

**Procedure for determining the tritium activity
concentration in surface water
following electrolytic enrichment**

C-H-3-OWASS-02

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1 Scope

The tritium activity concentrations in German surface water bodies noted in the early 1990's largely range below the detection limit of $10 \text{ Bq}\cdot\text{l}^{-1}$ demanded by the routine monitoring programme for the StrVG (1). Determining such low tritium activity concentrations via direct measurements (see procedure C-H-3-OWASS-01) is only possible by accepting high counting uncertainties.

For the purpose of radio-ecological studies, measuring dispersions as well as recording long-term trends, the sensitivity of tritium measurements can be substantially increased by enriching this nuclide in the water sample with electrolytic means prior to the actual measurement (2 – 7). This will decrease the decision threshold, $g_{\text{H-3}}^*$, by a factor of up to about 25 compared to the direct measurement, so that this procedure will facilitate detection of tritium activity concentrations of as little as ca. $0,2 \text{ Bq}\cdot\text{l}^{-1}$. However, considering the low radiotoxicity of this nuclide and the substantial technical effort required to reach decision thresholds as low as this, there are no radiological reasons for effecting this procedure within the regular framework of environmental monitoring.

2 Sampling

The sampling procedure is described in procedure C- γ -SPEKT-OWASS-01.

3 Analysis

3.1 Principle of the procedure

To determine low tritium activity concentrations in surface water, a sample with an original volume of 260 ml is distilled in the presence of sodium peroxide as an electrolyte and electrolytically split up at $0 \text{ }^\circ\text{C}$ to a final volume of 10 ml to 20 ml over a period of about 5 days. The electrolytic residue containing the tritium is then further evaporated to a dry extract in a still in order to separate its salty constituents. An aliquot of the distillate is then mixed with a gel scintillator at a fixed volume ratio to form a sample ("cocktail") and then measured in a scintillation spectrometer.

3.2 Setup for the electrolytic enrichment of tritium in water

An enrichment setup usually consists of up to 20 electrolytic cells that are arranged in a series and run in a chest cooler at $0 \text{ }^\circ\text{C}$. To make provision for possible malfunctions, a thermo-sensor is used to halt the electrolytic process if temperatures rise above $3 \text{ }^\circ\text{C}$. The chest cooler needs to be capable of reliably disposing of the heat emanating from the electrolytic process. The circulation of air inside the actual cooling chamber can be improved by employing a powerful fan.

The anode of an electrolytic cell consists of a V2A tube (inner diameter: 30 mm) with a welded-in bottom that concentrically takes in the cylindrical cathode (structural steel St. 37 with a phosphatized surface) (Figure 1).

A teflon spacer attached to the bottom end of the cathode and a bracket made from Trovidur mounted to its top end ensure the distance of 2 mm between the surfaces of the electrodes to remain constant and electrically insulate the two components of the cell from one another. An O-ring made from Perbunan or silicone rubber inserted into the Trovidur bracket seals the cell effectively enough. The electrical connections are made via simple plugs (banana plugs) to V2A-flanges affixed to anode and cathode (7).

The gaseous oxygen/hydrogen mix (detonating gas) that is produced during the electrolytic process is channelled via a gas release pipe into gas-washing bottles filled with silicone oil and on out into the open. Each electrolytic cell is connected to its own gas-washing bottle so that their imperviousness can be monitored and checked all the time. For reasons of safety, the sections and connections that will be filled with detonating gas during the process are to be secured with a Perspex shield at least 10 mm thick.

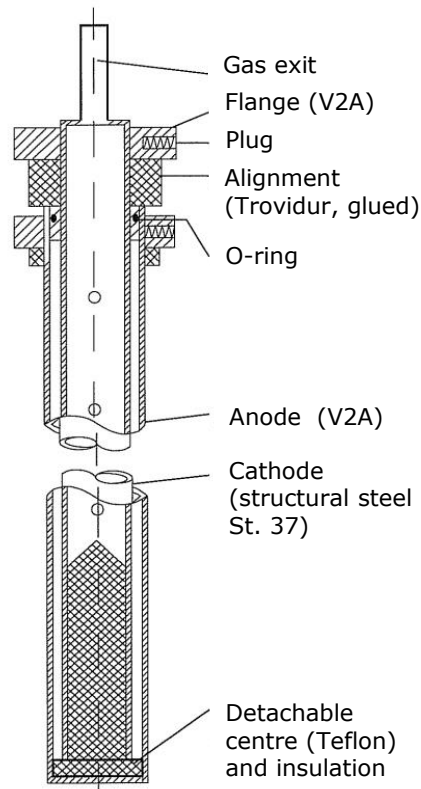


Fig. 1: Cross-section of an electrolytic cell for the enrichment of tritium in a water sample (7)

The original volume of the sample is 260 ml when the electrolytic cells are filled. Applying a current of 5 A, it is electrolytically split up to a final volume of ca. 15 ml over a period of 5 days. The progress of the electrolysis can be monitored via an ampere-hour-meter, but practical considerations suggest that weighing be given preference, because the specific energy consumption (ampere hours per ml) may exceed the theoretical value to a lesser or greater extent. Splitting up 1 ml of water electrolytically requires 2,98 A·h in theory. Electrolysis will furthermore cause

the sample to incur losses due to evaporation that amount to ca. 2 % and may need to be taken into consideration.

Prior to the first use of an electrolytic cell, some preparatory treatments are inevitable. This includes that the anode be carefully degreased with acetone and then dried in a drying oven at 105 °C. The cathode is likewise first degreased with acetone, then rinsed with distilled water, then submerged in half-concentrated hydrochloric acid (5 mol·l⁻¹), and treated in a bath of phosphoric acid (ortho-phosphoric acid, H₃PO₄, 85 %) at 40 °C to 50 °C for about 1 hour. Rinsed once more with distilled water, the cathode is finally dried in a drying oven at 105 °C.

Prior to the actual use, the electrolytic tritium-enrichment yields of the individual cells have to be determined from water samples with known tritium concentrations. Experience suggests that it will take 5 to 10 trial runs to establish sufficiently constant reference values. Affording them careful maintenance, electrolytic cells prepared thus will be fit for use for hundreds of electrolyses without changes in the enrichment yields becoming evident; the latter need to be checked from time to time notwithstanding. Every test run for determining the yield value needs to be followed up with the electrolysis of a nonvalent water counting source in order to demonstrate a possible contamination of the cell (memory effect).

3.3 Determining the tritium yield following electrolytic enrichment

The tritium yield from electrolytic enrichment depends on various influential factors (e. g. current density, electrode material, type and concentration of the electrolytic aids, structure of the cathode surface) and needs to be determined empirically with tritiated water with a known activity concentration, $c_{\text{H-3}}$, for each individual cell separately. To this end, a standard source is electrolysed, processed and measured under regular measurement conditions.

From the net count rate, $R_{\text{n,v}}$, measured for the mass ($m_{\text{w,v}} - m_{\text{E}}$) of the standard source prior to electrolysis and the count rate, $R_{\text{n,v}}$, metered for the mass ($m_{\text{w,n}} - m_{\text{E}}$) following electrolysis, the tritium yield, $\eta_{\text{A},i}$, is calculated for cell i as follows (7):

$$\eta_{\text{A},i} = \frac{R_{\text{n,n}} \cdot (m_{\text{w,n}} - m_{\text{E}})}{R_{\text{n,v}} \cdot (m_{\text{w,v}} - m_{\text{E}})} \quad (1)$$

Here, m_{E} corresponds to the mass of the electrolyte, sodium peroxide, used. With experience having shown that the tritium yields from electrolysis, $\eta_{\text{A},i}$, vary only to a minor extent from cell to cell (the standard deviation of the single values is typically ca. 3 %), corresponding means, $\bar{\eta}_{\text{A}}$, can be used as good approximations for analysing and determining tritium concentrations.

The yields obtainable by means of the tritium enrichment procedure described here will typically range around $\bar{\eta}_{\text{A}} = 0,95 \pm 0,03$ (\pm standard deviation).

The volume and mass reductions incurred in the electrolytic split-up of a water sample can be derived from the mass values $m_{\text{w,v}}$ and $m_{\text{w,n}}$ obtained before and after electrolysis and taking into account the added electrolyte, m_{E} . Combined, these factors are then used to calculate the corresponding reduction factor, $f_{\text{R},i}$, as follows:

$$f_{R,i} = \frac{(m_{w,v} - m_E)}{(m_{w,n} - m_E)} \quad (2)$$

This can then be taken further to derive the overall enrichment factor, $F_{A,i}$, for cell i resulting from determining the tritium activity concentration in an unknown sample from:

$$F_{A,i} = f_{R,i} \cdot \eta_{A,i} \approx f_{R,i} \cdot \bar{\eta}_A \quad (3)$$

3.4 Sample preparation

300 ml of an unfiltered water sample are over-distilled in a distilling apparatus (NS 29) with a Claisen head until it forms a dry extract. This residue will have retained dissolved salts and suspended matter. If a conventional still and heating mantles are used, this process will take ca. 1 hour. Processing several samples simultaneously is possible with setups designed for doing so.

Note

If the presence of I-131 in inorganic form is suspected, procedure C-H-3-OWASS-01 is to be followed.

3.5 Electrolytic enrichment

Using a glass beaker, 2,5 g of sodium peroxide (Na_2O_2) are dissolved in 260 ml (g) of the distillate obtained according to paragraph 3.4. The weakly alkaline solution is then filled into the well-cleaned and dried electrolytic cell (anode). The exact mass of the sample $m_{w,v}$, of the original sample is determined via differential weighing (weight (filled cell) minus weight (empty cell)). After the cathode has been inserted and locked in position, the cell – together with all other filled cells – are cooled down to $< 3 \text{ }^\circ\text{C}$ in a suitable cooler.

After the hoses for extracting the detonating gas that will emanate during the electrolytic process have been attached and all connections carefully checked for leaks, the electrolytic process is started by applying a direct-current voltage of ca. 3 V per cell. In order to curb the localised heating of the cells during electrolysis, which would lead to increased losses from evaporation, the current is to be limited to 5 A. Precautions that stabilize the current and monitor temperatures (thermo-sensor) are recommended for operational reliability. Continuing the electrolysis for about 120 hours will see the volume of the sample reduced to ca. 15 ml. The exact mass of the sample, $m_{w,n}$, is once more determined via differential weighing (weight (filled cell) minus weight (empty cell)).

The strongly alkaline residue is transferred to a 50 ml-round-bottomed borosilicate glass flask and the electrolyte separated by means of distillation to a dry extract in an apparatus with a Claisen head (NS 14.5). The pH of the distillate needs to be checked. If the pH is > 8 , which should not be the case if works have been effected with the necessary care, the distillation process is to be repeated. The emptied electrolysis cells are rinsed in hot water, flushed with distilled water, and finally dried in a drying oven at $105 \text{ }^\circ\text{C}$ over night.

3.6 Counting source preparation

8 ml of the distilled electrolysis residue are mixed and well homogenized with 12 ml of a gel scintillator ("cocktail") in a small plastic measuring bottle. After thermally adapting it in the cooled-down measuring instrument for ca. 1 hour, the measurement may commence. Amongst the commercially available gel scintillators, Insta-Gel by Packard-Canberra has advantages with regard to its sensitivity (8).

Note

When it comes to measuring extremely low tritium activity concentrations, measuring bottles made from low-pressure polyethylene are to be given preference, as they facilitate very low background count rates. Their disadvantage is, however, that the count rate tends to decrease gradually in a long-term measurement (> 1 week), which needs to be compensated for (8). Glass measuring bottles are of advantage if the measurement is to take place over extended periods of time and slightly increased background effects can be tolerated.

Further details can be found in procedure C-H-3-OWASS-01.

4 Measuring the activity

Calibration and adjustment of the measurement setup are described in procedure C-H-3-OWASS-01.

5 Calculation of the results

The tritium concentration, c_{H-3} , of a water sample can be determined from the following relationship:

$$c_{H-3} = \frac{R_g - R_0}{\varepsilon_{H-3} \cdot V \cdot f_{R,i} \cdot \eta_A} = \frac{R_n}{\varepsilon_{H-3} \cdot V \cdot f_{R,i} \cdot \eta_A} = \frac{R_n}{\varepsilon_{H-3} \cdot V \cdot F_{A,i}} \quad (4)$$

The long half-life of tritium of $t_{H-3} = 12,35$ a will not normally require that a correction factor for the radioactive decay between the point of time of taking a sample and its measurement be applied. However, the need of applying such a correction needs to be assessed on a by-case basis, especially for long holding periods before the measurement.

The achievable precision of a tritium analysis following electrolytic enrichment is determined in particular by the statistical uncertainty, $s(R_n)$, or $s^r(R_n)$, respectively, and an experimental error, s_{exp} or s^r_{exp} , respectively. Applying the Gaussian law of error propagation, this will produce the relative total error, s^r_g , in a tritium analysis from:

$$s^r_g = \sqrt{(s^r(R_n))^2 + (s^r_{exp})^2} \quad (5)$$

For its part, the experimental error, s_{exp} , consists of the following contributions (7):

- $s(\bar{\eta}_A)$ error in the mean tritium yield, $\bar{\eta}_A$;
- $\varepsilon(f_{R,i})$ weighing error in the determining $f_{R,i}$ of cell i ;
- $s(\varepsilon_{H-3})$ calibration error (error in the calibration solution, statistical count error in the calibration process, etc.).

The error contribution $s^r(\bar{\eta}_A)$ needs to be determined empirically on the basis of a larger number of the electrodes used. This will incorporate also those contributing errors that cannot be described mathematically (e. g., variations caused by different surface structures of the cathodes, amongst others). Experience suggests that this error ranges between $s^r(\eta_A) = 3\%$ to 4% for well prepared and maintained cells.

Owing to the errors incurred from weighing cell i , s_m , an error $s^r(f_{R,i})$ will be associated with $f_{R,i}$, which can be evaluated from an expression given elsewhere (7). This error, $s^r(f_{R,i})$, will be less than $0,5\%$ if a tolerance of $s_m = \pm 0,03\text{ g}$ is adhered to during the weighing process for specifying $f_{R,i}$ of cell i , and can usually be neglected.

The relative error $s^r(\varepsilon_{H-3})$ encountered in the calibration of the measurement setup is determined by the uncertainty specified for standard sources manufactured by the Phys.-Tech. Bundesanstalt as well as the corresponding statistical counting error incurred during the actual metering. Applying sufficiently long metering periods during the metering of the standard sources and carefully weighing in the standard solution ($\pm 0,01\text{ g}$) will easily reduce these error components to values below 1% , so that the error $s^r(\varepsilon_{H-3})$ is primarily determined by the calibration error, which will typically be given as $0,5\%$ to 1% . If the standard source is not prepared by means of weighing but by means of pipetting, the resulting error in determining the volume may amount to as much as 1% or even more.

The statistical count uncertainty, $s(R_n)$, of the net count rate, R_n , incurred in the analysis of a tritium concentration, can be calculated according to the following relationship:

$$s(R_n) = \sqrt{\frac{R_0}{t_0} + \frac{R_g}{t_m}} \quad (6)$$

with the relative uncertainty, $s^r(R_n)$, resulting from:

$$s^r(R_n) = \frac{s(R_n)}{R_n} \quad (7)$$

The relative total uncertainty, $s^r_g(c_{H-3})$, incurred from measuring a tritium activity concentration following electrolytic enrichment, can therefore be assessed after the following relationship:

$$s^r_g(c_{H-3}) = \sqrt{(s^r(R_n))^2 + (s^r(\bar{\eta}_A))^2 + (s^r(f_{R,i}))^2 + (s^r(\varepsilon_{H-3}))^2} \quad (8)$$

Using the purely statistical uncertainty that dominates the measurement of tritium at a low-level range, the corresponding error for the quantification of tritium, $s(c_{H-3})$, can be calculated as follows:

$$s(c_{H-3}) = \frac{s(R_n)}{\varepsilon_{H-3} \cdot V \cdot f_{R,i} \cdot \eta_A} = c_{H-3} \cdot \frac{s(R_n)}{R_n} \quad (9)$$

or, the relative standard deviation, $s(c_{H-3})/c_{H-3}$ (variation coefficient) from:

$$s^r(c_{H-3}) = \frac{s(c_{H-3})}{c_{H-3}} = \frac{s(R_n)}{\varepsilon_{H-3} \cdot V \cdot f_{R,i} \cdot \eta_A \cdot c_{H-3}} = \frac{s(R_n)}{R_n} \quad (10)$$

5.1 Worked example

Determining the tritium activity concentration in a water sample following electrolytic enrichment:

| | | |
|--|---------------------------------|------------------------|
| Detection efficiency: | $\varepsilon_{\text{H-3}}$ | = 0,25 |
| Duration of the background measurement: | t_0 | = 60 000 s |
| Duration of the counting source measurement: | t_m | = 6000 s |
| Background count rate: | R_0 | = 0,10 s ⁻¹ |
| Gross count rate: | R_g | = 0,20 s ⁻¹ |
| Aqueous content of counting source to measured ("cocktail"): | V | = 0,008 l |
| Mean yield during the enrichment process: | $\bar{\eta}_A$ | = 0,95 |
| Mass reduction factor, cell i : | $f_{R,i}$ | = 20 |
| Rel. error of $\bar{\eta}_A$ | $s^r(\eta_A)$ | = 0,04 |
| Rel. error of $\varepsilon_{\text{H-3}}$ | $s^r(\varepsilon_{\text{H-3}})$ | = 0,02 |
| Rel. error of $f_{R,i}$ | $s^r(f_{R,i})$ | = 0,005 |

According to equation (4), the tritium concentration, $c_{\text{H-3}}$, of the sample is calculated as:

$$c_{\text{H-3}} = \frac{0,2 - 0,10}{0,25 \cdot 0,008 \cdot 20 \cdot 0,95} \text{ Bq} \cdot \text{l}^{-1} = 2,63 \text{ Bq} \cdot \text{l}^{-1}$$

The relative counting uncertainty, $s^r(R_n)$, is calculated following equations (6) and (7) as:

$$s^r(R_n) = \frac{1}{0,2 - 0,10} \cdot \sqrt{\frac{0,10}{60000} + \frac{0,2}{6000}} = 0,059$$

and the relative total uncertainty, $s^r_g(c_{\text{H-3}})$, according to equation (8) reads:

$$s^r_g(c_{\text{H-3}}) = \sqrt{0,059^2 + 0,04^2 + 0,005^2 + 0,02^2} = 0,074$$

The result of the tritium analysis following electrolytic enrichment including a simple total uncertainty therefore reads:

$$c_{\text{H-3}} = (2,63 \pm 0,19) \text{ Bq} \cdot \text{l}^{-1}$$

or

$$c_{\text{H-3}} = 2,63 \text{ Bq} \cdot \text{l}^{-1} \pm 7,4 \%$$

6 Characteristic limits of the procedure

6.1 Decision threshold

The decision threshold, $g_{\text{H-3}}^*$, that can be achieved in the analysis of a tritium activity concentration following electrolytic enrichment, can be estimated as a good approximation according to the following relationship:

$$g_{\text{H-3}}^* = \frac{k_{1-\alpha}}{\varepsilon_{\text{H-3}} \cdot V \cdot f_{\text{R},i} \cdot \eta_{\text{A}}} \cdot \sqrt{\frac{R_0}{t_m} \cdot \left(1 + \frac{t_m}{t_0}\right)} \quad (11)$$

6.2 Detection limit

Accordingly, the following relationship applies to the detection limit, $g_{\text{H-3}}$:

$$g_{\text{H-3}} = \frac{(k_{1-\alpha} + k_{1-\beta})}{\varepsilon_{\text{H-3}} \cdot V \cdot f_{\text{R},i} \cdot \eta_{\text{A}}} \cdot \sqrt{\frac{R_0}{t_m} \cdot \left(1 + \frac{t_m}{t_0}\right)} \quad (12)$$

For example, this means that a measurement setup under realistic conditions ($R_0 = 0,10 \text{ s}^{-1}$; $t_0 = 60\,000 \text{ s}$; $t_m = 6000 \text{ s}$; $V = 0,008 \text{ l}$; $f_{\text{R},i} = 20$; $\varepsilon_{\text{H-3}} = 0,25$) for a confidence coefficient of $k_{1-\alpha} = 3$ (confidence interval 99,865 %), will have an achievable decision threshold of $g_{\text{H-3}}^* = 0,34 \text{ Bq}\cdot\text{l}^{-1}$. From this, the detection limit of the procedure for $k_{1-\beta} = 1,645$ (confidence interval 95 %) can be calculated as being $g_{\text{H-3}} = 0,52 \text{ Bq}\cdot\text{l}^{-1}$. Attention is explicitly drawn to particulars of the measurement conditions that limit the probability of the error β (type II error) occurring and ensure a power of $1 - \beta$.

7 Catalogue of chemicals and equipment

7.1 Chemicals

- Gel scintillator (e. g., Insta-Gel manufactured by Packard-Canberra);
- Sodium peroxide, Na_2O_2 , p.a.;
- Acetone, chemically pure;
- Silicone oil;
- Tritium-free water (activity-free water counting source);
- Tritium standard solution (activity standard) from the Phys.-Tech. Bundesanstalt, Brunswick;
- Ortho-phosphoric acid, H_3PO_4 , 86 %, chemically pure;
- Hydrochloric acid, HCl , $10 \text{ mol}\cdot\text{l}^{-1}$, chemically pure;

7.2 Equipment

- Setup for the enrichment of tritium in water samples (multi-cell apparatus) with cooling unit, constant-current supply, thermo-sensor, automatic switch-off in the case of a disrupted power supply, etc.;
- Liquid scintillation spectrometer with half-duplex transmission and units for tabulated and graphic output;

- Electronic quick scale, max. capacity 4000 g, display 0,01 g, accuracy 0,03 g;
- Automatic quick pipette for water and gel scintillator samples (e.g., EM-Dispenser, manufactured by Hirschmann Laborgeräte, Eberstadt);
- 50 ml-washing bottles, filled with silicone oil;
- Drying oven;
- 20 ml-measuring bottles made from ND-polyethylene;
- Basic laboratory equipment.

References

- (1) Umweltradioaktivität und Strahlenbelastung: Jahresberichte des Bundesministers für Umwelt, Naturschutz und Reaktorsicherheit, Bonn
- (2) Mundschenk. H., Krause, W. J.: Behaviour and radiological significance of tritium from nuclear power plants and other sources in the Rhine river basin. J. Environm. Radioactivity 14 (1991) pp. 341-360
- (3) Mundschenk. H., Krause. W. J.: Zur Bestimmung von Fließzeiten und longitudinaler Dispersion im Hoch- und Oberrhein mit ^3HHO als Tracer. Deutsche Gewässerkdl. Mitteilungen 35 (1991) S. 93-107
- (4) Cameron, J. F., Payne. B. R.: Apparatus for concentration and measurement of low tritium activities. Proc. of the 6th Int. Conf. on radiocarbon and tritium dating. Washington State University, Pullman, Wash., March 7-11, 1965, CONF-650652, p.45
- (5) Zutsbi, P. K., Sas-Hubicki, J.: A new cathode treatment for the reproducible electrolytic enrichment of tritium. Int. J. Appl. Radiat. Isotopes 17 (1966) 670
- (6) Hartley. P. E.: Design and Performance of tritium measurement Systems using electrolytic enrichment. Nucl. Instr. Meth. 100 (1972) 229
- (7) Krause. W. J., Mundschenk. H.: Elektrolytische Anreicherung und Bestimmung von Tritium in Grund- und Oberflächengewässern. Deutsche Gewässerkundl. Mitteilungen 22 (1978) 76-95
- (8) Krause. W. J.: Die Eignung verschiedener Meßfläschchen und Szintillatorflüssigkeiten zur Bestimmung von Tritium in Wasser. Z. Wasser-Abwasser-Forschung 18 (1985) S. 141-160