

Procedure for determining the activity concentration of tritium in wastewater

H-H-3-AWASS-01

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Procedure for determining the activity concentration of tritium in wastewater

1 Scope

The procedure outlined in the following is used for determining the activity concentration of tritium in wastewater from nuclear facilities according to the German Nuclear Safety Standards Commission standard 1504 [1]. This procedure is also applicable for water samples from other sources.

In this context, tritium (H-3 or T) needs to be present in the chemical form of water, i.e. HTO or T₂O. Non-volatile compounds are not determined by this method.

This procedure is suitable as a rapid determination method since results are available within the time of one working day.

2 Sampling

Details to representative sampling are given in procedure H- γ -SPEKT-AWASS-01.

Tightly closed or sealed glass or polyethylene sample containers should be used for transport and storage of samples. Prolonged contact of the sample with ambient air must be avoided to prevent isotopic exchange with water vapor from outside the sample. Such exchange would result in a change of the sample's tritium activity concentration.

3 Analysis

3.1 Principle of the procedure

The carriers sodium iodide, sodium sulfite and sodium carbonate are added to the sample for retaining volatile iodine compounds, carbon-14, phosphorus-32 or sulfur-35 which would compromise the result of the determination of the tritium activity concentration. Afterwards, the sample is distilled.

An aliquot of the distillate is mixed with a suitable scintillation cocktail and measured by liquid scintillation counting (LSC) [2].

Note:

If interfering beta emitters are identified during liquid scintillation measurements, the distillation must be repeated with suitable retention carriers.

If the presence of iodine isotopes can be excluded, e. g. groundwater or drinking water, the addition of sodium iodide carrier is not necessary.

3.2 Sample preparation

A sample preparation is not required.

3.3 Radiochemical separation

3.3.1 Approximately 50 ml of the sample are transferred into a completely dry 100-ml-ground flask, and about 100 mg sodium iodide, 100 mg anhydrous sodium sulfite and 500 mg anhydrous sodium carbonate are added as retention carriers.

3.3.2 The ground flask is connected to a completely dry micro-ground distillation apparatus with a column, e.g. Vigreux column (Figure 1). Subsequent distillation is carried out at a slow rate of approximately 1 drop per second.

Note:

Droplets of the starting liquid must be prevented from direct transport into the distillate, especially if the heated sample solution develops foam.

3.3.3 The first 10 ml of the distillate are discarded.

3.3.4 After a change of the distillate receiving flask, the following 20 ml to 30 ml are collected for later measurement.

Note:

Distillation should be stopped before the starting liquid is completely evaporated.

3.3.5 An aliquot of the distillate is transferred into a counting vial and the mass of the aliquot is determined. The counting vial is filled up with scintillation cocktail.

Note:

A common ratio is 8 ml of distillate mixed with 12 ml of scintillation cocktail. The ideal mixing ratio of distillate and scintillation cocktail has to be determined, if necessary; it depends on the purpose of measurement and on the manufacturer's specifications of the scintillation cocktail.

3.3.6 The counting vial is closed tightly and the mixture is homogenised by shaking.



Fig. 1: Parts of the distillation apparatus: Vigreux column and Liebig condenser

4 Measuring the activity

4.1 General

Tritium is a pure beta emitter with a maximum beta energy of 18,6 keV und a half-life of 12,312 years. The measurement of the sample preparation is carried out in an LSC in an energy range or energy window, respectively, from 0 keV to 18,6 keV. Additionally, the energy range above this window should be monitored for interfering beta emitters or raised background count rate.

The optimisation of this energy window via the maximisation of the so called 'figure of merit (*FoM*)' according to Equation (1) is recommended [2].

$$FoM = \frac{\varepsilon^2}{R_0} = \frac{(R_g - R_0)^2}{A^2 \cdot R_0} \quad (1)$$

Herein are:

- A* activity of the calibration source, in Bq;
- R*₀ background count rate, in s⁻¹;
- R*_g gross count rate of the calibration source, in s⁻¹;
- ε efficiency of the calibration source, in Bq⁻¹ · s⁻¹.

4.2 Calibration

The efficiency ε and the activity-related calibration factor φ_A respectively are commonly developed as a function of the so-called quench parameter. For this, tritium calibration sources with known activity concentrations are used that exhibit different grades of quenching. The calibration sources have to be of the same composition as the counting source.

Note:

The efficiency can alternatively be determined using a calibration source measured in each sample set. The quench of these calibration sources can be controlled and gradually raised by adding increasing amounts of nitromethane, whilst the overall composition, i.e. most importantly the water-scintillation cocktail-ratio, remains unchanged. Further information can be obtained in the General Chapter β -MESS/GRUNDL of this Procedures Manual. It is recommended to select the tritium activity concentration in such a way that the background doesn't contribute significantly to the gross count rate.

The activity-related calibration factor $\varphi_{A,i}$ is calculated for calibration sources with different quenching according to Equation (2).

$$\varphi_{A,i} = \frac{1}{\varepsilon_i} = \frac{A_i}{R_{g,i} - R_0} \quad (2)$$

Herein are:

$\varphi_{A,i}$ activity-related calibration factor of the calibration source i , in $\text{Bq} \cdot \text{s}$;

ε_i efficiency of the calibration source i , in $\text{Bq}^{-1} \cdot \text{s}^{-1}$;

A_i activity of the calibration source i , in Bq ;

$R_{g,i}$ gross count rate of the calibration source i , in s^{-1} ;

R_0 background count rate, in s^{-1} .

The so-called quench (correction) curve is calculated by linear or quadratic regression of the determined activity-related calibration factors. A typical quench curve using a device-specific quench parameter is shown in Figure 2.

Note:

The device-specific quench parameter is automatically calculated by the device software for each measurement. Depending on the calculation method applied, the name of the quench parameter differs, e. g. $tSIE$, SQP , $H\#$, SIS , SIE , SCR .

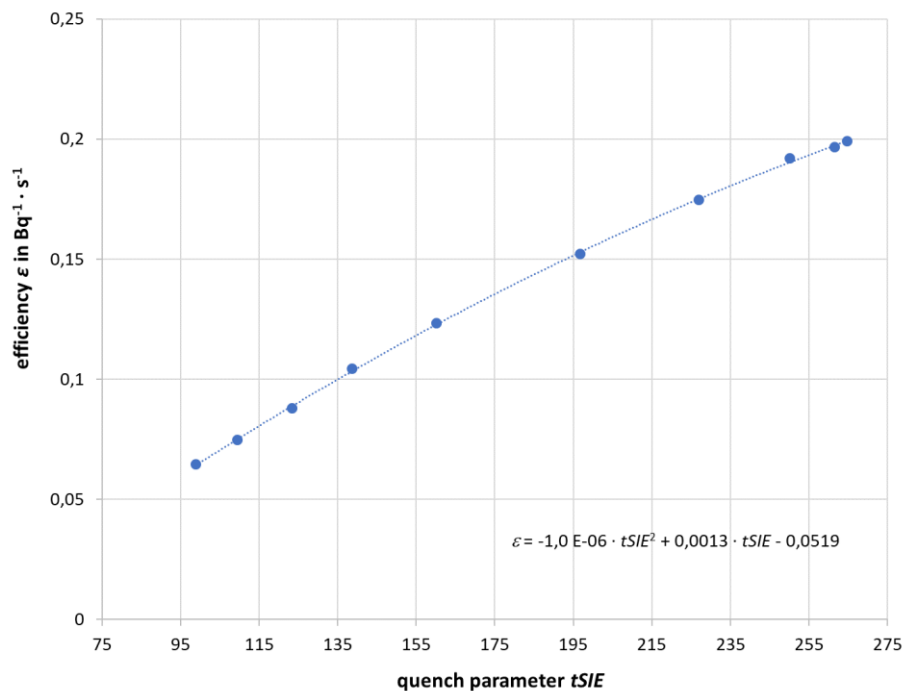


Fig. 2: Quench curve for tritium: efficiency as a function of the quench parameter $tSIE$

4.3 Measurement

Prior to the measurement, the counting source is stored dark and cool, e. g. in the liquid scintillation spectrometer, for a minimum of one hour to avoid interfering chemical luminescence effects. Then, the activity of tritium in the counting source is commonly measured for a duration of 100 minutes. Multiple measurements decrease measurement uncertainty as well as residual chemical luminescence. For each measurement series, tritium-poor water is used for determining the background count rate.

In general, counting vials made of polyethylene or glass are suitable for this purpose. Advantages and disadvantages of both materials should be considered [3]:

- If polyethylene vials are used, the stability of the counting source is limited to a few days due to the evaporation of volatile components of the scintillation cocktail. Therefore, cooling of the counting sources is recommended to decrease evaporation rates.
- The K-40 content in glass counting vials significantly increases background count rates. Special counting vials with low K-40 content are commercially available and their use is recommended for low-level measurements.

5 Calculation of the results

5.1 Equations

5.1.1 Output quantity

The activity concentration of tritium at the time of sampling is calculated according to Equation (3):

$$c = \frac{\varphi_A}{V} \cdot e^{\frac{\ln 2}{t_{H-3}} t_A} \cdot (R_g - R_0) = \varphi \cdot R_n \quad (3)$$

Herein are:

- R_g gross count rate of the prepared sample, in s^{-1} ;
- R_n net count rate of the prepared sample, in s^{-1} ;
- R_0 background count rate of the measurement system, in s^{-1} ;
- t_{H-3} half-life of tritium; in s;
- t_A time span between sampling (middle of sampling period) and measurement, in s;
- V volume of the aliquot used for measurement, in l;
- φ procedural calibration factor, in $Bq \cdot s \cdot l^{-1}$;
- φ_A activity-related calibration factor, in $Bq \cdot s$.

5.1.2 Standard uncertainty of the output quantity

The combined standard uncertainty of the activity concentration is calculated according to Equation (4):

$$u(c) = c \cdot \sqrt{u_{\text{rel}}^2(R_n) + u_{\text{rel}}^2(\varphi)} \quad (4)$$

The relative standard uncertainty of the net count rate, or type A uncertainty respectively, is obtained from Equation (5)

$$u_{\text{rel}}(R_n) = \frac{u(R_n)}{R_n} = \frac{1}{R_n} \cdot \sqrt{\frac{R_g}{t_m} + \frac{R_0}{t_0}} \quad (5)$$

and the relative standard uncertainty of the calibration factors, or the type B uncertainty respectively, is calculated according to Equation (6):

$$u_{\text{rel}}(\varphi) = \frac{u(\varphi)}{\varphi} = \sqrt{u_{\text{rel}}^2(\varphi_A) + u_{\text{rel}}^2(V)} \quad (6)$$

Herein are in both Equations (5) and (6):

- t_m duration of measurement, in s;
- t_0 duration of background measurement, in s;
- $u(c)$ standard uncertainty of the activity concentration, in Bq · l⁻¹;
- $u(R_n)$ standard uncertainty of the net count rate, in s⁻¹;
- $u(\varphi)$ standard uncertainty of the procedural calibration factor, in Bq · s · l⁻¹;
- $u_{\text{rel}}(R_n)$ relative standard uncertainty of the net count rate;
- $u_{\text{rel}}(V)$ relative standard uncertainty of the volume;
- $u_{\text{rel}}(\varphi)$ relative standard uncertainty of the procedural calibration factor;
- $u_{\text{rel}}(\varphi_A)$ relative standard uncertainty of the activity-related calibration factor.

5.2 Worked example

In the worked examples of the Sections 5.2 and 6.2, the interim results and the result are given with four significant digits. Deviations from the calculated values are possible when using another number of significant digits.

With the following values

R_g	=	0,075 s ⁻¹ ;	R_0	=	0,061 s ⁻¹ ;
t_m	=	6 000 s;	t_0	=	18 000 s;
t_A	=	10,37 · 10 ⁶ s;	$t_{\text{H-3}}$	=	0,3885 · 10 ⁹ s;
V	=	0,008 l;	$u_{\text{rel}}(V)$	=	0,02;
φ_A	=	4,17 Bq · s;	$u_{\text{rel}}(\varphi_A)$	=	0,10.

the procedural calibration factor is calculated as follows:

$$\varphi = \frac{4,17 \text{ Bq} \cdot \text{s}}{0,008 \text{ l}} \cdot e^{\frac{\ln 2}{10,37 \cdot 10^6 \text{ s}} \cdot 0,3885 \cdot 10^9 \text{ s}} = 511,7 \text{ Bq} \cdot \text{s} \cdot \text{l}^{-1}$$

With this, the activity concentration of H-3 according to Equation (3) is

$$c = 511,7 \text{ Bq} \cdot \text{s} \cdot \text{l}^{-1} \cdot (0,075 \text{ s}^{-1} - 0,061 \text{ s}^{-1}) = 7,164 \text{ Bq} \cdot \text{l}^{-1}$$

Both the relative standard uncertainty of the net count rate and the calibration factor are calculated according to Equations (5) and (6), respectively, as follows:

$$u_{\text{rel}}(R_n) = \frac{1}{0,075 \text{ s}^{-1} - 0,061 \text{ s}^{-1}} \cdot \sqrt{\frac{0,075 \text{ s}^{-1}}{6000 \text{ s}} + \frac{0,061 \text{ s}^{-1}}{18000 \text{ s}}} = 0,285$$

$$u_{\text{rel}}(\varphi) = \sqrt{0,10^2 + 0,02^2} = 0,102$$

After changing Equation (4) and using the values above, the standard uncertainty of the activity concentration is determined as:

$$u(c) = 7,164 \text{ Bq} \cdot \text{l}^{-1} \cdot \sqrt{0,285^2 + 0,102^2} = 2,169 \text{ Bq} \cdot \text{l}^{-1}$$

The tritium activity concentration for this worked example is then determined as

$$c = (7,164 \pm 2,169) \text{ Bq} \cdot \text{l}^{-1}$$

5.3 Consideration of the uncertainties

Uncertainty contributions arising from sampling are not taken into account in the framework of this Procedures Manual, as these can depend on many different and often not quantifiable factors.

The standard uncertainty of the calibration factor covers the standard uncertainties of the calibration source activity and the quench parameter. Enrichment effects caused by an incomplete distillation of the sample as well as the standard uncertainties of the measurement duration are negligible.

6 Characteristic limits of the procedure

The calculation of the characteristic limits follows the standard series ISO 11929 [4].

An Excel spreadsheet (see Section 7.1) as well as a project file for the software Uncert-Radio (see Section 7.2) are available on the website of this Procedures Manual.

Further considerations concerning the characteristic limits are to be found in the General Chapter CHAGR-ISO-01 of this Procedures Manual.

6.1 Equations

6.1.1 Decision threshold

The decision threshold of the tritium activity concentration c^* is calculated according to Equation (7):

$$c^* = k_{1-\alpha} \cdot \varphi \cdot \sqrt{R_0 \cdot \left(\frac{1}{t_m} + \frac{1}{t_0} \right)} \quad (7)$$

Herein, $k_{1-\alpha}$ is the quantile of the standard normal distribution of a type I error.

6.1.2 Detection limit

The detection limit of the tritium activity concentration $c^\#$ is calculated according to Equation (8):

$$c^\# = c^* + k_{1-\beta} \cdot \sqrt{[c^\# \cdot u_{\text{rel}}(\varphi)]^2 + \varphi^2 \cdot \left[\frac{c^\#}{t_m \cdot \varphi} + R_0 \cdot \left(\frac{1}{t_m} + \frac{1}{t_0} \right) \right]} \quad (8)$$

Instead of solving Equation (8) by iteration, it can be transformed to the explicit Equation (9)

$$c^\# = \frac{c^* \cdot \psi}{\theta} + \left[1 + \sqrt{1 - \frac{\theta}{\psi^2} \cdot \left(1 - \frac{k_{1-\beta}^2}{k_{1-\alpha}^2} \right)} \right] \quad (9)$$

with the following auxiliary quantities:

$$\theta = 1 - k_{1-\beta}^2 \cdot u_{\text{rel}}^2(\varphi) \quad (10)$$

$$\psi = 1 + \frac{k_{1-\beta}^2}{2 \cdot c^*} \cdot \frac{\varphi}{t_m} \quad (11)$$

Herein, $k_{1-\beta}$ is the quantile of the standard normal distribution of a type II error.

6.1.3 Limits of the coverage interval

In this procedure, the limits of the probabilistic symmetric coverage interval are used.

The lower and upper limits of the coverage interval are calculated according to Equations (12) and (13), respectively. The latter is used to control regulatory discharge limits [1].

$$c^< = c - k_p \cdot u(c) \quad (12)$$

$$c^{\triangleright} = c + k_q \cdot u(c) \quad (13)$$

In the Equations (12) and (13) are:

c^{\triangleleft} lower limit of the coverage interval of the activity concentration, in $\text{Bq} \cdot \text{l}^{-1}$;

c^{\triangleright} upper limit of the coverage interval of the activity concentration, in $\text{Bq} \cdot \text{l}^{-1}$.

k_p quantile of the standard normal distribution for probability p ;

k_q quantile of the standard normal distribution for probability q ;

Note:

In this case, the limits of the coverage interval are symmetrical with respect to the output quantity and the quantiles for $\gamma = 0,05$ are $k_p = k_q = k_{1-\gamma/2} = 1,96$. These can be calculated with Microsoft Excel® using the statistical formulae $\text{NORM.S.INV}(p)$ or $\text{NORM.S.INV}(q)$, approved for the versions 2010 to 2019.

Detailed information is available in Section 5.3 and Annex F of the General Chapter CHAGR-ISO-01 of this Procedures Manual.

6.2 Worked examples

Using the results of the worked example of Section 5.3 and $k_{1-\alpha} = 1,645$ [1], the following detection limit results from Equation (9):

$$c^* = 1,645 \cdot 511,7 \text{ Bq} \cdot \text{s} \cdot \text{l}^{-1} \cdot \sqrt{0,061 \text{ s}^{-1} \cdot \left(\frac{1}{6000 \text{ s}} + \frac{1}{18000 \text{ s}} \right)} = 5,87 \text{ Bq} \cdot \text{l}^{-1}$$

With $k_{1-\beta} = 1,645$ and the auxiliary quantities θ and ψ , determined according to Equations (10) and (11)

$$\theta = 1 - 1,645^2 \cdot 0,102^2 = 0,9718$$

$$\psi = 1 + \frac{1,645^2}{2 \cdot 5,87 \text{ Bq} \cdot \text{l}^{-1}} \cdot \frac{511,7 \text{ Bq} \cdot \text{s} \cdot \text{l}^{-1}}{6000 \text{ s}} = 1,0204$$

the detection limit is determined according to Equation (9) as follows:

$$c^{\#} = \frac{5,87 \text{ Bq} \cdot \text{l}^{-1} \cdot 1,0204}{0,9718} \cdot \left[1 + \sqrt{1 - \frac{0,9718}{1,0204^2} \cdot \left(1 - \frac{1,645^2}{1,645^2} \right)} \right] = 9,8 \text{ Bq} \cdot \text{l}^{-1}$$

Note:

Detection limits of approximately $10 \text{ Bq} \cdot \text{l}^{-1}$ are realistic for a minimum sample volume of 8 ml. Extending the measurement duration to approximately 500 minutes (sample and background likewise), a detection limit of about $5 \text{ Bq} \cdot \text{l}^{-1}$ can be achieved.

Calculating the lower and upper limits of the coverage interval according to Equations (12) and (13), using the quantiles $k_p = k_q = 1,96$, yields:

$$c^{\Delta} = 7,164 \text{ Bq} \cdot \text{l}^{-1} - 1,96 \cdot 2,169 \text{ Bq} \cdot \text{l}^{-1} = 2,913 \text{ Bq} \cdot \text{l}^{-1}$$

$$c^{\nabla} = 7,164 \text{ Bq} \cdot \text{l}^{-1} + 1,96 \cdot 2,169 \text{ Bq} \cdot \text{l}^{-1} = 11,42 \text{ Bq} \cdot \text{l}^{-1}$$

7 Software supported calculation

7.1 View of the Excel spreadsheet

Procedure for determining the tritium activity concentration in waste water

H-H-3-AWASS-01

Version June 2022

Procedures manual for monitoring of radioactive substances in the environment and of external radiation (ISSN 1865-8725)

SAMPLE IDENTIFICATION: sample 1

#Number of parameters p	8
k.alpha	1,645
k.beta	1,645
gamma	0,05

Create Excel variables!

User-Input:	Input of values
	Definition Excel variables
	Input of Excel formulae
Excel-VBA:	#Keywords
	Values from Vbasic

Data input:		variable names:			Uncertainty budget:		
	#Values of parameters p	Unit	Excel variable	Input values	StdDev	partial derivatives budget:	uncertainty budget in %
p 1	#Number of gross counts Ng		Ng	450	2,1213E+01	0,0884973	1,8773113
p 2	duration of measurement		tm	6000	0	-0,006637	0
p 3	background count rate		R0	0,061	1,8409E-03	-530,9838	0,9774847
p 4	duration of background measurement		t0	18000	0	0	0
p 5	half life of tritium		_tH3	3,89E+08	0	-3,54E-10	0
p 6	sampling period		tA	1,04E+07	0	1,326E-08	0
p 7	volume of aliquot used for measurement		V	0,008	1,6000E-04	-929,2207	0,1486753
p 8	activity-related calibration factor		_phiA	4,17	4,1700E-01	1,7826795	0,7433773
(List can be continued here)							
Model section		c = phix * Rn					
Auxiliary equations h		(Formulae)					
h 1	#Gross count rate Rg	1/s	Rg	0,075			
h 2	decay factor for tritium		_f1	1,0187E+00			
(List can be continued here)							
	#Net count rate Rn	1/s	Rn	1,4000E-02			
	#Calibration factor, proc.dep.	Bq*s/l	phix	5,3098E+02			
	#Value output quantity	Bq/l	Result	7,4338E+00	6,8645134	<-- output value modifiable by VBA	
	#Combined standard uncertain	Bq/l	uResult	2,2482E+00			
	#Decision threshold	Bq/l		3,2159E+00			
	#Detection limit	Bq/l		6,8645E+00			
further derived values							
	Auxiliary quantity Omega		Omega	9,9953E-01			
	Best estimate	Bq/l	BestEst	7,4376E+00			
	Uncertainty best estimate	Bq/l		2,2419E+00			
	Lower limit of the coverage interval	Bq/l		3,0449E+00			
	Upper limit of the coverage interval	Bq/l		1,1841E+01			

Calculate!

The corresponding Excel spreadsheet is available on the website of this Procedures Manual.

7.2 View of the UncertRadio result page

UR UncertRadio: Calculation of uncertainty budget and detection limits - H-H-3-AWASS-01_EN.bxp

File Edit Options Help

Procedure Equations Values, Uncertainties Uncertainty budget Results Text Editor

Final measurement result for c:

Value output quantity:	7.4338	Bq/l
extendend (Std.-)uncertainty:	2.2482	Bq/l
relative ext.(Std.-)uncertainty:	30.243	%
Best Bayesian Estimates:	<input type="checkbox"/> min. Coverage-Intervall	
Value output quantity:	7.4376	Bq/l
extendend (Std.-)uncertainty:	2.2419	Bq/l
lower range limit:	3.0449	Bq/l
upper range limit:	11.841	Bq/l

Coverage factor k: 1.0
Probability (1-gamma): 0.950

Decision threshold and detection limit for c:

Decision threshold (DT):	3.216	Bq/l	Iterations:	1
Detection limit (DL):	6.864	Bq/l	Iterations:	6

k_alpha=1.645, k_beta=1.645 Method: ISO 11929:2019, by iteration

Monte Carlo Simulation:

Number of simul. measurements	100000	<input type="checkbox"/> Values <0 included		
Number of runs:	1	<input type="checkbox"/> min. Coverage interval		
primary estimate:	7.4463	relSD%:	Bq/l	0.096
uncertainty primary estimate:	2.2626	Bq/l	0.224	
Value output quantity:	7.4484	Bq/l	0.096	
extendend uncertainty:	2.2592	Bq/l	0.224	
relative extd.(Std.-)uncertainty:	30.331	%		
lower range limit:	3.2163	Bq/l	0.593	
upper range limit:	12.081	Bq/l	0.158	
Decision threshold (DT):	3.2305	Bq/l	0.406	
Detection limit (DL):	6.7630	Bq/l	0.293	

active run: 1 IT: 9 Start MC

The corresponding UncertRadio project file is available on the website of this Procedures Manual.

8 Catalogue of the chemicals und equipment

8.1 Chemicals

The chemicals used should be of analytically pure quality.

- sodium carbonate, Na_2CO_3 ;
- sodium iodide, NaI: anhydrous;
- sodium sulfite, Na_2SO_3 : anhydrous;
- low-tritium water: e. g. deep groundwater from reservoirs with no exchange with the surface;
- scintillation cocktail: e. g. Quicksafe A.

8.2 Equipment

The following equipment is used for the procedure:

- typical equipment of a radiochemical laboratory;
- distillation apparatus made of glass with ground joints ST/NS 14/23, consisting of:
 - 50 ml-flask (receiving flask);
 - 100 ml-flask (distillation flask);
 - distillation adapter;
 - tube (approx. 30 cm long) as column, e. g. Vigreux column;
 - Liebig condenser;
 - head, e. g. Claisen head;
 - heating source;
- counting vials made of polyethylene (PE) or glass with low K-40 content, nominal volume 20 ml;
- liquid scintillation spectrometer.

References

- [1] KTA 1504:2017, *Monitoring and Assessing the Discharge of Radioactive Substances with Water*.
- [2] L'Annunziata, M. F., Kessler, M. J.: *Chapter 7 - Liquid Scintillation Analysis: Principles and Practice*. In: L'Annunziata, M. F. (Hrsg.): *Handbook of Radioactivity Analysis* Amsterdam: Academic Press, 2012, S. 423-573.
- [3] Krause, W. J.: *Die Eignung verschiedener Messfläschchen und Szintillatorflüssigkeiten zur Bestimmung von Tritium in Wasser*. Zeitschrift für Wasser- und Abwasser-Forschung, 1985, Vol. 18 (3), S. 141-160.
- [4] Standard series ISO 11929:2019, *Determination of the characteristic limits (decision threshold, detection limit and limits of the coverage interval) for measurements of ionizing radiation — Fundamentals and application (Parts 1 to 3)*.