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.
Contents

About this series
Warning to users
The determination of tritium (tritiated water) activity concentration by alkaline distillation and liquid scintillation counting

Introduction
1 Performance characteristics of the method
2 Principle
3 Hazards
4 Interferences
5 Reagents
6 Apparatus
7 Sample collection and preservation
8 Analytical procedure
9 Calculation

Table 1 Performance data

Analytical quality control

Address for correspondence

Members assisting with this method

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 requirements for performance generally relate to maximum tolerable values for total error (random and systematic error) or 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.

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 complied 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.

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

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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/l1. Activity concentrations of tritium larger than 100 Bq/l1 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/l 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 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 Environmental 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 mBq/l1.

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 ºC 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. (a) Check that the resulting solution is alkaline, for example by the use of broad range pH paper.

8.2 Add approximately 1 g of sodium carbonate (5.1) and several anti-bumping granules to each flask (note a). (b) For certain samples, this fraction may contain low boiling point tritium-containing compounds.

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). (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.

8.5 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) to produce a solution containing approximately 50 Bq/l. 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 ºC.

8.6 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.

8.7 Tritium (tritiated water) activity concentrations in 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.
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 $E_c = ((C_{std} / T_{std}) - (C_b / T_b)) / A_{std}$

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

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

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)

**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:

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>Mean</th>
<th>Standard deviation</th>
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</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>11.40</td>
<td>9.62</td>
<td>14.29</td>
<td>13.00</td>
<td>12.80</td>
<td>12.00</td>
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<tr>
<td>Sample B</td>
<td>34.70</td>
<td>33.09</td>
<td>34.47</td>
<td>32.00</td>
<td>34.60</td>
<td>33.48</td>
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<td>35.06</td>
<td>34.44</td>
<td>33.00</td>
<td>36.30</td>
<td>32.93</td>
</tr>
</tbody>
</table>

Units expressed as Bq/l 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 ± 3s) or two consecutive values exceed the warning limit (at ± 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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