

# ELECTROLYTIC TRITIUM ENRICHMENT OF NATURAL WATER SAMPLES FOR TRITIUM ANALYSIS

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**ABSTRACT.** Electrolytic tritium ( $^3\text{H}$ ) enrichment in a batch process has proved to be suitable for low-level  $^3\text{H}$  determination. However, all available electrolysis systems have a reproducibility error (3–6%), which limits greatly the accuracy of the total measurement process and, thus, the scale of possible hydrogeological conclusions. These fluctuations are caused by  $^3\text{H}$  losses from incomplete isotopic separation in the cathodic processes and evaporation. Several electrolysis systems show the development of the cathodes' capacity to catalyze the isotopic exchange reaction,  $^1\text{H}^3\text{H} + ^1\text{H}_2\text{O} \rightleftharpoons ^1\text{H}_2 + ^1\text{H}^3\text{HO}$ , to be the essential parameter for developing separation factors and their fluctuations. Extremely high separation factors are made possible by the consecutive reaction sequence of the cathodic processes and the isotope exchange reaction. A further improvement of enrichment accuracy can be reached by an efficient technique to reduce evaporation.

## INTRODUCTION

The cosmogenic-technogenic radionuclide, tritium ( $^3\text{H}$ ), is widely used to study hydrogeological behavior. As part of the water molecule,  $^3\text{H}$  is an ideal tracer. The  $^3\text{H}$  method was established when nuclear bomb testing strongly increased  $^3\text{H}$  concentration in precipitation, so that it was comparatively easy to detect. Since the nuclear test ban treaty (1963),  $^3\text{H}$  concentration in precipitation has been declining. Thus, the enrichment of  $^3\text{H}$  in a water sample prior to radiometric measurement has become necessary for most hydrogeological applications since the 1970s.

## MEASUREMENT METHODS FOR TRITIUM

The classical method of determining the natural  $^3\text{H}$  content in water is measurement in a proportional counter tube after inclusion of the sample hydrogen into a suitable counter gas. The sensitivity of this method is such that the  $^3\text{H}$  content in the water sample can still be determined directly (*i.e.*, without enrichment) for many hydrogeological problems in central Europe (Fig. 1). Disadvantages include time-consuming preparation and low throughput.

In tandem with preliminary  $^3\text{H}$  enrichment, the liquid scintillation counting (LSC) technique has proven to be a method of high-performance measurement for natural  $^3\text{H}$  concentrations. Major advantages are simple sample preparation and cyclical measurement; the resulting optimization of measurement time per sample promotes increased throughput.

However, LSC cannot be used to measure natural  $^3\text{H}$  levels without preliminary enrichment of  $^3\text{H}$  in the sample (Fig. 1). In spite of its much higher sensitivity, the mass spectrographic  $^3\text{H}$  measurement determining its decay product,  $^3\text{He}$ , is not available for widespread application in hydrogeology.

Given the declining differentiation of  $^3\text{H}$  concentrations in groundwater, better measurement accuracy is needed to obtain hydrogeological information in the future. Error analysis has shown that, for young groundwater ( $0.1\text{--}3 \text{ Bq kg}^{-1}$ ), the main source of error is the  $^3\text{H}$  enrichment process (Morgenstern 1992). Thus, improved overall accuracy can be achieved only by improving the precision of  $^3\text{H}$  enrichment.

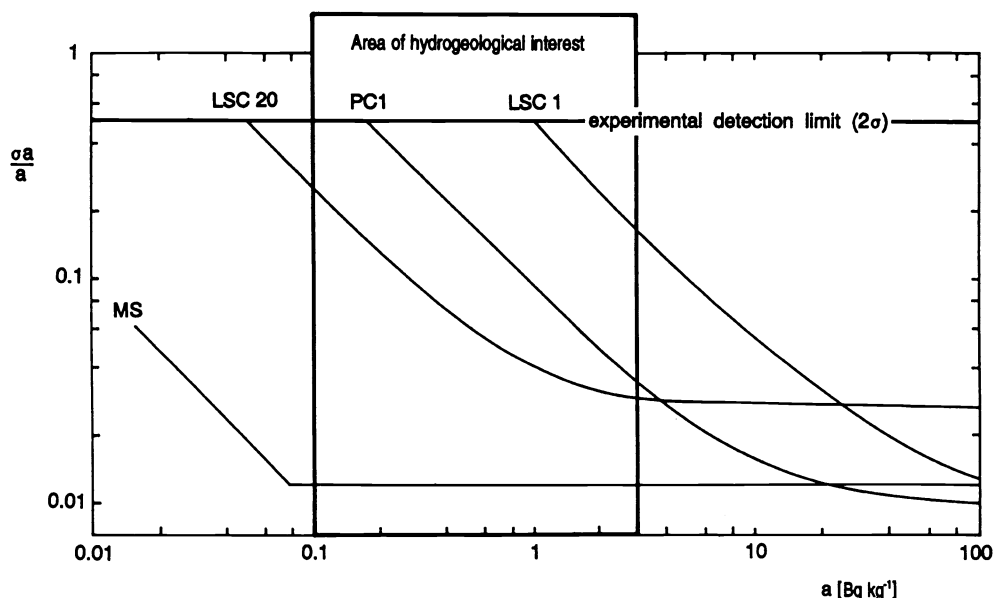


Fig. 1. Relative measurement error of specific  $^3\text{H}$  activity,  $a$  (2 standard deviations ( $2\sigma$ )); PC = gas proportional counter (Wolf, Rauer & Weigel 1981); LSC = liquid scintillation counter (Laboratory of Natural Radionuclides, Bergakademie Freiberg); MS =  $^3\text{He}$  ingrowth method (Jenkins 1981). Enrichment factor  $A = 1-20$ .

## ELECTROLYTIC TRITIUM ENRICHMENT IN A BATCH PROCESS

### Enrichment Systems

To increase  $^3\text{H}$  sensitivity for a given detector volume, the low  $^3\text{H}$  concentration of natural waters must be enriched in a prescribed, reproducible way designed to reduce protium ( $^1\text{H}$ ) highly preferentially to  $^3\text{H}$  atoms. The isotopic effects used for this isotope separation are based on the high relative mass differences between  $^1\text{H}$  and  $^3\text{H}$ , and resulting differences in physical and chemical properties that lead to an isotopic concentration shift between phases 1 and 2 according to

$$\beta = \frac{(^3\text{H}/^1\text{H})_1}{(^3\text{H}/^1\text{H})_2}$$

with the isotope separation factor,  $\beta$ . In terms of  $^3\text{H}$  retention and routine safety, we found the electrolytic decomposition of water was particularly suitable for the preferential reduction of  $^1\text{H}$  in large samples, compared to  $^3\text{H}$ . Other methods, such as gas chromatographic or thermodiffusive enrichment (Roether 1981; Roether & Weiss 1981), were not introduced in spite of their high  $^3\text{H}$  retention and enrichment factor.

The fourth IAEA measurement survey of low-level  $^3\text{H}$  laboratories in 1985 (Hut 1986) showed that 82% of the 66 participating laboratories enrich the sample  $^3\text{H}$  before the radiometric measurement; they use water electrolysis exclusively for routine operations. The most common cell type (48%) is the so-called IAEA type (Cameron 1967) with iron cathodes, stainless steel anodes and NaOH as electrolyte.

Östlund (1977) and Taylor (1977) discussed several possible types of electrolysis cells. At present, the batch cell is used predominantly because of its relatively simple and robust operation and high

$^3\text{H}$  retention. In these cells, the entire initial amount of water is decomposed continuously. The reduction in volume and, thus, the maximum attainable enrichment, is restricted by a limited concentration range of the electrolyte in the batch process. One can achieve volume reductions by a factor of 30 for most electrode materials without electrode corrosion, electrolyte saturation and increased ohmic losses.

Although electrolytic  $^3\text{H}$  enrichment is used widely, the mechanism of preferential  $^1\text{H}$  deposition at the cathode is not completely clear. This leads to variations of enrichment parameters both within one electrolytic system and between different electrolytic systems, resulting in high reproducibility errors of 3–6% (e.g., Hut 1986). For example, the  $^3\text{H}/^1\text{H}$  separation factors not corrected for vapor losses vary from 8–46 (Cameron 1967; Theodórsson 1974; Taylor 1977; Östlund 1977; Florkowski & Grabczak 1977; Florkowski 1981; Inoue & Tanaka-Miyamoto 1987). To avoid long series of experiments, most laboratories use well-established electrolytic systems; thus, the literature on the parameters influencing the electrolysis process is sparse. Until now, we have not established which of these parameters exerts the decisive influence on the separation factor.

According to Taylor (1977),  $^3\text{H}$  enrichment,  $A$ , is

$$A = \frac{c_f}{c_i} = \left( \frac{m_i}{m_f} \right)^{[r_E(1 - 1/\beta) - r_v(1-1/\beta_v)]} \quad (1)$$

where

$c_i/c_f$  = initial/final  $^3\text{H}$  concentration in the electrolyte

$m_i/m_f$  = initial/final mass of electrolyte

$r_E/r_v$  = rate of electrolysis/evaporation of the total water loss

$\beta/\beta_v$  = isotopic separation factor of cathodic processes/evaporation.

According to Morgenstern (1992), the reproducibility errors during the electrolysis process are caused by  $^3\text{H}$  losses due to incomplete isotope separation of the cathodic processes

$$L_s = 1 - \left( \frac{m_i}{m_f} \right)^{-1/\beta} \quad (2)$$

and  $^3\text{H}$  losses by evaporation

$$L_v = 1 - \left( \frac{m_i}{m_f} \right)^{-r_v/\beta_v} \quad (3)$$

These differ from run to run and from cell to cell. Thus, to improve the reproducibility of  $^3\text{H}$  enrichment, we need to find electrolysis parameters that guarantee minimum  $^3\text{H}$  losses and, thus, minimum fluctuations.

### $^3\text{H}$ Loss Due to Incomplete Isotopic Separation of Cathodic Processes (Separation Loss)

Because water decomposition is linked to a high isotopic separation factor, its fraction,  $r_E$ , of the total water loss should be as high as possible (usual systems = 97–99%). To minimize the separation loss,  $L_s$ , of  $^3\text{H}$  (usual systems = 6–30%), we must be able to guarantee a high isotopic separation factor of the cathodic processes.

Until recently, most researchers assumed that the isotopic factor is influenced only by electrochemical parameters, such as overvoltage, current density and the type of hydrogen recombination at the cathode. However, Morgenstern (1992) showed that these electrochemical conditions are constant for suitable electrode materials and electrolyte concentrations, and thus, cannot change isotopic separation behavior. Apart from this, we observe spontaneous changes of the separation factor, independent of electrochemical processes.

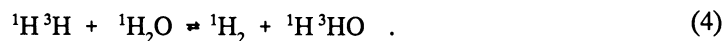
To obtain a good isotopic separation factor, the cathode must have a pronounced porous surface. The impact of the surface condition becomes obvious if the separation factor of iron cathodes is observed during the start-up period (formation of a porous surface), under otherwise unchanged electrochemical conditions. Table 1 demonstrates the increase of the separation factor of several IAEA-type electrolysis systems.

TABLE 1. Increased Separation Factor ( $\beta_1, \beta_i$  - First/ith Run) During Formation of a Porous Cathode Surface

System/author	Cell	No. of runs i	$\beta_1$	$\beta_i$	$\beta_i/\beta_1$
Florkowski (1981)	11	19	14	50	3.6
	13	15	13	37	2.9
	14	15	11	29	2.7
	Big	12	10	28	2.9
Taylor (1977)	1	16	12	29	2.4
	2	12	10	29	2.9
	18	11	12	29	2.4
TriCarLab BA	18	12	9	38	4.2
Freiberg (1988)	26	13	8	33	4.3

The separation factor increased 2–4 times due to the formation of a porous layer in the first few runs. The fact that the separation factor increases many times with increasing porosity of the cathode surface justifies the assumption that an isotopic exchange reaction is catalyzed by the cathode surface activity, which increases with porosity.

Molecular hydrogen in contact with water undergoes isotopic exchange according to



The equilibrium separation factor  $\beta_1$  of this reaction at 2°C is 8.5 (Fiek, Romaker & Schindewolf 1980). However, equilibration requires several days at this temperature, and has no noticeable impact on the overall separation factor of electrolytic water decomposition. On the other hand, suitable metals (Pd, Pt, Fe, Ni) can be employed to catalyze reaction (Eq. 4), so that equilibrium occurs within a few minutes (Buttlar, Vielstich & Barth 1963).

The potential catalysts are the same metals that provide high separation factors; thus, the increased separation factor with high porosity can be interpreted to mean that the related increase of the cathode's activity leads to more effective catalysis of the isotope exchange reaction (Eq. 4). The higher the activity of the cathode for the reaction, the closer the isotope rate between gas and water approaches the equilibrium value.

With iron, the formation of this active layer leads to an enormous increase of the separation factor (see below). In contrast, this effect lacks with nickel because of the absence of such a catalytically active layer.

The great increase of the separation factor during the formation of the porous cathode surface occurs by combining the isotope exchange reaction (Eq. 4) with all preceding isotopic effects in a consecutive reaction sequence. If the separation factor of cathodic hydrogen deposition is  $\beta_c = c_l/c_{g,ab}$ , and that of the catalytic isotopic exchange is  $\beta_i = c_{g,ab}/c_g$ , the overall separation factor of the consecutive reactions is

$$\beta = \frac{c_l}{c_g} = \beta_c \times \beta_i \quad (5)$$

where

$c_l$  = <sup>3</sup>H content in the electrolyte

$c_{g,ab}$  = <sup>3</sup>H content in the H<sub>2</sub> molecules absorbed at the cathode

$c_g$  = <sup>3</sup>H content in the hydrogen gas additionally depleted in <sup>3</sup>H by the isotopic exchange.

Thus, the separation factor of the entire electrolysis increases by the factor,  $\beta_i$ , depending on the efficiency of the catalytic isotopic exchange. This allows very large separation factors for electrodes fulfilling the above electrochemical and catalytic conditions. Table 2 illustrates the increased isotopic separation factor and the related reduction of separation losses.

TABLE 2. Electrolysis conditions and enrichment parameters of the electrolysis system of the Laboratory of Natural Radionuclides, Bergakademie Freiberg. The values are averages of 12 IAEA-type cells. Cathode: mild steel; anode: stainless steel; initial electrolyte (NaOH) concentration: 0.32%; current: 8 A; cell filling degree: 85%; cooling bath temperature: 12°C; cathode cleaning: warm water rinsing.

Year	Electrolysis no.	$m_i$ (g)	$m_f$ (g)	$\beta$	$L_s$ (%)	$L_v$ (%)
1980	2	249	22.6	12.1	18.0	0.5
1985	92	249	10.2	31.3	9.7	3
1988	165	249	9.7	39.8	7.8	4
1991	234/236	249	10.6	68.5	4.5	4

Figure 2 shows the electrolytic enrichment parameter,  $1-1/\beta$ , which is increased by the greater separation factor, together with the reduced reproducibility error,  $\sigma(1-1/\beta)$ . Here, it is intriguing that the enrichment behavior of the cell set improves over an 11-yr interval. This also means improved enrichment reproducibility, even though some of the cathodes required replacement (average replacement: 1 cathode in the set of 12 cells in 2 yr) and thus, have not yet reached a high separation factor.

### <sup>3</sup>H Loss Due to Evaporation (Vapor Loss)

Cathodes with a high isotopic exchange activity develop such high separation factors that isotopic separation by cathodic processes is almost complete. This means that the fraction of the vapor loss increases in the remaining overall <sup>3</sup>H loss. Table 2 shows that for extremely high separation factors ( $\beta \sim 70$ ), about one-half of the remaining <sup>3</sup>H loss is caused by evaporation.

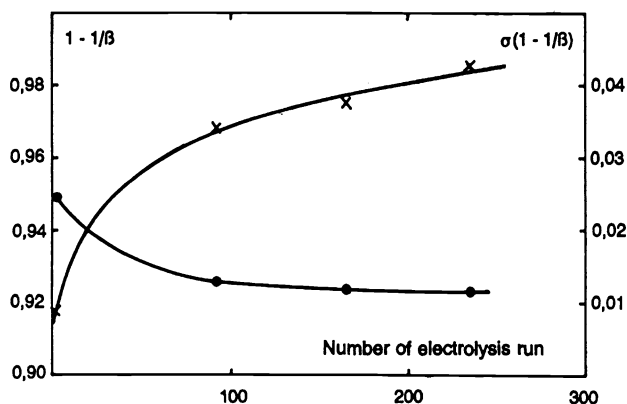


Fig. 2. Enrichment parameter,  $1 - 1/\beta$  (x), and reproducibility error,  $\sigma(1 - 1/\beta)$  (o)

To further increase the reproducibility of  $^3\text{H}$  enrichment, this component of  $^3\text{H}$  loss must also be minimized. In a test run, the reduction of the cell temperature to almost  $0^\circ\text{C}$  proved sufficient to reduce the vapor losses to 0.4 of the initial value, equivalent to a reduction of the enrichment error to 0.6.

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