

**Procedure for determining the  
activity concentration of tritium  
in surface water**

C-H-3-OWASS-01

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# Procedure for determining the activity concentration of tritium in surface water

## 1 Scope

The content of water bodies with tritium is based on both natural and anthropogenic sources and emitters, respectively (1 – 4). In order to monitor long-term consequences in areas used for the recovery of drinking water in particular, the routine measurement programme of the StrVG and the guideline for the monitoring of emissions and immissions of nuclear installations demand that adequate measurements be taken.

The procedure described here allows measuring nuclide activity concentrations of about  $5 \text{ Bq}\cdot\text{l}^{-1}$  under practical conditions and thus complies with the required detection limit of  $10 \text{ Bq}\cdot\text{l}^{-1}$  (5 – 8).

## 2 Sampling

The sampling procedure is described in procedure C- $\gamma$ -SPEKT-OWASS-01.

## 3 Analysis

### 3.1 Principle of the method

The sample collected by appropriate means is distilled. An aliquot of the distillate is mixed with a commercially available gel-scintillator to form a "cocktail" counting source and then measured in a liquid scintillation spectrometer.

### 3.2 Sample preparation

About 100 ml of an unfiltered water sample is over-distilled in a conventional distilling apparatus with a Claisen head until it forms a dry extract. If a device with an electric heating mantle is used, this will take ca. 1 hour per sample. Commercially available multi-heating mantle arrays facilitate the processing of several samples simultaneously.

#### Note

If the presence of inorganic I-131 is suspected, the sample needs to be fortified with 100 mg of sodium sulphite, 10 mg of potassium iodide, and 10 mg of silver nitrate in solid form and then treated with a little sodium carbonate (solid) until the alkaline reaction (pH ca. 8) sets in, prior to the distillation process.

### 3.3 Counting source preparation

8 ml of the distilled water sample are mixed with 12 ml of a gel-scintillator (e. g., Instagel by Packard-Canberra) to a "cocktail" in a small measuring plastic bottle. Following an about 1 hour-period of thermal adaptation in the cooled measuring chamber of the liquid scintillation spectrometer, the actual measurement may commence (5 – 7).

**Note**

Compared to measuring bottles made from glass, those made from plastic (low-pressure polyethylene) have a much-reduced background effect. Their disadvantage is, however, that the count rate tends to decrease slightly in long-term measurements and may need to be compensated for. Glass measuring bottles are therefore of advantage if the measurement is to take place over extended periods of time and an increased background effect can be tolerated (6).

**3.4 Interferences**

Chemoluminescence may be noted during the counting source preparation, and these would disturb the measurement. Experience has shown, however, that these effects will have subsided within an hour after the preparation of the counting sources. Random checks should nevertheless be performed, in particular when a new scintillation solution has been used.

**3.5 Activity-free water counting source**

The background count rate always needs to be determined by using counting sources of tritium-free or -poor water ("activity-free water counting sources"). Activity-free water counting sources contaminated with tritium causes systematic errors in determining the tritium activity concentration. This was repeatedly noted by individual participants involved in the comparative analyses conducted by the BfG (8, 9). Activity-free water counting sources can be recovered from old groundwater deposits, but have to be verified to ensure their tritium activity concentrations are negligible. Small quantities of activity-free water counting sources with a tritium concentration of  $c_{\text{H-3}} < 0,02 \text{ Bq}\cdot\text{l}^{-1}$  may also be obtained from the BfG.

**4 Measuring the activity****4.1 Adjusting of the measurement setup**

A sample containing tritium is measured using a liquid scintillation spectrometer. For a given amplification, the lower and upper discrimination thresholds have to be set carefully to ensure an optimal ratio between the beta spectrum of tritium and the background. It is recommended to identify the differential distributions of the pulse heights of both the beta spectra of tritium and the background.

The background count rate is largely determined by the quality of the photo multipliers (multi alkaline cathodes), the manner and extent of the shielding used, the temperatures applied during the measurement, and the local dose rate at the position of the counter. In general, measurements should only be performed with measuring instruments that are specifically designed for low-level measurements. The electronic background count rate of the device that is based upon random coincidence should range below  $0,005 \text{ s}^{-1}$  (to be verified with a measuring bottle filled with black indian ink).

**4.2 Calibration**

To determine the tritium activity concentration of a water sample it is necessary to know the efficiency for defined measurement conditions. This in turn requires that the calibration of the measurement setup and the measurement of the actual sample be always effected under identical conditions (device settings, composition of the sample, scintillator used, etc.). Certified standard solutions (activity standards) have to be used for calibration.

The measured net count rate of the standard sample  $R_n$  ( $s^{-1}$ ) of a known activity concentration  $c_{H-3}$  ( $Bq \cdot ml^{-1}$ ) and a given sample volume,  $V$  (ml), together produce the efficiency for the measurement of tritium,  $\varepsilon_{H-3}$ , from:

$$\varepsilon_{H-3} = \frac{R_g - R_0}{\varepsilon_{H-3} \cdot V} = \frac{R_n}{\varepsilon_{H-3} \cdot V} \quad (1)$$

The count rate,  $\varepsilon_{H-3}$ , of the measurement setup needs to be checked for possible drift effects at weekly intervals. The background effect should be monitored constantly in order to detect possible interferences or device malfunctions early.

### 4.3 Quality of the measurement

The quality of a measurement for a setup can be characterized by quality values such as the "figure of merit" (FOM) discussed in literature (5, 6). The FOM of a fixed composition of a sample (water/scintillator) in a counting setup is defined as follows:

$$FOM = \frac{\varepsilon_{H-3}^2 \cdot V^2}{R_0} \quad (2)$$

This indicates that the quality of a counting setup is improved more effectively by increasing the efficiency or increasing the sample volume rather than by reducing the background count rate. Carefully adjusting the counting setup, utilizing Instagel as a scintillator, and measuring in plastic bottles makes it possible to reach a FOM of at least  $10^{-4} l^2 \cdot s$ . Applying this FOM helps to effectively optimise the settings of the measurement setup and the composition of the sample to be measured.

## 5 Calculation of the results

The tritium concentration,  $c_{H-3}$ , of a water sample is determined according to the following relationship:

$$c_{H-3} = \frac{R_g - R_0}{\varepsilon_{H-3} \cdot V} = \frac{R_n}{\varepsilon_{H-3} \cdot V} \quad (3)$$

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 statistical uncertainty,  $s_n$ , caused by the net count rate,  $R_n$ , of the measurement of tritium is calculated according the following relationship:

$$s_n = \sqrt{\frac{R_0}{t_0} + \frac{R_g}{t_m}} \quad (4)$$

This produces the statistical uncertainty of the tritium activity concentration,  $s(c_{\text{H-3}})$ , as:

$$s(c_{\text{H-3}}) = \frac{s_n}{\varepsilon_{\text{H-3}} \cdot V} = c_{\text{H-3}} \cdot \frac{s_n}{R_n} \quad (5)$$

and the relative standard deviation,  $s(c_{\text{H-3}})/c_{\text{H-3}}$  (variation coefficient) as:

$$\frac{s(c_{\text{H-3}})}{c_{\text{H-3}}} = \frac{s_n}{\varepsilon_{\text{H-3}} \cdot V \cdot c_{\text{H-3}}} = \frac{s_n}{R_n} \quad (6)$$

The errors in weighing, pipetting and calibrating encountered in the quantification of tritium activity concentrations can usually be neglected vis-à-vis the statistical uncertainty caused by counting uncertainties.

### 5.1 Worked example

Quantification of the tritium concentration,  $c_{\text{H-3}}$ , in a sample of river water

Duration of background measurement:	$t_0$	= 60 000 s
Duration of counting source measurement:	$t_m$	= 6000 s
Detection efficiency:	$\varepsilon_{\text{H-3}}$	= 0,25
Background count rate:	$R_0$	= 0,050 s <sup>-1</sup>
Gross count rate:	$R_g$	= 0,13 s <sup>-1</sup>
Volume of the water sample:	$V$	= 0,008 l

Applying equation (3), this shows the tritium concentration of the water sample,  $c_{\text{H-3}}$ , as:

$$c_{\text{H-3}} = \frac{0,13 - 0,05}{0,25 \cdot 0,008} \text{ Bq} \cdot \text{l}^{-1} = 40,0 \text{ Bq} \cdot \text{l}^{-1}$$

The statistical uncertainty associated,  $s(c_{\text{H-3}})$ , is obtained from equations (4) and (5) in the following manner:

$$s(c_{\text{H-3}}) = \frac{\sqrt{\frac{0,05}{60000} + \frac{0,13}{6000}}}{0,25 \cdot 0,008} \text{ Bq} \cdot \text{l}^{-1} = 2,4 \text{ Bq} \cdot \text{l}^{-1}$$

The result of the tritium activity concentration in river water with a simple statistical count uncertainty therefore reads:  $c_{\text{H-3}} = (40 \pm 2,4) \text{ Bq} \cdot \text{l}^{-1}$

$$c_{\text{H-3}} = (40 \pm 2,4) \text{ Bq} \cdot \text{l}^{-1}$$

or

$$c_{\text{H-3}} = 40 \text{ Bq} \cdot \text{l}^{-1} \pm 6,0 \%$$

## 6 Characteristic limits of the procedure

### 6.1 Decision threshold

The detection threshold,  $g_{\text{H-3}}^*$ , for a measurement of the tritium activity concentration that can be achieved under realistic conditions can be calculated as a good approximation from the following relationship:

$$g_{\text{H-3}}^* = \frac{k_{1-\alpha}}{\varepsilon_{\text{H-3}} \cdot V} \cdot \sqrt{\frac{R_0}{t_m} \cdot \left(1 + \frac{t_m}{t_0}\right)} \quad (7)$$

### 6.2 Detection limit

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

$$g_{\text{H-3}} = \frac{(k_{1-\alpha} + k_{1-\beta}) \cdot \sqrt{\frac{R_0}{t_m} \cdot \left(1 + \frac{t_m}{t_0}\right)}}{\varepsilon_{\text{H-3}} \cdot V} \quad (8)$$

For example, this means that a measurement setup under realistic metering conditions ( $R_0 = 0,05 \text{ s}^{-1}$ ;  $t_0 = 60000 \text{ s}$ ;  $t_m = 10\,000 \text{ s}$ ;  $V = 0,008 \text{ l}$ ;  $\varepsilon_{\text{H-3}} = 0,25$ ) for  $k_{1-\alpha} = 3$  (confidence interval 99,865 %), will have an achievable decision threshold of  $g_{\text{H-3}} = 3,5 \text{ Bq} \cdot \text{l}^{-1}$ . From this, the detection limit of the procedure for  $k_{1-\beta} = 1,645$  (confidence interval 95 %) can be calculated, resulting in  $g_{\text{H-3}} = 5,4 \text{ Bq} \cdot \text{l}^{-1}$  (chapter IV.5). Attention is explicitly drawn to particulars of the measurement conditions that limit the probability of the error  $\beta$  (type II error) occurring and ensure a power of  $1 - \beta$ .

## 7 Catalogue of chemicals and equipment

### 7.1 Chemicals

- Tritium-free water ("Activity-free water counting source");
- Sodium sulphite, ultra-pure ( $\text{Na}_2\text{SO}_3$ );
- Sodium carbonate, ultra-pure ( $\text{Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O}$ );
- Gel scintillator (e. g., Instagel manufactured by Packard-Canberra);
- Tritium standard solution (activity standard) from the Physikalisch-Technische Bundesanstalt, Brunswick;
- Potassium iodide solution, p. A. (KI);
- Silver nitrate, p. A., ( $\text{AgNO}_3$ ).

### 7.2 Equipment

- Liquid scintillation spectrometer with half-duplex transmission and units for tabulated and graphic output;
- Multi-heating mantle array;
- Automatic quick pipette for water samples;
- Dispenser for gel scintillator;
- 20 ml-measuring bottles made from ND-polyethylene;
- Basic laboratory equipment.

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