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