



ENVIRONMENT AGENCY

Guidance on the measurement of tritium in environmental samples (2005)

Methods for the Examination of Waters and Associated Materials

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This booklet contains guidance on the measurement of tritium in environmental matrices.

Whilst this booklet may report details of the materials and equipment actually used, this does not constitute an endorsement of these products but serves only as an illustrative example. Equivalent products are available and it should be understood that the performance characteristics of the method might differ when other materials are used. It is left to users to evaluate methods 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, soil (including contaminated land) 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. 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 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.

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 booklet are listed at the back of the booklet.

Publication of new or revised methods will be notified to the technical press. If users wish to receive copies or advance notice of forthcoming publications, or obtain details of the index of methods then contact the Secretary on the Agency's internet web-page (<http://www.environment-agency.gov.uk/nls>).

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
August 2004

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 the Radioactive Substances Act 1993, and all regulations made under these Acts, particularly the Ionising Radiations Regulations 1999 (SI 1999/3232) together with the associated Approved Code of Practice and Guidance (L121) and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). 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.

Glossary

Batch correction factor	A correction factor used to adjust the results of a batch of samples based on the recovery of a standard solution analysed as part of the analytical batch. For example, if the recovery of the standard solution is 90%, the correction factor would be 100/90.
Beta emitter (β -emitter)	In an unstable nucleus, a neutron is converted to a proton, a negative electron and an anti-neutrino. The electron is emitted from the nucleus, and this is termed negative beta emission.
Conversion efficiency	The effectiveness by which the method converts tritiated organic compounds contained in a sample to tritiated water.
Counting windows	These are set up within the software of the liquid scintillation counter. They enable the counts in different energy regions within the spectrum to be integrated.
Dead water	Water with a negligible tritium content (less than 0.1 Bq/l) often obtained from deep bore-holes.
Fouling	The process by which the surface of the catalyst becomes physically blocked, reducing its active surface area.
Hydrogen isotopes	Three isotopes of hydrogen exist, i.e. tritium (^3H or T) deuterium (^2H or D) and hydrogen (H). The latter isotopes are not radioactive and occur in relative abundances of approximately 0.015% and 99.985% respectively.
Liquid scintillation cocktail	A mixture of substances that absorbs the energy of beta radioactive decay and produces light flashes.
Liquid scintillation cocktail external standard	Usually, a high activity radioactive source, for example ^{133}Ba or ^{226}Ra forming part of the liquid scintillation counter. At the beginning of the counting period, the external standard is placed in a position next to the sample. The resultant shape of the spectra that the instrument software package produces provides a measure of the degree of quenching of the sample.
MeV	Million electron volts.
Sintering	The process by which the active surface area of a catalyst is decreased. This is often due to heating-cooling cycles that increase the crystal size in the catalyst, effectively reducing surface area.
Trapping efficiency	A mathematical expression used to calculate the efficiency of the process used for trapping tritiated water at the post-oxidation stage. For example, if the amount of tritiated water in the trap is 90 % of the theoretical amount, the correction factor would be 100/90.
Tritiated water	A mixture of one or more of the following compounds, $^3\text{H}_2\text{O}$ (T_2O); $^3\text{H}^2\text{HO}$ (TDO); ^3HHO (THO).

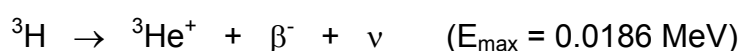
Guidance on the measurement of tritium in environmental samples

1 Aim

The aim of this document is to provide readers with guidance on the complex issues surrounding the measurement of tritium (especially in environmental samples) and to encourage best practice. This booklet gives an overview of the two most common techniques used for measuring tritium in environmental samples and complements guidance given elsewhere in this series⁽¹⁾. Guidance on making valid measurements and liquid scintillation counting (which plays a vital role in such measurements) is also given.

2 Background

Tritium (^3H) is a low energy (weak) β -emitter with a half-life of 12.33 years, decaying with a β -emission of:



Tritium occurs naturally in the environment in low concentrations and is produced in the upper atmosphere by the interaction of high-energy cosmic neutrons:



In the upper atmosphere, tritium is oxidised to tritiated water, $^3\text{H}_2\text{O}$, $^3\text{H}^2\text{HO}$ and ^3HHO (sometimes written as T_2O , TDO and THO respectively) and eventually mixes with surface water. For water isolated from the atmosphere, tritium is a major source of ^3He . The natural abundance of tritium is often expressed in tritium units (TU).

$$1 \text{ TU} = \begin{array}{l} 1 \text{ } ^3\text{H} \text{ atom per } 10^{18} \text{ H atoms} \\ 1.100 \times 10^{-19} \text{ mol/g of pure water (H}_2\text{O)}. \end{array}$$

More commonly, in environmental measurements, tritium concentrations are expressed in terms of activity.

$$1 \text{ TU} = 0.118 \text{ Bq/l}$$

Since the 1950s, tritium has been discharged into the environment as a result of routine emissions by the nuclear power industry, as a consequence of nuclear weapons production and testing, and from civilian uses often related to the production of isotopically-labelled organic compounds. Chemical compounds containing tritium vary widely, and whilst much tritium is found as tritiated water, there is increasing interest in organically bound tritium (OBT).

3 Definition of organically bound tritium

Whilst there have been many attempts to define organically bound tritium, there is still great debate over these definitions and the interpretations given to them. Organically bound tritium may be regarded as being 'exchangeable' or 'non-exchangeable'. Most organic compounds (for example amines, alcohols and thiols) and compounds containing α -keto groups contain some exchangeable hydrogen atoms; some contain non-exchangeable hydrogen atoms. The carbon-tritium bond ($^3\text{H-C}\equiv$) is generally stable except in the presence of strong acids, strong bases or catalysts. Tritium bonded in this stable

manner is generally referred to as non-exchangeable OBT⁽²⁾.

An alternative definition widely used in industry is based on the analytical procedures used to measure total tritium and tritiated water. Generally, total tritium is measured by a technique involving combustion or wet oxidation procedures, and tritiated water is measured following a distillation technique⁽¹⁾. The difference in these measurements is then defined as OBT. Thus:

$$\text{OBT} = \text{total tritium} - \text{tritiated water}$$

The term, OBT, is a general term and may cover or include many hundreds of organic compounds, many of which possess greatly differing chemical and/or biological properties. In addition, there is a range of techniques that can be used to separate the tritiated water and OBT components. These techniques include distillation, fractional distillation and specific solvent or solid phase extraction procedures. In view of the wide range of techniques available, and the range of organic compounds that may be present (especially in liquid samples) it is unlikely that a single technique will be appropriate for all of the tritiated organic chemicals that may need to be considered. For example, when methanol is tritiated, the tritium may be present in exchangeable (³HO-) and non-exchangeable (³HC≡) forms. Hence, if tritium is to be determined the aqueous methanolic distillate may contain non-exchangeable tritium (as a result of the co-distillation of tritiated methanol) as well as exchangeable tritium (as tritiated water). However, the result will be determined and reported as tritiated water. Thus it may be that volatile forms of OBT will be present in the fraction that is assumed to be tritiated water. This fraction will therefore be over-reported in terms of its tritiated water content, and the OBT fraction (when calculated by difference of the total tritium and tritiated water) will consequently be under-reported in terms of its OBT content.

4 The difficulties of tritium measurements

Tritium can be extremely difficult to measure, especially when bound up in a complex environmental matrix. Its beta emissions are of such low energy that the energy may be attenuated before it is able to reach a suitable detector, or may not even be detected. Also, techniques, such as liquid scintillation counting, which are used routinely to measure low-energy beta emissions, suffer from an effect referred to as quenching. This quenching effect further reduces the chances of detection. Some tritiated compounds are very volatile and may evaporate prior to analysis. Other tritiated compounds may not be oxidised completely, especially if the temperature of oxidation or combustion is not sufficiently high. For these reasons, it is important that appropriate techniques are used to separate and quantitatively detect tritium in complex environmental matrices.

4.1 Potential interferences

Prior to analysis, it is essential that analysts possess a thorough understanding of the sample types and matrices that need to be analysed. This will facilitate the determination of tritium and help ascertain whether the presence of other radionuclides interferes in the analysis. Analytical methods for tritium measurements should be robust and interfering radionuclides should be eliminated or be taken into account. Examples of potential interferences include:

²²²Rn: When ²²⁶Ra is present in the sample, the interference from ²²²Rn can be relatively easy to identify, i.e. via the alpha component of the liquid scintillation spectrum, and

can be eliminated from water at the end of the oxidation stage by purging the water with nitrogen.

²¹⁰Pb: This interference should be easily identified by its spectrum. If this radionuclide is found to be a problem, a distillation (of the water collected post-oxidation) carried out at low temperature should eliminate this.

⁹⁹Tc: This interference should be readily identified by its spectrum. If this radionuclide is found to be a problem, a subsequent distillation stage can be introduced under alkaline conditions, which should retain the technetium.

5 Total tritium measurements

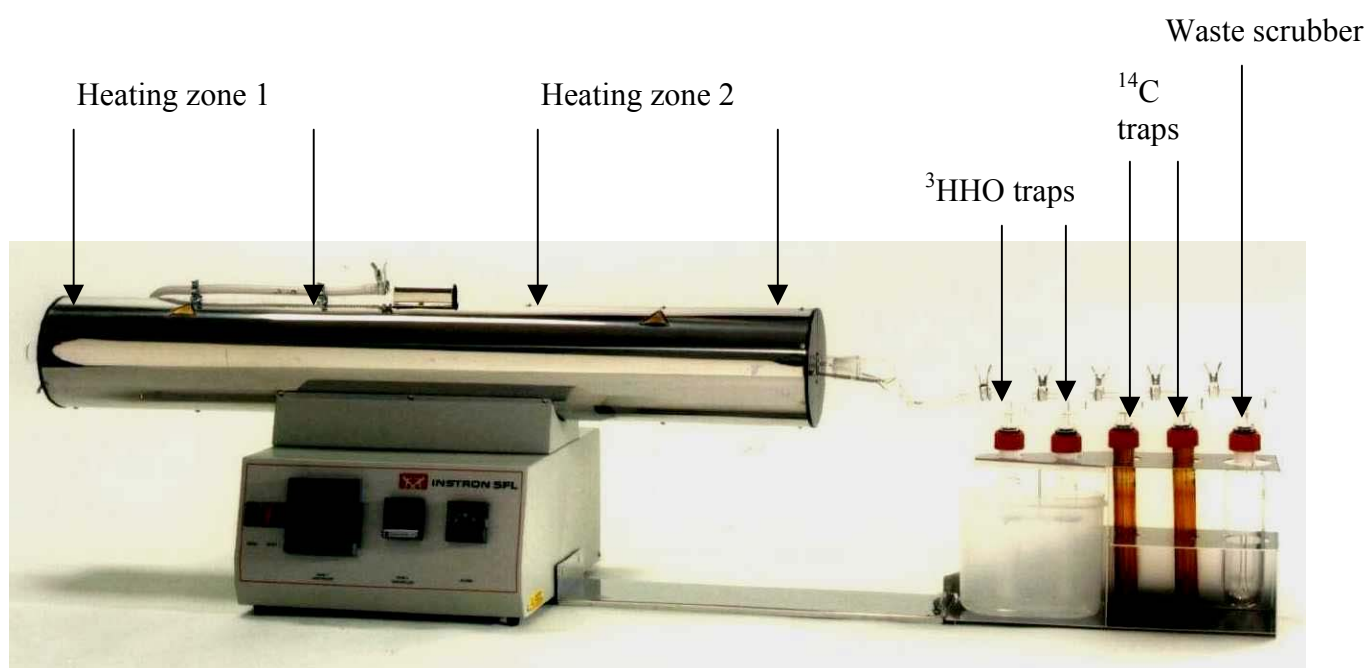
5.1 Combustion techniques

Combustion techniques rely on the controlled and complete oxidation of organic compounds, at elevated temperatures in an oxygen-rich environment. The tritium (as tritiated water) and other forms of water are removed and subsequently measured by liquid scintillation counting. For example, the combustion of tritiated methane with oxygen can be represented as:



Several furnace systems are available commercially, but all rely on the same general principle. One such system, the Instron-SFL™ system, is shown below (Figure 1) for illustrative purposes only. This system represents a typical combustion furnace used for the simultaneous measurement of ³H and ¹⁴C.

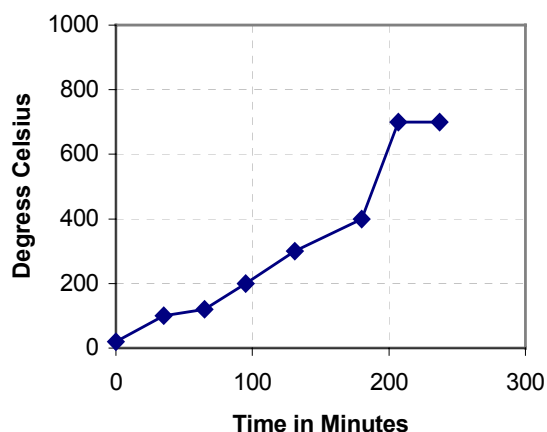
Figure 1 Typical in-line combustion furnace layout



Heating zone 1

The sample is placed in this area of the furnace. The temperature in this zone is capable of being ramped to 750 °C. Sample sizes are typically up to 20 g of fresh moist material. If the material appears very dry, “dead water” may be added to the sample to act as a carrier. The temperature control enables a variety of temperature profiles to be programmed to suit different sample matrices. Nitrogen is initially passed over the sample to ensure the sample is not too rapidly combusted and approximately mid-way through the oxidation, oxygen is introduced into the system to ensure complete combustion of the sample. A typical temperature profile for a grass sample is shown in Figure 2.

Figure 2 Example of a temperature profile used in the combustion of grass



It is essential that the conditions used are optimised for each matrix to ensure that the rate of combustion is controlled, and that complete combustion of the sample is achieved. The profile should show a series of temperature “ramps” (i.e. periods of increasing temperature) and “dwells” (i.e. periods where a constant temperature is maintained), each of which is optimised for the type of matrix being analysed.

Heating zone 2

This area contains the catalyst, which is maintained at 750 °C for the duration of the combustion, with a flow of oxygen entering the system at an inlet situated between the heating zones. The catalyst used by different manufacturers may differ, and some comprise 0.5 % platinum-coated beads of alumina or copper. Whilst in use, the catalyst can suffer degradation due to processes such as “fouling” or “sintering”, and when these processes begin to occur the catalyst should be replaced. Failure to do so will result in a reduction of the conversion efficiency. Typically, platinum catalysts should be replaced after 20 samples have been combusted. However, this should be verified for different sample matrices.

Tritiated water traps

These traps generally comprise collection tubes contained within an ice bath that facilitates the removal (or trapping) of tritiated and other forms of water. The amount or yield of water trapped should be determined. The tritiated water should be quantitatively transferred to a sample vial and the tritium determined by a suitable technique, for example a liquid scintillation counting technique. Sufficient water should be produced from the combustion

of the sample to enable a suitable count to be made. If the sample is “dry” or low in hydrogen content, then “dead water” should be added to the sample prior to combustion.

¹⁴C traps

Where these traps are fitted, they generally comprise tubes containing an aqueous solution of a suitable amine. This solution absorbs carbon dioxide and hence traps the ¹⁴CO₂. The amount of ¹⁴C is then determined by a suitable technique.

Waste scrubber

Depending on the system, some of the amine solution can evaporate. In order to avoid release of this vapour (and possibly other hazardous vapours caused as a result of the combustion) into the atmosphere these vapours are removed (scrubbed) from the emerging gas stream. Any remaining gases should then be vented via a suitable fume cupboard, or extraction system fitted with a suitable filter.

5.1.1 System evaluation

When the system is set up and prior to undertaking routine analysis, it should be evaluated to identify potential sources of error. In addition, the system should be re-evaluated after a catalyst has been replaced. The system may be evaluated by the combustion of known samples, one of which contains tritium and one which does not. The known organic compounds containing the tritium should be representative of those compounds most likely to be present in the samples requiring analysis. For certain samples, it has been shown that tritiated-glucose and tritiated-sucrose are suitable for use for calibration purposes as these compounds contain tritium in a non-exchangeable form. In other cases where compounds do not easily combust more suitable tritiated compounds should be considered and used as calibration compounds. Hence the choice of compound used for calibration is important. After combustion of the known tritiated compound, the “trapping efficiency” should be calculated. This factor should then be applied to the analysis of unknown samples. When a catalyst is replaced, or other conditions changed, a new factor should be determined.

5.1.2 Useful information

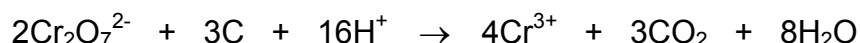
The following information will be useful to analysts setting up combustion systems.

- The system should be properly sealed, as the presence of leaks in the system between the furnace and the waste-scrubber bottles will result in losses of tritium that cannot be estimated.
- The furnace should not be overloaded. Samples containing high levels of fats or oils tend to combust rapidly if not properly controlled.
- The correct temperature profile should be used that is appropriate for the sample matrix being oxidised.
- All glassware should be clean. This will prevent or reduce cross contamination.
- The catalyst should be replaced at appropriate intervals.
- Primary standards often possess a level of activity that is too high for routine use. Dilution of these materials to a suitable working dilution should therefore be carried out, and this should be done in a different location or part of the laboratory to where the analysis is undertaken.
- Some tritiated compounds, for example tritium-thymidine, exhibit unusual reactivity

for the catalyst, especially platinum catalysts, and are not easily combusted. Where samples contain high levels of tritium in these types of compounds, it may be necessary following the first combustion process to carry out a second combustion using “dead water”. This second stage combustion should enable the quantitative recovery of the tritium to be determined.

5.2 Wet oxidation techniques

The principle of this technique is similar to the widely established procedure used to determine chemical oxygen demand⁽³⁾ and relies on the oxidation of organic matter to form carbon dioxide and water under acidic conditions in the presence of dichromate:



where C represents the organic matter in the sample.

The water, including tritiated water, formed as a result of the oxidation process is then distilled and collected in a trapping system.

The sample size used in the analysis depends upon the matrix and the organic matter of the sample, and also on the quantities of reagents used. Typically, 60 ml of the chromic acid reagent may be sufficient to completely oxidise approximately 5 g of wet fish muscle or approximately 10 g of sediment containing low levels of organic matter. The sample should be digested by gently heating the solution for about 2 hours. After the digestion stage is completed, typically, 20 ml of “dead water” is added to the reaction mixture and the whole contents distilled and the water collected. This water should then be distilled a second time, under alkaline conditions, to remove all potential interferences. A suitable technique should then be used to determine the tritium content of the distillate. If results are to be reported on a dry-weight basis, it will be necessary to determine the moisture content of the original sample.

5.2.1 System evaluation

The conditions used should be optimised to ensure that complete oxidation of the sample is achieved. In addition, blank determinations and the recovery of tritiated water in samples containing known amounts of tritiated water should be carried out for each batch of reagents. Typically, a batch of chromic acid reagent may be made for the analysis of up to 100 samples. The recovery factor should be used to determine the batch correction factor. The method should also be validated using the same type of tritiated compounds as described in section 5.1.1.

5.2.2 Useful information

The following information will be useful to analysts setting up wet oxidation techniques. The reaction mixture should not be overloaded (i.e. the volume of chromic acid reagent should be appropriate to the amount of sample requiring oxidation). For example, the appearance of droplets of oil or fatty material in the water following distillation may indicate incomplete oxidation. If this occurs, the analysis should be repeated using smaller quantities of sample or larger volumes of reagents. If smaller amounts of sample are being considered, the analyst should be cognisant of whether the sample still remains representative of the original sample submitted for analysis. When analysing a new

sample matrix, it may be necessary to assess a range of sample sizes to ensure complete oxidation occurs.

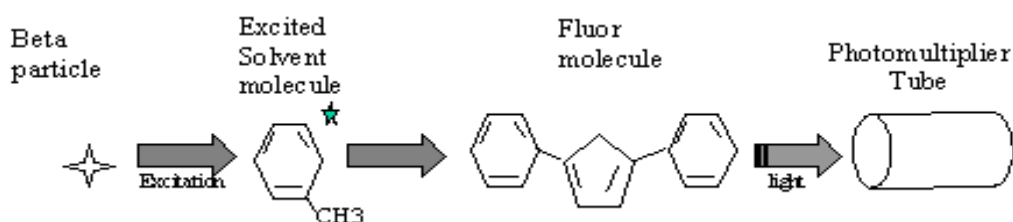
6 Measurement of tritiated water

There are numerous techniques used for the measurement of tritiated water in environmental samples. Most of these are based upon a distillation technique. One method⁽¹⁾ employs an alkaline distillation procedure, followed by liquid scintillation counting of the distillate. Other methods utilise freeze-drying techniques, where the tritiated water is trapped at low temperature and then distilled under alkaline conditions.

7 Liquid scintillation counting

This section describes useful information to enable analysts to avoid some of the pitfalls of the liquid scintillation counting technique. The radioactive sample (for example, the tritiated water following combustion) should be combined with a liquid scintillation cocktail, so that it is in direct contact with a substance possessing the propensity to fluoresce when excited, thus producing scintillations (i.e. photons). A substance, commonly referred to as “fluor” has been shown to be suitable. Figure 3 shows the process whereby a beta particle excites a solvent molecule which then imparts its energy to fluor, the resultant photon being detected by the photomultiplier tube. When a beta-emitting isotope is dissolved in a solvent each radioactive emission results in an excited solvent molecule (i.e. the molecule possesses a higher energy). The excited solvent molecule transfers its energy to the scintillation cocktail, forming electronically excited molecules, which return to an un-excited state by the emission of photons (scintillations). The photomultiplier tube (PMT) converts the photons into electronic pulses (i.e. electric signals), the intensity of which is proportional to the energy of the radiation transferred (i.e. activity present) to the liquid scintillation cocktail. Each emission is termed an event. Most modern liquid scintillation counters employ two PMTs, and are termed coincidence counters. These will record only those counts originating from the sample, and not background, if both PMTs receive the electronic signal within a very small time period.

Figure 3 Summary of liquid scintillation process



The technique relies on the efficient transfer of energy (both electronic and light). Any process, that interferes with these processes (which are not accounted for) are likely to produce erroneous results. The most common process by which the effectiveness of these energy / light transfer processes is reduced is termed “quenching”. This is mainly due to compounds or substances in the sample that interfere with the processes leading to the production and transmission of light. The result is a reduction in the number of photons produced during beta particle energy transfer observed as a reduction in counting efficiency, and a shift of the energy spectrum to lower energy. There are a number of causes of quenching, the most important of which are briefly described in the following

sections. When these effects are ignored, results may be produced that under-estimate the true value.

7.1 Colour quenching

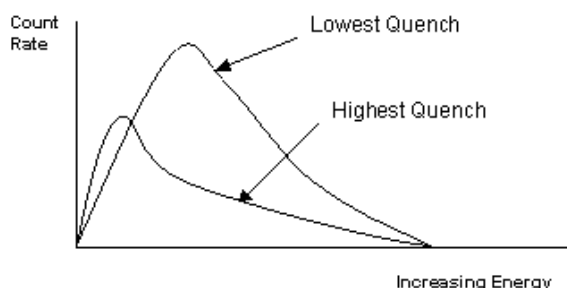
Colour quenching depends on factors such as the colour of the interfering chemical and the path length that the photons travel. These factors need to be taken into account otherwise the true value of the tritium concentration will be under-estimated. The interference occurs after production of photons in the solution. Events that take place close to one PMT will give rise to a large pulse and a smaller pulse in the other PMT. Colour quenching can often be visually identified prior to a sample even being loaded onto the liquid scintillation counter. Normally, if colour is present in the solution, for example in the distillate or after a sample has been combusted in the furnace, this may indicate that the oxidation/combustion process has been incomplete.

7.2 Chemical quenching

Chemical quenching results from the absorption of beta energy (before being converted to photons) by organic molecules that have not been completely oxidised or combusted. In a chemically quenched sample, all energy radiations appear to be equally affected, shifting the spectrum to lower energies. This type of quenching should be highlighted by the instrument software package as a quench-indicating-parameter used in the liquid scintillation counter.

In Figure 4, the effect of quenching is shown. The count rate is reduced as the quenching increases. The sample spectrum indicates that the lowest quenched sample spectrum can be regarded as being the true observed spectrum for the sample. Where the highest quenched sample spectrum is shown represents the situation where there has been chemical quenching that has resulted in a shift in the spectra to lower energy and a reduction in the efficiency, as indicated by a reduced area under the spectral curve.

Figure 4: Example of chemical quenching effect



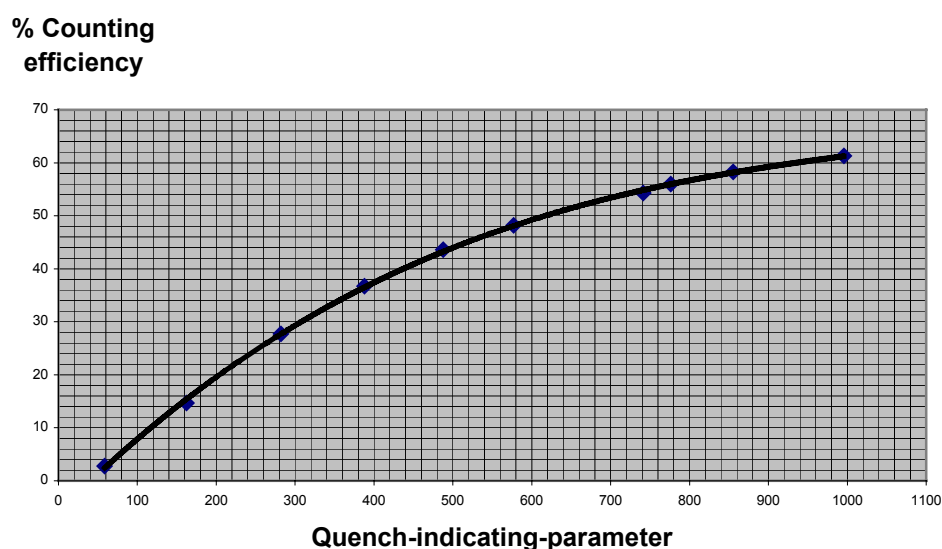
7.3 Quench-indicating-parameters

Modern liquid scintillation counters generally include software packages that provide a simple numerical indication that a significant quenching effect has occurred in the sample. Usually, this numerical indication is often not taken into account by analysts. The value for

the counts per minute (cpm.) in the counting window of interest is often assumed to be absolute. Whilst it is acknowledged that the quench-indicating-parameter may be difficult to interpret for samples that possess activities close to the background value, i.e. samples containing very low levels of tritium, it is possible to generate a meaningful value on which to determine a more accurate value. For samples with very low levels of activity, these samples should be counted first for the desired count time, without using the external standard (built into the counter) and then recounted for 60 seconds, this time using the external standard, to produce the quench-indicating-parameter for each sample. The counting procedure should be carried out in this order since the use of the external standard can result in a slight elevation of the limit of detection. Counting samples in the way indicated reduces this risk.

A quench curve, which is basically a plot of the counting efficiency against the quench-indicating-parameter (specific to the liquid scintillation counter) should be plotted. A typical example of such a curve for ^3H generated on a liquid scintillation counter is given in Figure 5.

Figure 5 Quench curve for ^3H



Quench sets, essentially reference compounds possessing a known quenching effect, are commercially available, and the quench curve should be determined using the same liquid scintillation cocktail as is used for samples analysed routinely. It has been shown that if different liquid scintillation cocktails are used, systematic errors of the order of 20% can result.

When making environmental measurements, the instrument used should be used with the appropriate spectral software package. The “counting windows” set up and fixed by individual manufacturers should not be used, without being optimized for particular combinations of sample and liquid scintillation cocktail. The spectral software package should enable the user to identify potential interferences from other radionuclides that may be present as contaminants. Analytical methods should be robust and potential interferences identified during validation of any analytical procedure.

7.4 Scintillation cocktails

It is very important to choose the correct liquid scintillation cocktail to ensure that a stable counting medium is achieved. Many liquid scintillation cocktails are available commercially, and it is essential that the one chosen is able to cope, for example in the determination of tritiated water, with the amount of water generated from the sample. Where low levels of environmental tritium are to be measured, it is often a compromise between the background signal and the counting efficiency. This relationship is usually called the “figure of merit”, which mathematically is expressed by:

$$\text{Figure of merit} = \frac{\text{Efficiency}^2}{\text{Background}}$$

This relationship is used to optimize the liquid scintillation cocktail and the “counting window”. The larger this value, the lower the limit of detection.

8 Quality control

8.1 Validation of methods

Whilst there are many good references describing procedures for method validation, key issues that the analyst should consider (during the validation of a method for determining tritiated water) include the following:

- (i) Scope – This section describes details of the method’s intention, for example, the measurement of tritium in a range of stated matrices.
- (ii) Repeatability – Analysts should compare the precision of their results, and how consistent the procedure is when analysing the same sample (or different samples) over a period of time using the same equipment, reagents etc.
- (iii) Accuracy – Analysts should compare their results of a reference material with a known value. In some cases, the known value may be a consensus value rather than a true value.
- (iv) Uncertainty of measurement – The overall uncertainty to be applied to the final result should not only relate to the counting uncertainty. An uncertainty, at the 95% confidence level, is normally used, and may include a wide variety of sources including the reference material, calibration of the counter, etc.
- (v) Limit of detection – A number of calculations can be used to calculate the limit of detection. All possess individual advantages and disadvantages.
- (vi) Selectivity – This relates to the specificity of the procedure used for the measurement.
- (vii) Interferences – This is related to a certain extent to the selectivity. For example does the method generate results that are regarded as false positives? It may be that at low concentrations the interference is not significant; but at higher concentrations the interference may have a more significant impact. Robust analytical methods should be developed to minimise all interference effects.
- (viii) Linearity – This should define the operating and calibration range of the detection system.
- (ix) Robustness – This should assess the ability of the method to tolerate small variations in the analytical procedures used. These may include the effects of different operators, different equipment etc.

- (x) Storage – Samples should be analysed as soon as possible after collection. This however, may not always be possible. The conditions of storage can have a crucial effect on the result. For example, if tritiated water is to be measured, samples should not be freeze-dried, unless as part of the determination (see section 6).
- (xi) Supporting documentation – This is an essential part of any validation process.

Any method used routinely in a laboratory should have been properly validated in that laboratory. This will demonstrate that the laboratory can achieve the stated performance of that method.

8.2. Inter-laboratory comparisons

A laboratory should not rely entirely on internal quality control procedures, but should also participate in appropriate and independently organised inter-laboratory comparison exercises. These exercises play a crucial role in demonstrating the laboratory's capabilities. Some of the more important factors for consideration include:

- Is the sample matrix (provided by the scheme organiser) or activity level relevant to the laboratory's needs?
- Are "real" samples provided, or are samples spiked with the determinand of interest?
- Are the reference tritium-containing organic compounds relevant and appropriate to the laboratory's needs?
- Are time-scales appropriate? The time between distribution of the sample and the reporting of results should be controlled so that any problems that arise can be addressed.

8.3 Routine liquid scintillation counting

The performance of any liquid scintillation equipment should be checked on a regular basis to ensure that it operates correctly and is within acceptable limits.

9 References

1. Standing Committee of Analysts, 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*, in this series, Environment Agency.
2. An overview of tritium behaviour in the Severn estuary (UK). *Journal of Radiological Protection*, J L Williams, R M Russ, D McCubbin and J F Knowles, 2001, **21**, pp337-344.
3. Standing Committee of Analysts, Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters 1986 (second edition), *Methods for the Examination of Waters and Associated Materials*, in this series, ISBN 0117519154. A revised draft is being prepared.

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. In addition, if users would like to receive advance notice of forthcoming publications please contact the Secretary on the Agency's web-page.

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