

# The determination of tritium (tritiated water) activity concentration by alkaline distillation and liquid scintillation counting 1999

## Methods for the Examination of Waters and Associated Materials

This booklet contains a method for the determination of tritium (tritiated water) activity concentration. Limited performance data are available and it is left to users to evaluate the method in their own laboratories.

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# About this series

## Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, waste water and effluents as well as sewage sludges, sediments and biota. In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

## Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests reported. These methods should be capable of establishing within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results encompassing at least ten degrees of freedom from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available. An indication of the status of the method is shown at the front of this publication on whether the method has undergone full performance testing.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

## Standing Committee of Analysts

The preparation of booklets within the series "Methods for the Examination of Waters and Associated Materials" and their continuing revision is the responsibility of the Standing Committee of Analysts. This committee was established in 1972 by the Department of the Environment and is now managed by the Environment Agency. At present, there are nine working groups, each responsible for one section or aspect of water quality analysis. They are:

- 1 General principles of sampling and accuracy of results
- 2 Microbiological methods
- 3 Empirical and physical methods
- 4 Metals and metalloids
- 5 General non-metallic substances
- 6 Organic impurities
- 7 Biological methods
- 8 Biodegradability and inhibition methods
- 9 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with this method are listed at the back of this booklet.

Publication of new or revised methods will be notified to the technical press. An index of methods is available from the Secretary.

Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary.

Dr D Westwood  
*Secretary*

July 1999

## Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements compiled with. This should include compliance with the Health and Safety at Work etc Act 1974 and all regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 1988 (SI 1988/1657). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety. These should be consulted and be readily accessible to all analysts. Amongst such publications are; "Safe Practices in Chemical Laboratories" and "Hazards in the Chemical Laboratory", 1992, produced by the Royal Society of Chemistry; "Guidelines for Microbiological Safety", 1986, Portland Press, Colchester, produced by Member Societies of the Microbiological Consultative Committee; and "Safety Precautions, Notes for Guidance" produced by the Public Health Laboratory Service. Another useful publication is "Good Laboratory Practice" produced by the Department of Health.

# The determination of tritium (tritiated water) activity concentration by alkaline distillation and liquid scintillation counting

## Introduction

Tritium in the environment is of natural or man-made origin. Tritium of natural origin is fairly uniform in terms of its activity concentration being produced by cosmic radiation. However, the most significant source of tritium in the environment results from nuclear weapons testing in the atmosphere carried out during the late 1950s and early 1960s. To date, the most important new sources of tritium in the environment are those relating to emissions from nuclear engineering establishments, such as power stations and reprocessing plants. Other contributions arise from the application and processing of isotopes. Despite the low toxicity of tritium, monitoring for its activity concentrations in the environment is necessary in order to follow its circulation in the hydrosphere and biosphere.

## 1 Performance characteristics of the method

1.1 Substance determined	Tritium (tritiated water) activity concentrations in water.
1.2 Type of sample	All types of water including seawater.
1.3 Basis of method	The sample is made alkaline by the addition of sodium carbonate and then distilled. An aliquot of the distillate is mixed with a scintillation solution and counted on an anti-coincidence liquid scintillation counter.
1.4 Range of application	Tritium (tritiated water) activity concentrations from 5 – 10 Bq <sup>l</sup> <sup>-1</sup> . Activity concentrations of tritium larger than 100 Bq <sup>l</sup> <sup>-1</sup> can be accommodated by taking a smaller sample aliquot.
1.5 Standard deviation	See Table 1.
1.6 Limit of detection	The limit of detection depends on the high water capacity liquid scintillation cocktail solution and the liquid scintillation counter. In the inter-laboratory trial, "natural" tritium-containing water with a value of 4 Bq <sup>l</sup> <sup>-1</sup> was reported with 19 degrees of freedom.
1.7 Time required for analysis	Approximately 10 hours per sample, but dependent on the level of activity and the amount of counting required. Analytical output can be improved by use of multiple distillation apparatus, and cycling samples on the liquid scintillation counter.

## 2 Principle

The sample is made alkaline by the addition of sodium carbonate and then distilled. An aliquot of the distillate is mixed with a scintillation solution in a counting vial and then counted on an anti-coincidence liquid scintillation counter.

## 3 Hazards

Regulations set out in the Radioactive Substances Act 1993 control, through site specific authorisations and registrations, the accumulation and disposal of radioactive waste and the keeping of radioactive materials. The regulatory authorities are the Environment Agency for England and Wales and the Scottish Environment Protection Agency for Scotland. The Ionising Radiation Regulations govern the hazards to users of radioactive materials in laboratories.

## 4 Interferences

None are known which are not accounted for in the method.

## 5 Reagents

All reagents should be of analytical grade quality.

- 5.1 Sodium carbonate. Anhydrous.
- 5.2 Tritiated water standard. Tritiated water standards are commercially available at activity levels of between 2 – 50 kBq<sup>l</sup><sup>-1</sup>.

5.3 Low tritiated water standard. A suitable quantity of tritiated water standard (5.2) should be diluted with low tritium-containing water (5.4) to produce a solution containing approximately 50 Bq<sup>l</sup><sup>-1</sup>. A bulk quantity of this solution should be prepared and used with each batch of samples and stored in air-tight amber glass containers at approximately 5 °C.

5.4 Low tritium-containing water. This is water that has been characterised with a low tritium content. This may be produced from de-ionised water using commercially available systems or obtained commercially.

5.5 High water capacity liquid scintillation cocktail solution. This may be obtained commercially, but should be used so that, for example equal volumes of sample and liquid scintillation cocktail solution remain in a stable homogenised single-phase state.

## 6 Apparatus

- 6.1 Liquid scintillation counter. This should, preferably, be of a low background type.
- 6.2 Distillation equipment. For example, 150 ml distillation flasks and other distillation glassware, such as Leibig condensers and distillation heads.
- 6.3 Low background liquid scintillation vials. For example, plastic vials with a capacity of approximately 25 ml.

## 7 Sample collection and preservation

The water sample should be taken in glass bottles and stored at approximately 5 °C in the dark. Analysis should be carried out as soon as possible after sampling.

## 8 Analytical procedure

Step	Procedure	Notes
8.1	Measure approximately 75 ml of a well-shaken sample, a low tritiated water standard (5.3) (for quality control purposes) and a low tritium-containing water blank (5.4) and transfer to separate 125 ml round-bottom distillation flasks.	
8.2	Add approximately 1 g of sodium carbonate (5.1) and several anti-bumping granules to each flask (note a).	(a) Check that the resulting solution is alkaline, for example by the use of broad range pH paper.
8.3	Assemble each distillation apparatus and distil the solutions. Reject the initial fraction of distillate, ie up to approximately 20 ml (note b) and when the temperature has stabilised collect approximately 30 ml of distillate. Discard the remaining solution in the distillation flask (note c).	(b) For certain samples, this fraction may contain low boiling point tritium-containing compounds. (c) For certain samples, this fraction may contain high boiling point tritium-containing compounds.
8.4	Prepare duplicate counting vials for each sample, quality control sample and blank solutions. Dispense 10.00 ± 0.01 ml of the distillate into high performance counting vials. To these vials, add 10 ml of a high water capacity liquid scintillation cocktail solution (5.5). Secure the caps on the vials and shake well.	

Step	Procedure	Notes
8.5	A counting vial is also prepared containing a standard calibration solution using 1.00 ± 0.01 ml of a tritium standard solution (5.2), 9.00 ± 0.01 ml of low tritium-containing water (5.4) and 10 ml of a high water capacity liquid scintillation cocktail solution (5.5). Secure the cap on the vial and shake well.	
8.6	The vials are loaded onto a low background liquid scintillation counter, (note d) and allowed to "dark" acclimatise for at least 1 hour.	(d) The counter should be optimised for counting tritium. It should be noted that higher energies may be present.
8.7	The vials are counted for at least 500 minutes (note e). Using manufacturer's procedures, check whether quenching has occurred. For example, compare the channel ratio for the sample against the ratio obtained for the standard to ensure no quenching has occurred in the sample vials.	(e) Alternatively, a preset condition of 10,000 counts can be used.
8.8	If no quenching has occurred, calculate the tritium activity of the sample, as described in section 9.1.	
8.9	If quenching has occurred, one of the vials can be spiked with 0.100 ± 0.001 ml of a tritiated water standard (5.2). The solution is re-acclimatised and re-counted. The difference in counts enables the counts due to the spike to be determined, and therefore, a counting efficiency. Hence, the activity concentration of the sample can be calculated as described in section 9.2.	

## 9 Calculation

9.1 Activity concentration if no chemical quenching occurs is given by:

$$C_c = (C_s / T_s) - (C_b / T_b)$$

where  $C_c$  is the corrected counts per second  
 $C_s$  is the count obtained for the sample  
 $C_b$  is the count obtained for the blank  
 $T_s$  is the count time of the sample (seconds)  
 $T_b$  is the count time of the blank (seconds)

and  $E_c = ((C_{std} / T_{std}) - (C_b / T_b)) / A_{std}$

where  $E_c$  is the efficiency of counting (tritium)  
 $C_{std}$  is the count obtained for the standard  
 $T_{std}$  is the count time of the standard (seconds)  
 $A_{std}$  is the activity of the standard counted (Bq)

and  $T_a = (C_c \times 1000) / (E_c \times V)$

where  $T_a$  is the tritium activity (Bq/l)  
 $E_c$  is the efficiency of counting (tritium)  
 $V$  is the volume of sample counted (ml), normally 10 ml.

9.2 Activity concentration if chemical quenching occurs is given by:

$$C_c = (C_s / T_s) - (C_b / T_b)$$

where  $C_c$  is the corrected counts per second  
 $C_s$  is the count obtained for the sample  
 $C_b$  is the count obtained for the blank  
 $T_s$  is the count time of the sample (seconds)  
 $T_b$  is the count time of the blank (seconds)

and  $C_{cs} = (C_{spk} / T_{spk}) - (C_s / T_s)$

where  $C_{cs}$  is the corrected count per second for the spike  
 $C_{spk}$  is the count obtained for the spike  
 $T_{spk}$  is the count time of the spiked sample

and  $E_c = (C_{cs} - (C_b / T_b)) / A_{std}$

where  $E_c$  is the efficiency of counting (tritium)  
 $A_{std}$  is the activity of the standard counted (Bq)

and  $T_a = (C_c \times 1000) / (E_c \times V)$

where  $T_a$  is the tritium activity (Bq/l)  
 $E_c$  is the efficiency of counting (tritium)  
 $V$  is the volume of sample counted (ml), normally 10 ml.

**Table 1 Performance data**

The following results were obtained in an inter-laboratory trial using two natural waters, prepared by spiking water with tritiated water standards:

Laboratory	1	2	3	4	Mean	Standard deviation
Sample A	11.40	9.62	14.29	13.00	12.16	2.10(19)
	12.80	12.00	9.14	18.00		
	12.60	12.07	14.12	12.00		
	10.90	10.81	12.43	14.00		
	11.40	11.29	8.27	13.00		
Sample B	34.70	33.09	34.47	32.00	33.78	1.71(19)
	34.60	33.48	34.99	34.00		
	36.90	33.32	31.27	30.00		
	36.00	35.06	34.44	33.00		
	36.20	32.93	32.12	33.00		

Units expressed as Bq l<sup>-1</sup> unless otherwise specified. Figures in brackets represent degrees of freedom.

The collaborative trial was organised by LGC (Teddington).

Participating laboratories included Centre for Environment, Fisheries and Aquaculture Science; NNC Ltd, Waste Checking Laboratory; LGC (Teddington); BNFL, Magnox Generating Group, Technology and Central Engineering Division.

## Analytical Quality Control

- 1 Routine control**

Once a method has been selected for routine use, a system of analytical quality control should be adopted in order to validate the analysis. At least one control standard should be analysed with each batch of samples and the results plotted on a control chart. Corrective action should be taken if one value falls outside of the action limit (at  $\pm 3s$ ) or two consecutive values exceed the warning limit (at  $\pm 2s$ ). As more data are acquired, the standard deviation,  $s$ , should be updated and the control chart limits re-calculated.
- 2 Estimation of the accuracy of analytical results using these procedures**

None of the procedures given in this booklet has been thoroughly investigated for all types of samples and before general use, the accuracy achievable should be known. It would be of great value if analysts using these procedures would estimate the accuracy of their own analytical results and report their findings to the Secretary of the Standing Committee of Analysts.

## Address for correspondence

However well procedures may be tested, there is always the possibility of discovering hitherto unknown problems. Analysts with such information are requested to contact the Secretary of the Standing Committee of Analysts at the address given below.

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