



The measurement of tritium in environmental water samples

1. Introduction

The Hidex 300 SL automatic TDCR liquid scintillation provides an excellent solution for the determination of H-3 in drinking water. Due to the physical characteristics of H-3 ($E_{\beta \max} = 18.5$ keV) this application is traditionally seen as highly demanding.

The German DIN 25482, Teil 1 and international ISO 11929 part 1 describe detection procedures and detection limits for measurement of radioactivity in environmental water samples. To achieve acceptable results we therefore recommend close conformance with these methods. In addition, the general and specific rules and instructions relating to liquid scintillation counting (LSC) that form part of good laboratory practice should be observed.

2. Positioning of Hidex 300 SL

It is important that the measuring instrument's place of operation is not subject to fluctuations in temperature, and that the sun does not shine directly onto the instrument at a particular time of day. A constant temperature, if possible in an air-conditioned laboratory, is a most important pre-requisite for good measurement results.

The place of operation should further be selected such that the gamma dose rate is as low as possible and that the values of radon and radon decay products coming from building materials are minimal.

If possible, the laboratory and/or the room in which the measurements are made should not be equipped with strongly fluorescent lamps. Luminescence from such lights during the transport of vials from the storage area to the counter can affect the results.

3. Sample handling and measurement

Instructions on sampling and sample preparation are given in the general recommendations for the analysis methods mentioned above.

The following points are worth emphasizing. In principle the samples should be stored in a cool, dark place. However, the storage conditions should not be so cold that separation of the water and cocktail can occur. Temperatures around 18°C are optimal. When cocktail is added to the water sample it is important to ensure that the temperatures of sample and cocktail are the same.

Sample preparation steps can cause strong luminescence effects. To avoid problems with luminescence, samples should be left for at least 4 hours before measurement (or longer in



the case of strong luminescence); this particularly applies for low level samples. The preparation of the samples should not take place in bright light and not in the vicinity of strongly fluorescent lamps.

For the avoidance of static electricity effects (frequently encountered with plastic vials) the Hidex 300 SL features a mechanism to discharge the static from the sample directly before measurement; this adds 1 to 2 seconds to the sample processing time.

4. Detection limits of the Hidex 300 SL for H-3 measurements

The calculation of the detection limit is made for a 20ml vial. The formula used is the proximity formula with the settings, $\alpha = \beta = 0.05$, with the result that $k_{1-\alpha} = 3$ and $k_{1-\beta} = 1.645$. The counting time for the determination of the background, t_0 is set to equal the counting time for the sample, t_b :

$$DL = V^{-1} * K (k_{1-\alpha} + k_{1-\beta}) \sqrt{\frac{2 \cdot R_0}{t_b}} \text{ in Bq/l}$$

K = Calibration factor (1 / Efficiency)

$k_{1-\alpha}$ = Quantile of the standard – normal distribution for probability of error of 1st type (= 3)

$k_{1-\beta}$ = Quantile of the standard – normal distribution for probability of error of 2nd type (= 1.645)

t_b = Measuring time of the sample in seconds

R_0 = Background

V = 0.008 l sample volume

This equation is derived from the general equation given below, and reflects the special case in which $t_0 = t_b$.

For the detection limit for tritium, g_{H-3} :

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

Under practical measuring conditions ($R_0=0.05\text{s}^{-1}$, $t_0=60000\text{s}$, $t_m=10000\text{s}$; $V=0.008\text{ l}$, $\varepsilon_{H-3}=0.25$) for $k_{1-\alpha} = 3$ (99.865% confidence limit) the detection limit attainable is $3.5\text{ Bq}\cdot\text{l}^{-1}$. For $k_{1-\beta} = 1.645$ (95% confidence limit) the detection limit of the procedure becomes $5.4\text{ Bq}\cdot\text{l}^{-1}$. It is important to maintain measurement conditions so as to limit the β error probability (type 2 error) and ensure a predetermined confidence level, $1 - \beta$.



5. Determination of efficiency and backgrounds

For the determination of the activity of an unknown sample the efficiency and background must be accurately known. For this, two additional samples need to be prepared using the same chemistry and conditions as for the unknowns (e.g. 8 ml aqueous sample + 12 ml water-soluble cocktail).

Background

For the determination of the background, activity-free water is used as the sample. The counting time used will be the same as that used when the unknown samples are measured.

Efficiency

For efficiency measurement, certified activity standards must be used and their measurement must be carried out under the same conditions as those of the unknown samples.

The efficiency of the tritium measurement, $\epsilon_{\text{H-3}}$ is obtained from the measured net count rate of the standard sample, R_n (s^{-1}); the known activity concentration, $c_{\text{H-3}}$ ($\text{Bq}\cdot\text{ml}^{-1}$); and the predetermined sample volume, V (ml):

$$\epsilon_{\text{H-3}} = \frac{R_b - R_o}{c_{\text{H-3}} \cdot V} = \frac{R_n}{c_{\text{H-3}} \cdot V}$$

To detect any drift the performance of the measuring device should be monitored weekly using activity standards. Similarly the background radiation levels should be kept under constant review.

When measuring activities roughly 1000 times higher than the background, the effects of the background can be ignored.

6. Determination of activity of the sample

The tritium concentration ($c_{\text{H-3}}$) in an aqueous sample is given by the following equation:

$$c_{\text{H-3}} = \frac{R_b - R_o}{\epsilon_{\text{H-3}} \cdot V} = \frac{R_n}{\epsilon_{\text{H-3}} \cdot V} \text{ Bq}\cdot\text{l}^{-1}$$

Given the long half-life of tritium ($t_{\text{H-3}} = 12.35$ y) correction for the radioactive decay between the time of sampling and that of measurement is usually not required. However, half-life correction does need to be considered in some situations, for example, if the sample has been left for a long time before measurement.

In the measurement of tritium the statistical counting error s_n for the net count rate R_n is calculated using the following formula:



$$s_n = \sqrt{\frac{R_o}{t_o} + \frac{R_b}{t_m}} \quad s^{-1}$$

From this we obtain the statistical error of the tritium determination, $s(c_{H-3})$:

$$s(c_{H-3}) = \frac{s_n}{\epsilon_{H-3} \cdot V} = c_{H-3} \cdot \frac{s_n}{R_n} \quad \text{Bq} \cdot \text{l}^{-1}$$

The coefficient of variation is then:

$$\frac{s(c_{H-3})}{c_{H-3}} = \frac{s_n}{\epsilon_{H-3} \cdot V \cdot c_{H-3}} = \frac{s_n}{R_n}$$

Errors due to weighing, pipetting and calibration are typically negligible in comparison to the statistical counting error.

7. Determination of H-3 activity with Hidex 300 SL with MicroWin 2000

There are three parameter files corresponding to the three measuring tasks:

Determination of the efficiency

Determination of the background and detection limit

Determination of the sample activity

Note: Parameter files default settings are based on vials containing 8 ml sample volumes and 12 ml cocktail. If different proportions are used, the appropriate parameter file must be changed.

Determination of the Efficiency

For the determination of the Efficiency a sample with calibrated standard activity is counted. This activity (the counting rate should preferably be large, otherwise background becomes significant and needs to be considered) for the appropriate label must be recorded in DPM (it may be necessary to correct the radioactive half-life). We recommend to use the water soluble H3 capsules available from Hidex Oy.

For this measurement four repeat measurements are needed. The associated parameter file is:



Efficiency Determination H-3 4Repeat 1W.par

The activity of the standard must be recorded in the Standard in DPM

Click **Standard in DPM**, choose position A1 and enter the activity value in the field for the formula, Press **Enter**.

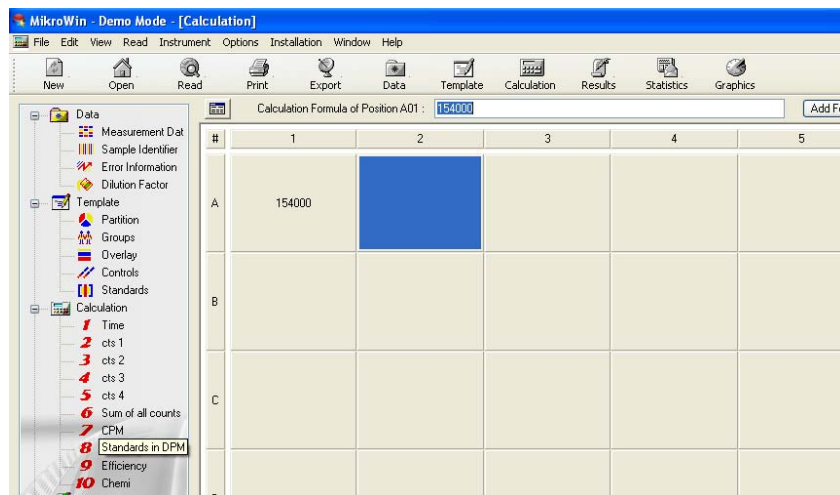


Figure 2. Data field for supplying the value for the standard.

After counting the Efficiency is automatically calculated:

Efficiency = count rate/standard activity

Alternatively it is possible to utilize the TDCR method. The TDCR value is shown automatically after the measurement as the average of the TDCR values for the 4 repeat measurements.

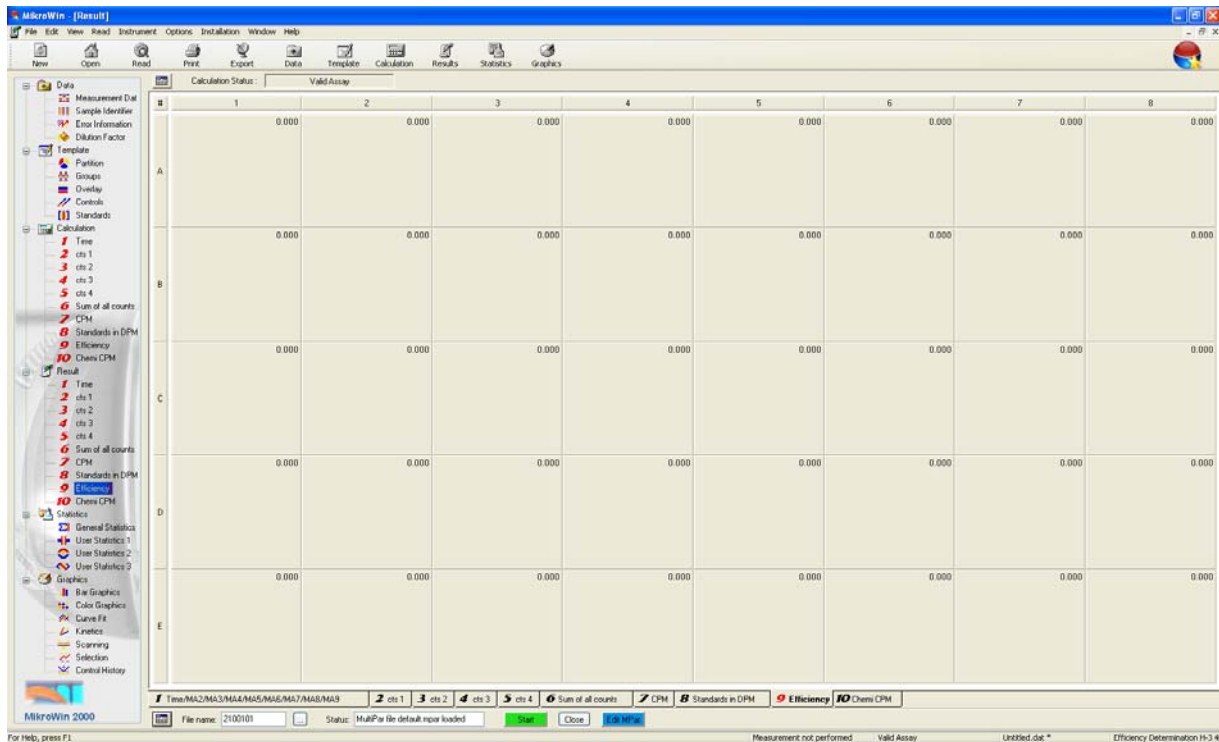


Figure 3. View of parameter file for the Efficiency determination.

After the measurement the data are stored as a dat file and can be printed.

The data can also be exported automatically into an Excel file, together with the parameters and characteristics of the measurement. Additionally, the data are also stored as a csv file. Thus at any time “the render software” can be called on to display the spectrum, allowing its use for further, individual calculations.

Determination of the background and the detection limit

4 repeat measurements are again required. The associated parameter file is:



H3 4 repeat llod and bkg.par

The counting time is parameterized; the Efficiency, ε (or the TDCR value) has to be entered as a value in the appropriate field.

In connection with the measurements the background is also calculated together with the detection limit:



$$DL = V^{-1} * \varepsilon^{-1} (k_{1-\alpha} + k_{1-\beta}) \sqrt{\frac{2 \cdot R_0}{t_b}} \text{ in Bq/l}$$

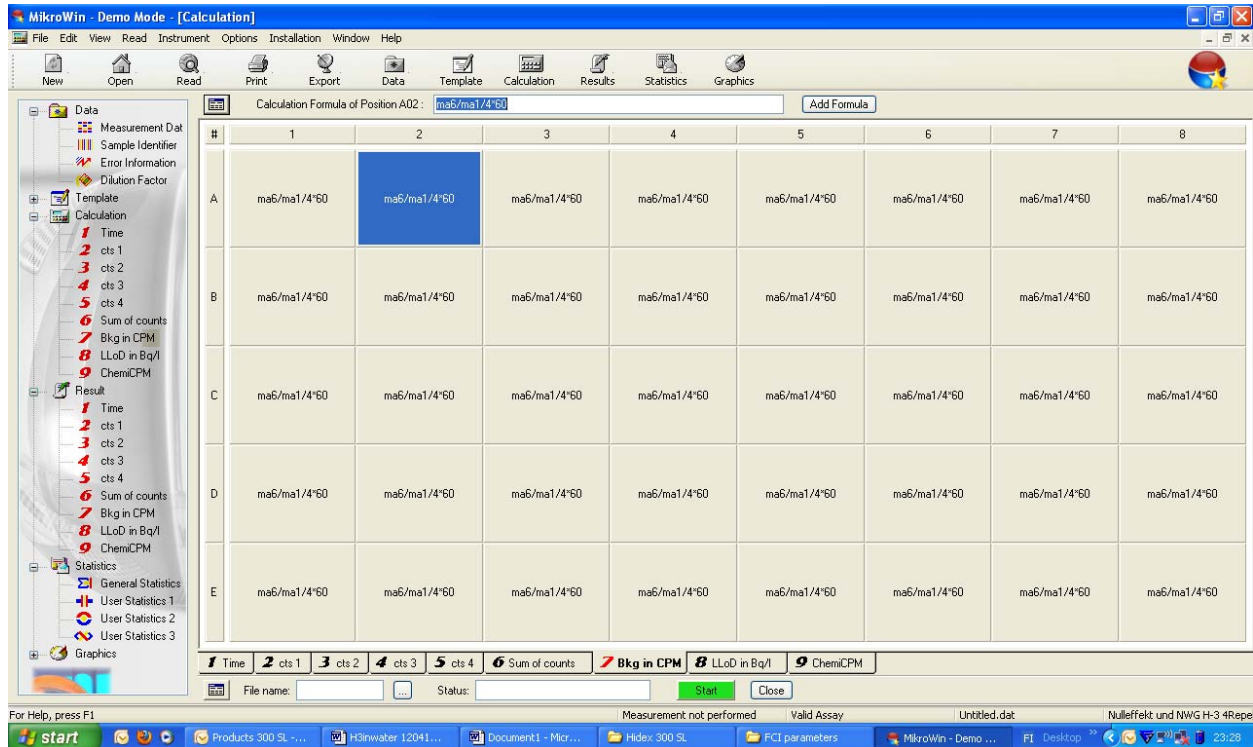


Figure 4. View of parameter files for the Efficiency determination.

After the measurement the data are stored as a dat file and can be printed.

The data can also be exported automatically into an Excel file, together with the parameters and characteristics of the measurement. Additionally, the data are also stored as a csv file. Thus at any time “the render software” can be called on to display the spectrum, allowing its use for further, individual calculations.

Determination of the activity of samples

4 repeat measurements are again made. The associated parameter file is:



Determination of H-3 4Repeat 20 mL.par

The counting time is parameterized; the Efficiency, ε (or the TDCR value) has to be entered as a value in the appropriate field; the TDCR value is calculated directly from the measurement.

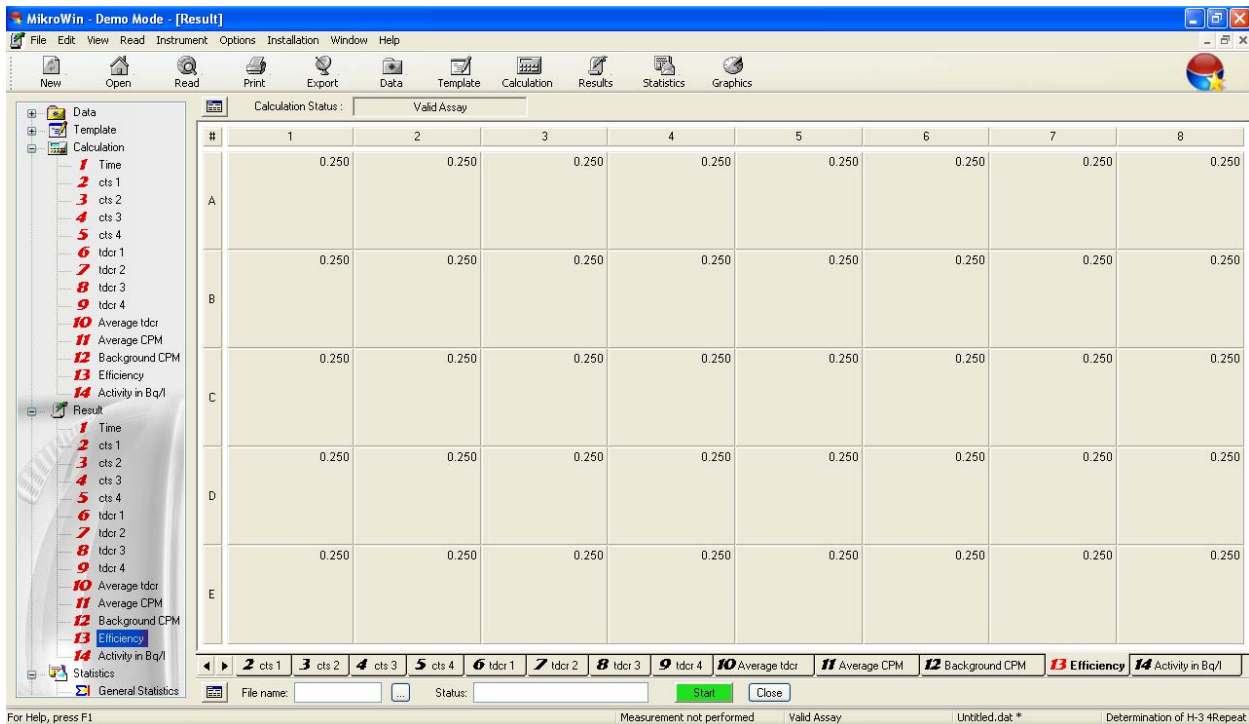


Figure 5. View of parameter files for the Efficiency determination.

In accordance with the previously mentioned guidelines, the calculation of the tritium concentration c_{H-3} , in an aqueous sample is performed using the following equation:

$$c_{H-3} = \frac{R_b - R_o}{\epsilon_{H-3} \cdot V} = \frac{R_n}{\epsilon_{H-3} \cdot V} \text{ Bq} \cdot \text{l}^{-1}$$

Given the long half-life of tritium ($t_{H-3} = 12.35 \text{ y}$) correction for the radioactive decay between the time of sampling and that of measurement is usually not required. However, half-life correction does need to be considered in some situations, for example, if the sample has been left for a long time before measurement.

On this basis the sample activity is also computed with the TDCR value determined during the measurement.

Optionally the statistic counting error in Bq/l can also be computed:

In the measurement of tritium the statistical counting error s_n for the net count rate R_n is calculated using the following formula:



$$s_n = \sqrt{\frac{R_o}{t_o} + \frac{R_b}{t_m}} \quad s^{-1}$$

From this we obtain the statistical error of the tritium determination, $s(c_{H-3})$:

$$s(c_{H-3}) = \frac{s_n}{\epsilon_{H-3} \cdot V} = c_{H-3} \cdot \frac{s_n}{R_n} \quad \text{Bq} \cdot \text{l}^{-1}$$

After the measurement the data are stored as a dat file and can be printed.

The data can also be exported automatically into an Excel file, together with the parameters and characteristics of the measurement. Additionally, the data are also stored as a csv file. Thus at any time “the render software” can be called on to display the spectrum, allowing its use for further, individual calculations.

8. Recommended equipment and material

- 425-201 Hidex 300 SL liquid scintillation counter
- 425-018 Low Level PM tube option
- 425-2001 Cooling option
- 461-008 5 L Aqualight cocktail
- 463-130 20 ml plastic vials 500 pcs
- 462-011 H3 water soluble internal standard capsules