Radiometric techniques for the detection and assessment of tritium in aqueous media - a review

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Abstract

Tritium (^{3}H) is one of the hardest isotopes to detect by most traditional radiometric means due to the low energy of the β^- emission, (β^-_{MEAN} 5.67 keV, β^-_{MAX} 18.59 keV). The high mobility of the isotope in groundwater environments and subsequent entry into the food chain constitutes a radiation safety risk justifying assessment. Accordingly, there is a need to measure ^{3}H accurately and efficiently, often in low concentrations, both in laboratory settings and on-line flow-cells for potential *in situ* measurement requirements. This review covers technologies developed to assess aqueous tritium-containing samples. Of the techniques reviewed, liquid scintillation counting (LSC) is the best performing means of aqueous ^{3}H detection with a minimal detectable activity of 6×10^{-4} Bq L^{-1} for a 195-minute counting time. LSC is also established as the industry standard and is the basis of the first, commercially-available, real-time ^{3}H detection system. This review also covers the other means described in literature for the detection of tritium in aqueous samples, including the use of plastic and inorganic scintillators, imaging plates, both in off-line and on-line modes of operation. Whilst most of these techniques lag LSC in terms of technological maturity, several offer detection sensitivities that could rival LSC, without the need for the sample preparation and waste generation associated with LSC, and providing real-time *in situ* measurements.
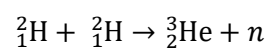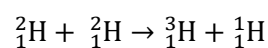
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Introduction

History and Production

Tritium (^{3}H) is a radioactive isotope of hydrogen, with a nucleus consisting of a proton and two neutrons. It was first observed by Oliphant *et al.* (1934) following the bombardment of deuterium-(^{2}H) containing compounds with high-energy deuterium nuclei using one of the earliest particle accelerator built by Sir John Cockcroft and Ernest Walton [1]. Oliphant *et al.* postulated the products from the reaction between the colliding deuterium being either a protium and tritium, or a neutron and helium-3 (see Equation 1). However, they could not isolate the products nor determine whether the tritium or ^{3}He was radioactive. Around the same time other research groups also reported the discovery of tritium [2], [3]. Tritium was identified in isolation by Lozier *et al.*, who measured its relative abundance in a heavy water sample [4]. The determination that tritium, rather than ^{3}He, was radioactive was made by Luis Alvarez in 1939 who noticed the proportion of ^{3}He to be the same in both helium obtained from oil wells and from atmospheric sources was the same, despite the well-borne helium being 70-million-years-old during which time the helium would have decayed if it were radioactive. Alvarez then surmised and proved the radioactivity of ^{3}H, correctly identifying the very low-energy β particles produced in its decay [5],

$$^2_1\text{H} + \ ^2_1\text{H} \rightarrow \ ^3_1\text{H} + \ ^1_1\text{H}$$

$$^2_1\text{H} + \ ^2_1\text{H} \rightarrow \ ^3_2\text{He} + n$$

Eq. 1

Given the low energy of the β emission from tritium, observing the precise radioactive characteristics of tritium proved challenging, with an early estimate of the half-life being 31 ± 8 years [6]. With World War 2 and the Manhattan Project occupying many of the fields' nuclear physicists at the time, further work on the isotope was not restarted until the late 1940s when refined values for its half-life became close to what is now accepted, 12.35 years [7]. Also, around this time, mass production of tritium began as the isotope was used in weapon production, either as gaseous tritium or in the form of solid lithium tritide. The atmospheric testing of these nuclear weapons, from 1945 until the Partial Nuclear Test Ban treaty in 1962, led to the highest of tritium levels in the environment in the form of

radioactive fallout [8]. Following the ban on atmospheric testing, levels of tritium in the environment have steadily decreased to almost pre-testing levels because of its radioactive decay [9].

Aside from the legacy contributions from nuclear weapons testing, anthropogenic tritium (^{3}H) is arises mainly as a by-product of the nuclear fuel cycle, and is formed in nuclear reactors as a result of: neutron capture on hydrogen (predominantly in pressurised water reactors), activation of deuterium in heavy water reactors, in reactors dedicated to the production of tritium itself, as a result of the reprocessing of nuclear fuel and via ternary fission at a rate of approximately 1 tritium atom per 10,000 fissions [10]. Commercial reactors produce about 2 grams of ^{3}H per year (equivalent to 714 TBq), with the ternary fission contribution incorporated predominantly into the fuel pellets and/or cladding surrounding the fuel elements. Activation of ^{10}B, used in control rods and in chemical shim necessary to quench reactivity in light water reactors, produces ^{3}H directly or indirectly via ^{7}Li, see Equation 2 [11], and further via lithium hydroxide used to control pH [12],

$$^{10}\text{B} + n \rightarrow {}^3\text{H} + 2\alpha$$

$$^{10}\text{B} + n \rightarrow {}^7\text{Li} + \alpha$$

$$^7\text{Li} + n \rightarrow {}^3\text{H} + \alpha$$
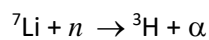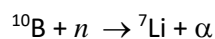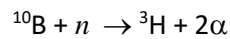
Eq. 2

Thus, the management and treatment of cooling waters leads to the production of tritium, which can be upwards of six times higher in PWRs than BWRs [13]. In line with national government regulations, most nuclear power stations dispose of this tritium via controlled releases to the environment, either by liquid discharge or gaseous release [14]. The distribution of the majority of significant environmental ^{3}H is, therefore, localised to the vicinity of nuclear sites, particularly reprocessing facilities [15], legacy nuclear sites or those that have been affected by significant accidents, e.g., La Hague [16], Sellafield [17] and Fukushima [18]. Following the Fukushima Daiichi nuclear disaster in 2011, large volumes of boric acid infused sea water were used to cool the stricken reactor cores which was retained on-site in vast storage tanks. Given the latent reactivity and heat in the damaged cores, 1.25 million m^3 (containing 870 TBq of ^{3}H) of tritiated water (HTO) was produced as a result.

Radiological Characteristics and Safety Hazard.

Tritium decays by beta emission with an average energy (E_{avg}) of 5.67 keV and a maximum energy (E_{max}) of 18.59 keV [10], Figure 1 shows the energy spectrum of the beta emission from tritium. The very low energy decay means the range of ^{3}H beta particles is very short, its mean being approximately 6 mm in air. As such, ^{3}H presents a negligible external radiation hazard as the β particles cannot

penetrate the outer layer of dead skin. The same radiological properties that make ^{3}H a negligible external radiological hazard render it difficult to detect. The E_{avg} 5.7 keV, E_{max} 18.6 keV β particles do not have sufficient energy to penetrate detector housing materials (typically aluminium) and are therefore unable to reach the detection media inside, e.g., scintillation crystal, gas chamber etc.
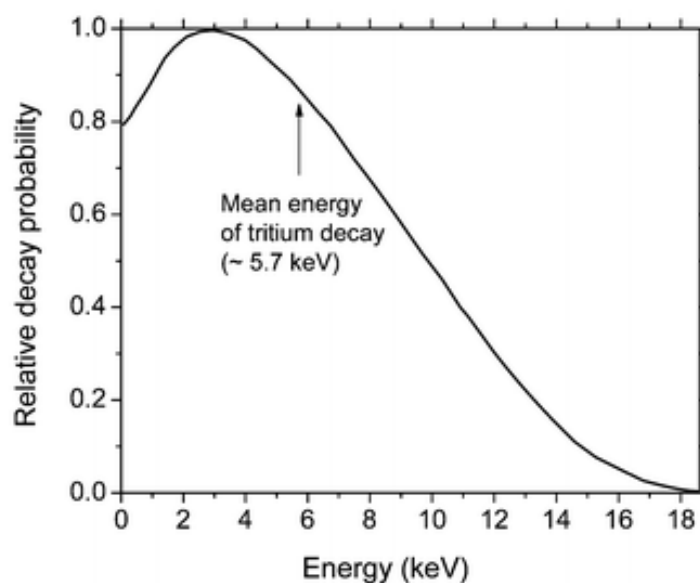

Figure 1. Energy spectrum of the tritium beta emission.

Hazardous exposure to tritium is most likely to occur if tritium is ingested. Due to its chemical equivalence with protium (^{1}H), tritium binds readily with hydroxyl radicals to form tritiated water (HTO). As a result, tritium becomes mobile in the environment particularly in areas of high rates of groundwater flow. It also well known to displace hydrogen in organic matter, forming organically bound tritium (OBT). This displacement of hydrogen for tritium in OBT is a very stubborn reaction to reverse, with 80% of tritium atoms in OBT being bound irreversibly [19]. Based on these characteristics, the potential radiological hazard to humans from ^{3}H comes from internal exposure, via ingestion or, albeit less probable, via inhalation. The beta emission of tritiated water has been calculated to give committed effective dose factor of 1.8 x 10^{-11} Sv Bq^{-1} for ingested HTO and 4.2 x 10^{-11} Sv Bq^{-1} for ingested OBT (values for inhaling these forms are very similar [20]). Consequently, regular consumption of tritium-contaminated food stuffs would likely expose a person to only very low doses of radiation, though at present, this remains a risk that should be mitigated.

When evaluating the risk from ionising radiation, international (ICRP, IAEA, etc.) and national organisations (NRC, HSE) have long adopted the conservative *linear no threshold* (LNT) model. The LNT-model is based on genetics research in the early-mid twentieth century, and controversially, long-term studies of the Hiroshima and Nagasaki bomb survivors [21]. Fundamentally, it assumes any dose of radiation, regardless of magnitude, increases the lifetime risk of developing cancer linearly.

Accordingly, regulatory agencies have established limits on the mass of radioactive materials in food stuffs and drinking waters to ensure that seeks to minimise exposure to the public, weighing the radiological risk against the technical difficulties, time and money needed to control it. This regulatory philosophy has different names in different jurisdictions, *As Low As Reasonably Practicable* (ALARP) in the UK, in the USA it is *As Low as Reasonably Achievable* (ALARA), *So Far As Is Reasonably Practical* (SFAIRP) in Australia. The World Health Organisation have set a limit of 10,000 Bq L^{-1} for tritium in drinking water, national authorities often set even lower limits (100 Bq L^{-1} in the European Union) [22], [23]. Using the limits and the dose coefficients above, a person consuming 2 litres of tritium-contaminated water daily would receive an annual dose of 131 µSv and 1.31 µSv, respectively. As a reference, epidemiological studies have shown increased likelihood of lifetime cancer becoming observed at doses above 100,000 µSv (100 mSv) [24].

Advances in cellular biology, genetics and our understanding of cellular mutations, have increased discussion on the applicability of the use of the LNT model for low dose exposure, such as those commonly received when exposed to tritium [21], [25]. Based on the changing perception of the LNT at low doses and the imminent discharge of significant volumes of HTO from the Fukushima site, researchers have begun to focus on the issue and develop hypersensitive assay systems allow investigators to make estimates of the risks accruing from very low-level HTO exposures [26].

Despite this, the fact remains that in the view of nuclear and safety regulatory agencies there is a hazard to worker and public health posed by tritium, with the principal difficulty being accurate measurement of it. As such, there remains a need for technology to offer a robust and efficient method of detecting tritium in aqueous media. This article seeks to offer a review on the technologies reported in scientific literature and the state-of-the-art for the detection of aqueous tritium.

Detector Performance Measures

For the purposes of comparing the various tritium detection techniques discussed below, it is pertinent to understand the general performance criteria of radiation detectors: efficiency, resolution, and minimal detectable activity.

Efficiency

In simple terms, the absolute efficiency (ϵ_{abs}) refers to the proportion of radioactive quanta detected (q_D) compared all the radioactive quanta emitted from a source (q_E) [27], as per,

$$\epsilon_{abs} = \frac{q_D}{q_E}$$

Eq. 3

There are several factors that influence absolute efficiency, including the geometry of the source-detector setup, the likelihood of radioactive quanta interacting with the detection media, and the energy of the radiations itself. The geometric efficiency can be maximised by having a detector intersect as much of a radiation emission as possible. For an isotropic source, ideally, this would be surrounding a source in all directions covering a solid angle of 4π steradian (4π).

The material efficiency can be improved by selecting a detection media that has a higher likelihood for causing interactions with the anticipated radioactive emissions. For gamma rays this would typically be a material with a high atomic number, i.e., CsI(Tl), for fast neutrons this may be a hydrogenous material, i.e., organic polyvinyl toluene. For low-energy beta particles, this may be materials with a low Z number and a material that produces little backscatter.

The efficiency of a scintillation detector is also affected by *quenching*, particularly in the case of liquid scintillation techniques. Quenching is a term that describes several mechanisms that reduce the transfer of energy between the incident radiation and the resultant energy reaching the PMT. This term includes, *physical quenching*, where physical barriers prevent either the interaction of the radioisotope and the scintillant or block scintillation light from reaching the PMT; *chemical quenching*, where beta particles are absorbed by materials in the solutions that do not cause scintillation, or interaction of a quenching agent with the beta-excited scintillant before the scintillant has relaxed back to its ground state; and *colour quenching* (or optical quenching), where the scintillation light is absorbed within the sample before it reaches the photocathode and PMT.
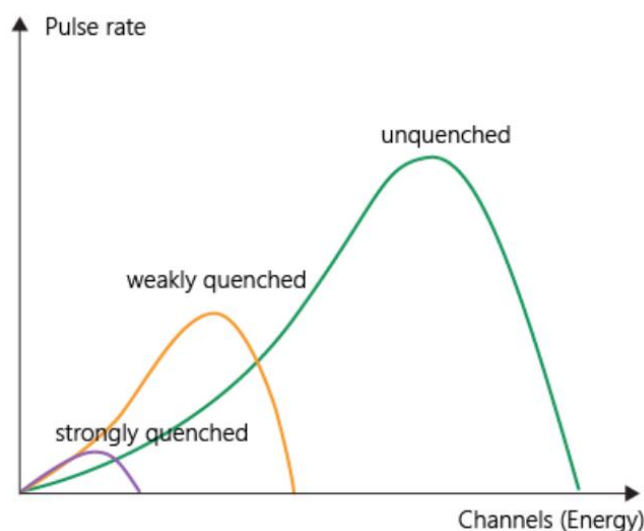

Figure 2. The effects of quenching on a hypothetical energy spectrum [28]*.*

In addition to reducing the overall detected count rate from a sample, quenching also shifts the energy spectrum toward lower energies and can be seen in the output from a Multi-Channel Analyser (MCA).

A simple example of quenching, both the reduction in count rate and spectral shift, can be seen in Figure 2, whereas the effects of quenching get stronger the spectrum shifts towards lower energy channels and decreases in overall area.

Resolution

The measure of the ability of a radiation detector to discern incident particles of differing energy is referred to as its *energy resolution*. The better the resolution of a detector, the better it will distinguish between particles of different energies. Energy resolution is typically measured in keV or as a percentage of the full-width half maximum of the corresponding photopeak.

Not all radiation detectors can distinguish radiations in terms of energy, and in some instances, they cannot discern different radiation types, as in the case of the Geiger Müller (GM) counter. In these cases, just the count rate is returned and, as such, these instruments are unable to discriminate between the count from a source of interest and any contamination that may be present from another isotope. However, non-specific detector technologies often exhibit very high detection efficiencies.

Minimal Detectable Activity

Most detection techniques can also be characterised by the minimal detectable activity (MDA) that they can detect, sometimes referred to as the Limit of Detection (LOD). This is the lowest level of radioactivity that can be determined, above background levels, and within given statistical confidence intervals (typically 2σ). The standard approach to calculating the MDA was proposed by Currie in 1968 [29]. The MDA is the smallest amount of radioactivity in a sample what will be detected with a 5% probability of non-detection risk and a 5% probability of false detection risk, as per,

$$MDA = \frac{2.71 \ \times 4.65 \times \sqrt{C_b T_b}}{\varepsilon \times V_s \times T_s \times 60}$$

Eq. 4

Where the 2.71 and 4.65 values are used to account for statistical uncertainties present in counting data, C_b is the background count rate, T_b is the duration of the background count, ε is the detector efficiency (%), V_s is the volume of the sample (grams or mL), and T_s is the duration of the active sample count, all durations are in minutes, with the final MDA value expressed in Bq g^{-1} or Bq ml^{-1}, depending on the volume unit used. Though extending counting times will provide greater ability to detect low levels of radioactivity, regardless of MDA, Equation 2 can also be used to compare the sensitivity performance of different detectors.

Tritium Detection Techniques

Liquid Scintillation Counting

Technique Overview

Liquid scintillation counting (LSC) is a technique used across many different industries to analyse samples for radioactive content, often in trace amounts. The technique involves mixing a sample of interest with a scintillation cocktail (a solution containing scintillants, solvents, and emulsifiers in varying ratios) and placing a vial of the mixture in a darkened enclosure (typically a light-tight compartment that is shielded from background radiation) where it is exposed to one or more photomultiplier tubes (PMTs). The PMTs are sensitive to visible light produced from the interaction between the sample and scintillant, and convert the visible light photons into an electrical signal which can be measured and analysed in a variety of ways depending on purpose. Figure 3 shows a simple diagram of a common LSC setup.
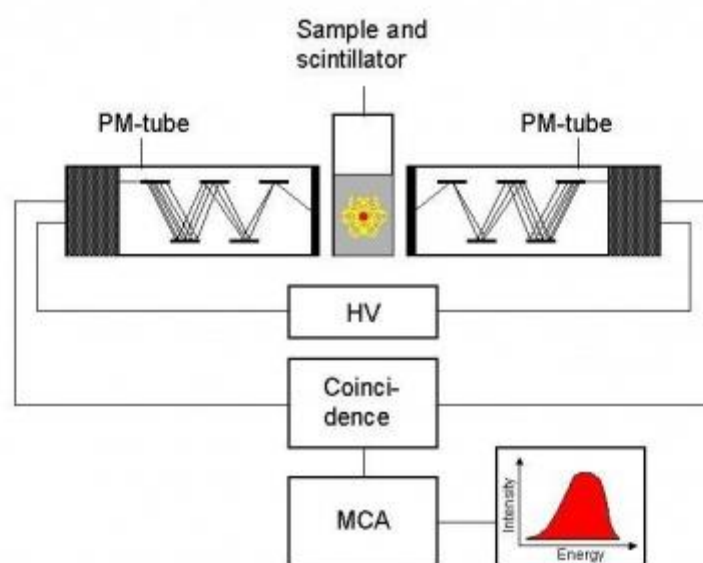
Figure 3. A schematic of a two-PMT LSC system. A vial is placed between two PMTs which are powered from the high voltage supply (HV), wired in coincidence, and connected to a multichannel analyser (MCA) [30]*.*

When calibrated with known reference sources, the radioactivity and the isotopic content of the samples can be determined [27]. As the sample and scintillant are brought into direct contact with one another, LSC is particularly useful for analysing low-energy beta emissions, such as those produced by ^{3}H, ^{14}C, or alpha particles. Furthermore, LSC has high geometric efficiency (often quoted as 4π) as the sample is mixed with the scintillant, meaning that there is a very high probability that a disintegration in the sample will cause scintillation light to be produced, and that the vial is surrounded

by at least two photomultiplier tube(s) so that any scintillation photons produced have a high chance of reaching the PMTs.

There is abundant volume of literature spanning the previous 70 years describing the use of LSC for the analysis of various ^{3}H source types [31]–[33]. There are works that seek to offer improvement or refinement of the technique, particularly for low-activity samples. Given the scope of this review, the number of prior reviews on LSC [34]–[36], and for brevity, a concise history of the developments in LSC pertinent to aqueous ^{3}H analysis will be outlined and only the LSC approaches with the lowest levels of detection will be discussed.

History

One of the earliest reports of LSC for tritium counting was by Hayes *et al.* (1952) at Los Alamos, USA [37], prior to this, ionisation chambers where the primary means for detecting tritium. Hayes *et al.* reported the development of a new solute (2, 5-Diphenyloxazole) for LSC that is suited to the low operating temperatures (~ 0°C) needed for the detection of the low energy beta emissions of ^{3}H and ^{14}C. In a subsequent paper, in 1953, Hayes and Gordon reported the further development of specialist LSC features for low-energy beta emissions, including multiple photomultiplier (PMT) tubes and cooling of the PMTs coincidence circuitry to minimise electrical noise which increases the background count. They also reported the LSC counting efficiency for a toluene-HTO-^{14}C solution, with the maximum efficiency for ^{3}H being 4.6%. Further work by Rosenthal and Anger (1954) provided measures of the counting efficiency of early LSC in the use of ^{3}H and ^{14}C detection. with the efficiency of counting ^{3}H containing stearic acid was in the order of 33%, while the efficiency for HTO was approximately 16%. A full history of the development of liquid scintillation at Los Alamos was provided by Ott in 1980 [38].

Within 5 years, LSC techniques had become the primary means of analysing liquid samples for ^{3}H content and, by 1962, counting efficiencies of 25% had been reported for HTO [35]. The technique was demonstrated to be used effectively for the analysis of ^{3}H in water [39], urine [39], blood and other bodily tissues [40], organic matter [41], as well as environmental water samples. By 1962, Benson and Maute had adapted light guides, taken from gamma spectrometers, to increase the light transmission from the scintillant vial to the PMTs resulting in a calculated efficiency of up to 44% for HTO sample in LSCs [42]. The sensitivity of this technique was also demonstrated by Butler (1960) who used LSC to analyse HTO samples with activities as low as 20 Bq L^{-1} [39]. A full early history of the technique was reported by Rapkin (1964) and a comprehensive survey of tritium in water analysis techniques was published by Cameron (1967) [43], [44]. At the time of their publication, Cameron noted that proportional gas counters were able to detect tritium activity an order of magnitude lower

than LSC, (approximately 10 Bq L^{-1} for proportional gas counters as opposed to 100 Bq L^{-1} for LSC over a 5-hour counting period [44]).

Over the early decades of LSC development and as the properties of ^{3}H were still being explored, a variety of mechanisms were developed to correct count data for the effects of quenching. The very low energy of the beta emission from ^{3}H (E_{avg} = 5.67 keV) makes it particularly susceptible to quenching. As such, concerted efforts were made to reduce or correct quenching. Early efforts included the use of internal and external source standardisation [45], [46], and the channel ratio method [47]–[49].

The channel ratio (CR) method utilises the shifting energy spectrum, due to sample quenching, to determine the overall efficiency of the detected count, and thereby assuming the true radioactivity of a sample. The method takes a set of calibrated radioactive samples and adds a differing level of quench to each. The samples are then analysed using the same detector. The spectra produced are split into two channel regions which form the basis of the CR, using Eq. 1. The CR is also referred to as Quenching Indicator Parameter (QIP).
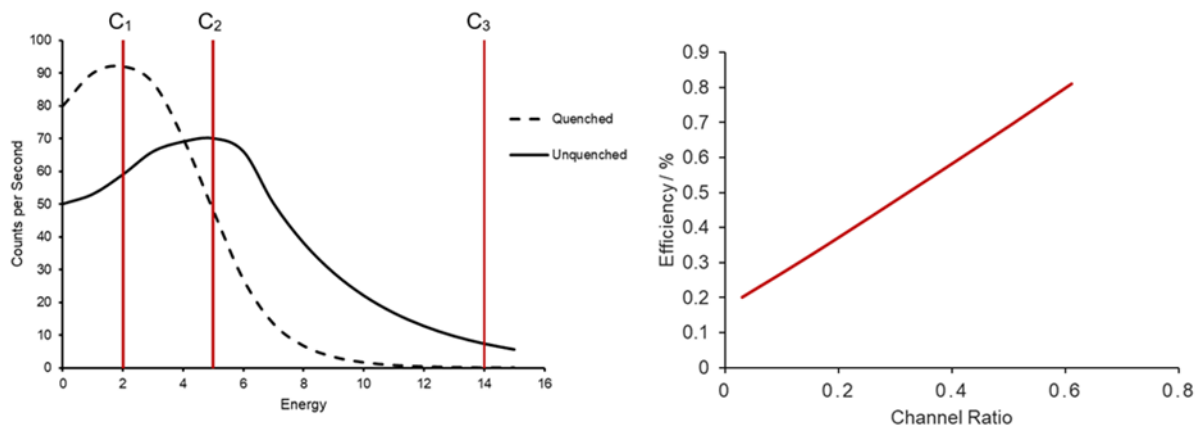
Figure 4. Channel ration (left) and calibration curve (right).

$$CR = \frac{\text{Total counts between C3 and C2}}{\text{Total counts between C3 and C1}} \qquad \text{Eq. 5}$$

As the degree of quench in the calibration standards increases, the ratio CR will change as fewer counts are registered in the upper channel region, and there are fewer counts overall. This will result in the detected counts-per-second (CPS) in the sample being less than its, known, true number of disintegrations-per-second (DPS), and thus the efficiency (Eff = CPS/DPS) can be determined for each level of quench. A *quench calibration curve* can be made showing the relationship between the CR and

the efficiency. Samples of unknown activity can then be analysed, its CPS, CR, and efficiency determined, allowing its true activity can be calculated (DPS = CPS/Eff). The method benefits from the calibration process only needing to be conducted once if using the same detector and sample sizes. However, preparing the samples, and performing the calibration can be onerous.

A second method that allows the calculation of absolute DPM from understanding the degree of quench in the sample is the *internal standard method* (ISM), reported as early as Hayes *et al.* (1957) [45]. For the ISM, a known amount of non-quenching radioactivity is added to all the sources, both calibration and the unknown sources. The calibration is then based on the ratio of quench between the internal sample and the unknown source. The detector counting efficiency for the sample is calculated using Eq. 2.

$$\text{Eff} = \frac{C_{ST} - C_{SA}}{D_{ST}}$$

<div align="right">Eq. 6</div>

Where C_{ST} is the count from combined sample and standard, C_{SA} is the count from the sample, and D_{ST} is the calculated disintegration rate of the standard. ISM has been shown to be more accurate than the external standard method [49], however it has several significant disadvantages over other techniques, namely: the creation of additional radioactive waste, the preparation and use of the standard is time consuming, and once mixed the original sample is lost. To combat the latter two points, by 1979 commercially available standards were marketed in the form of micro-gram quantity compounds that could be dissolved in the vial to expedite the ISM process [50]. Periodic comparisons of a wide range of tritium standards for LSC have demonstrated apparent consistency between the standards [51], [52]. The user must be careful in the choice of standard for use in ISM, factors effecting the decision include: it must be radiologically distinct from the sample, clearly resolved in the data output, have a suitably long half-life, be readily available, and ideally is eluted following analysis.

The *External Standard Method* (ESM), described by Higashiura *et al.* (1962), uses a second radioactive source, commonly a mid-energy gamma emitter (i.e., [133]Ba or ^{137}Cs), that is counted in tandem with the sample of interest [53]. Unlike the ISM, the second source is not mixed with the samples of interest, hence the term *external*. The gamma radiation from the external source produces Compton scattering within the sample, which is very similar to beta radiation and produces the same scintillation effects in the sample. The energy spectrum is processed and the relationship between counts at two pulse height channels on the spectrum, correlating to where 10 % and 20% of counts are found, is used to determine the *Transformed External Standard* sample (tSIE) value.

As the sample quench changes, the tSIE changes. Using a set of samples with known quench and radioactivity, a calibration curve is developed between tSIE and the counting efficiency. In similar fashion to the Internal Standard Method, a sample of unknown activity can be analysed, the tSIE determined, checked against the known calibration curve, and the true activity of sample calculated. In most modern systems the external source is held within the counter itself and the quenching calibration is performed automatically. In some systems, the fixed windows used for the channels can limit the useful range of quench determination or produce unacceptable statistical uncertainty [54].

The development of the *Triple-to-Double-Coincidence-Ratio* (TDCR) method for liquid scintillation counting in 1979 by Pochwalkski and Radoszewski [55], allowed for the determination of specific activity for pure beta emitting isotopes without the need for any addition source validation, either the external or internal source methods. TDCR uses a three-PMT setup, arranged symmetrically around a sample, see **Error! Reference source not found.**. The PMTs are then linked to a timing and coincidence circuit to capture the signals from the PMTs and process them accordingly to produce a ratio of the number of Triple events (all 3 PMTs recorded an event within a set time window) to the number of double events (2 PMTs recording an event within the time window).

The determination of the specific activity using TDCR is accomplished using a physical and statistical model of the photon distribution emitted by the source, a full description of the models can be found in the relevant references. The absolute measurement of the activity relies on three assumptions on the statistics of emitted light, detector thresholds, and the non-linearity of scintillation. TDCR also allows for automatic quench correction, when there are sufficient counts, as the ratio between the triple and double coincidence provides a measure of the quenching.
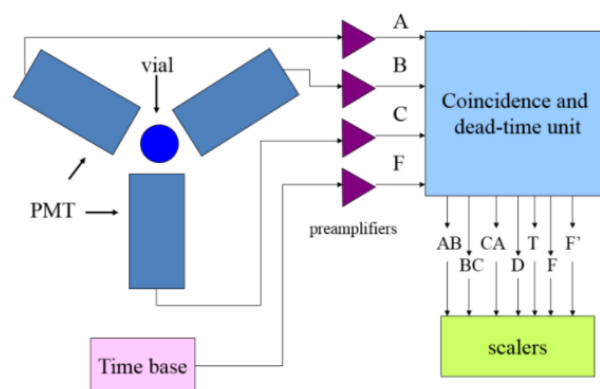

Figure 5. Simplified schematic of the TDCR coincidence circuitry.

Recent work on understanding TDCR coincidence timing windows by Dutsov *et al.* (2021) shows that extending the coincidence window (up to 2 µs) to include delayed fluorescence leads to an over estimation of activity in low-energy beta emitters [56]. The authors conclude that it is not advisable

to extend resolving time beyond what is necessary to register all prompt-fluorescence events, with a coincidence window between 10 ns and 200 ns utilised commonly.

Like other aspects of radiation measurement, the incorporation of new computing technology from the 1960s into LSC systems expanded the techniques sensitivity and ease of use [57]. Early adoption of Fortran codes were used to compute decays-per-minute and quench calibration curves, expanding to the incorporation of programs to automatically run the channels ratio and ESM in the early 1970s calculating the effects of isotope interference and quenching [58], [59]. With further advances in microprocessor technology in the 1980s being incorporated into LSC systems [60], in-built data processing, calibration, and quench correction have become rudimental aspects of any off-the-shelf LSC system. However, studies have shown that the automated choice of calibration curves, without user input, for low-energy beta emitters by the systems does not always produce the best results [61].

As of 2021, advances in computing technologies, such as neural networks and artificial intelligence, are still being applied to LSC to improve the performance of the technique. Joung *et al.* (2021) demonstrated how the application of artificial neural networks (ANN) can reduce measurement times, increase statistical accuracy in analysis, while dealing with fluctuating low-energy beta spectra [62]. Further, analysis of the time-domain with respect to the pulses produced by the PMTs has been shown to offer an estimation of the efficiency of the detector itself [63].

Real-Time Monitoring

Given the need for the sample to be mixed with the liquid scintillant and the need for prolonged counting durations, real-time LSC detectors have not been reported frequently in literature nor has the widespread commercial realisation of real-time LSC systems become apparent. Sigg et al (1994) appear to be the first to propose such a system, developing a computer-controlled pump system that automatically mixes sample solutions with the liquid scintillation cocktail before pumping the combined solution through the 2.5 ml flow-cell [64]. The flow cell is viewed by dual PMTs in coincidence; 0.12 mL min^{-1} of sample solution is mixed with 0.15 mL min^{-1} of the liquid scintillant. The detector was reported to have a MDA for 5-minute counting of approximately 0.6 Bq ml^{-1} with a full response to change in environmental tritium concentrations being detectable in 30 minutes. The system-maintained quench correction using the external standard method.

More recently, the *Wilma Online Radiation Monitor* system (LabLogic Ltd., UK) has been developed, which is another real-time LSC system. The system uses an integrated fluid-handling system to mix 5 ml samples with a LSC cocktail, which is then counted and subsequently disposed automatically. Wilma is a commercial product and, as yet, no results have appeared in the scientific literature. However, the commercial literature states it reaches an MDA of 0.081 Bq g^{-1} in 5 minutes with a counting

efficiency 15% and a background count rate <5 cpm, which is a significant improvement of the work of Sigg *et al.* [65]. This MDA is very close to the activity limit specified in the NEMI 7500-3H B standard. However, it should be noted that this performance is reported on commercial materials rather than peer-review literature.

Liquid Scintillation Cocktails

In tandem with the components and electronic development of liquid scintillators, there has been research into the optimal liquid scintillator solutions for counting low-energy beta emissions. In concurrence with the development of the counter, Hayes *et al.* (1955) also reported a comprehensive analysis of hundreds of organic compounds for their use in LSC [66]. The solution cocktails for analysing aqueous tritium samples are, typically, a combination of solvent, surfactant and scintillant(s) that aim to incorporate the sample homogeneously throughout the solution, maximise the scintillation output whilst minimising the level of quench [35].

Solvents act as the medium for dissolving samples, making up 60-99 % of the overall scintillation cocktail by volume, and where the initial excitation occurs in the solvent molecules. Molecules with available low-lying energy levels and non-binding electrons which require little energy for promotion into higher energy levels make good liquid scintillation solvents. The aromatic solvents meet these requirements and as such toluene, benzene and dioxane, became common solvents early in the history of liquid scintillation counting and remain common today [67]. Toluene, a common liquid scintillator material itself [68], is most often used in LSC as the solvent containing small quantities of additional scintillant, typically between 0-1 % by volume. However, in recent years there has been a focus on bio-degradable and/or disposable, such as di-isopropyl naphthalene (DIN), or linear alkyl benzene (LAB), which have shown excellent performance and robust long-term stability [69].

Surfactants are required due to aqueous solutions and aromatic hydrocarbon solvents being immiscible. One of the more common reported from early in the history of LSC is Triton-X100 (2-[4-(2,4,4-trimethylpentan-2-yl)phenoxy]ethanol), an ionic surfactant that allows the aqueous ^{3}H samples to form a homogeneous emulsion with solvents such as toluene. Work by Turner (1969) and Collins *et al.* (1977) has demonstrated that for aqueous tritium samples, Triton-X100 can act as the only solvent and that no additional toluene is required [70] [71]. Despite this, the use of an aqueous tritium, toluene and Trition-X100 cocktail has been reported frequently [72]–[74], [75], [76]. Further, the sensitivity of the detection systems using Triton surfactants was shown by Lieberman and Moghissi (1970), achieving a sensitivity of 7.4 Bq L^{-1} of tritium in water [77]. However, since 4th January 2021 the use of Triton-X100 within the European Union has been limited due to its hazard to human health [78].

To allow for the optical detection of radioactivity, a scintillant (or solute, fluor) must be added to the solvent if it not itself a scintillator. One of the earliest adopted was the oxazole 2,5-Diphenyloxazole (PPO), which remains one of the most widely used scintillators (see Table 1) and is still found in commercially available LS cocktails [79]. The scintillant act as *acceptors* of the excited energy produced by incident radiation in the solvent, becoming excited themselves. In the process of de-excitation of the scintillant, a photon of optical wavelength is released, which then may be recorded by the PMT.

In addition to the primary scintillator, it is not uncommon to use a further scintillator as a wavelength shifter so that the wavelength of the scintillation photons matches the absorption wavelength of the photocathode, increasing the number of optical photons detected. 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP), a common example of a wavelength shifter, absorbs shorter wavelength photons produced by the primary scintillant and emits a longer wavelength photon at 410 nm [80].

The development of solgel scintillators for LSC of aqueous and non-aqueous samples was proposed by Benson (1976) however this never seemed to progress into mainstream analysis, and recent advances in liquid scintillation solutions have explored the use of ionic liquids as replacements of common liquid scintillants [81], however the use of this is not widespread.

Today, liquid scintillation cocktails are available commercially that incorporate the three main components, with the ratios of the different components selected for specific counting and analysis requirements, i.e., low-energy beta or gamma rays. Furthermore, even the distinct components, such as the solvent can be a composition of various solvents. As an example, Table 1 shows the chemical composition of the commercially available Ultima Gold XR (PerkinElmer) cocktail which includes six different solvents/surfactants and two scintillants. Ultima Gold LLT (PerkinElmer) is a cocktail developed specifically for the analysis of low-level ^{3}H in aqueous solutions [82].

Table 1. Chemical composition of Ultima Gold XR liquid scintillation cocktail, taken from Dianu and Podina (2007) [79]

Component	Name	Composition (weight %)
Solvents	di-isopropyl naphthalene (DIN)	40 - 60
	ethoxylated alkylphenol	20 - 40
	bis(2-ethylhexyl) hydrogen phosphate	2.5 - 10
	triethyl phosphate	2.5 - 10
	sodium di-octylsulphosuccinate	2.5 - 10
	3,6-dimethyl-4octyne-3,6-diol	1.0 - 2.5
Scintillators	2,5 diphenyloxazole (PPO)	0 - 1.0
	1,4-bis (2-methylstyryl)-benzene (Bis-MSB)	0 - 1.0

The final considerations to make regarding the liquid scintillation cocktail is the total sample volume and the ratio of cocktail to sample used. Early work on identifying the best solvents for LSC, by Patterson and Greene (1965), discussed the dichotomy in choosing solvents [83]. The highest light output solvents like the alkylated benzenes which give the highest yield of photons per ß particle do not dissolve significant quantities of many biological materials, and that water and some biological compounds are good quenching agents. As such, merely increasing the sample size, relative to the solvent can decrease the overall counting efficiency.

A commonly reported ratio between the sample and cocktail that offers optimal results is 8:12 ml ratio in a 20 ml vial [75]. However, the specific ratio of sample-to-cocktail is often specific to the needs of the sample to be analysed, such as the number of isotopes present in the sample and the likely range of the energy spectra. Several works over the decades have approached this subject, in a general view of process optimisation [84], [85], [86], [87] and the tailored commercially-available cocktails also come with recommended sample-to-cocktail ratios [82].

Channel Window Selection

LSC counters use multichannel analysers to generate the energy spectra of the emissions present in the sample, and thus enable the presence and mass of individual isotopes to be discerned. The ability to refine and optimise the windows (the range of channels encompassing an emission) can improve the sensitivity of the detector system, particularly with regard to ^{3}H, as noted by Theodorssan (1999) [88].

Further, statistical methods haves also been used to improve the counting efficiency of LSC in the analysis of aqueous tritium samples. Verrezen and Hurtgen (2000) report the use of a multiple window deconvolution technique, in parallel with the internal standard method, that allows for the accounting for and removal of spectral contributions from high-energy beta impurities that may be present in low-energy beta samples, such that the activity of the isotope of interest can be determined [89].

Low Background LSC

Even with enrichment separation and concentration processes discussed later, environmental samples typically posses very low levels of radioactivity that make detection very difficult. To further enhance the low-level detection capabilities, methods, sample preparation processes and equipment have been developed and optimised, such as to reduce the influence of background count.

One of the first non-electronics areas for background reduction was to evaluate the materials used to make sample vials [90]. Standard glass vials contain trace levels of potassium. Natural potassium contains the naturally occurring radioactive isotope ^{40}K, with typical activity of 32.1 Bq g^{-1} of potassium

[20]. The presence of ^{40}K in the glass can cause a range of phenomena that can contribute to increased background radiation, not just from its own decay, e.g., fluorescence of the glass vial itself [91].

Even milligram quantities of potassium in standard glass will produce counts which will affect counting statistics negatively, especially when counting durations are long (> 5 hours). As such, using materials with low, or no, potassium content removes a principal source of background count in low-counting analysis. One of the most adopted materials for low-background LSC vials is borosilicate glass, such as Pico Glass Vial [82], used in various LSC-based studies, an example is shown in Figure 6 [92]. Other materials include quartz, Teflon^{TM}, and high-density polyethylene vials [93], [94].

The presence of naturally occurring radioactive materials (NORM) in building materials is the most common source of background radiation that affects counting data. As such, further reductions in the background count can be achieved using passive shielding. This includes: the use of low-Z materials (e.g., copper) to shield against low-energy emissions, such as beta particles, x-rays; the use of high-Z materials (tungsten, lead, etc.) to attenuate gamma rays [27].

Figure 6. 7 ml borosilicate Pico Glass Vials, Perkin Elmer.

In addition to passive measures, active measures have also been implemented to remove background counts. These measures include using multiple photon detection systems (e.g., multiple PMTs) used in coincidence counting mode to reduce the number of false events not originating from the interaction of the beta particles with the scintillation cocktail. A counting event would need to be recorded within a given time window (typically the order of a few nanoseconds) in both photomultiplier tubes for it to be recorded. Any counting events that occur in only one of the photon detectors within the defined time window are discarded.

The coincidence method is used in the work of Feng *et al.* (2020) in their analysis of environmental tritium samples [95]. The authors used the AccuFlex LSC-LB7 that contains five separate photomultiplier tubes used in coincidence to eliminating false signals. Erchinger *et al.* (2017) report

perhaps the lowest background rate recorded for LSC systems, as low as 10 counts per-day. This is approximately two orders of magnitude lower than other common low-background LSC systems (e.g., AccuFlex LSC-LB7 or Quantulus GCT 110 V) [92], which leads to a reduction in the expected MDA, recorded as 6 x 10^{-4} Bq g^{-1} for a 195-minute counting duration.

The reduction in background count was achieved through a combination of low-background materials, passive shielding of beta particles, neutrons, and gamma rays, and coincidence counting. Figure 7 shows a depiction of the ultra-low background LSC setup. The authors located the detector setup in a shallow underground laboratory to reduce the influence of cosmic radiation; however, it has been noted that this can lead to increased background count rates due to the presence of NORM in the soils and rock that can be released into the local atmosphere, e.g., radon.
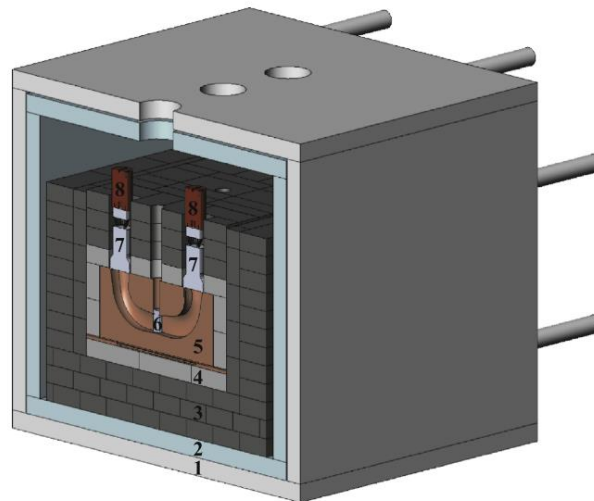

Figure 7. Cutaway diagram of the low-background Liquid Scintillator counter designed by Erchinger et al. 2015. 1) Outer layer of plastic scintillator veto panels (grey), 2) borated polyethylene (teal), 3) lead shielding (dark grey), 4) low background lead shielding (grey), 5) hollow copper light guide (orange), 6) liquid scintillation vial (grey), 7) photomultiplier tubes (light grey), 8) PMT bases (red) [92]

Similarly, the use of anti-coincidence detectors can be used to remove extraneous counts, produced by incomplete energy deposition or secondary scattering. Anti-coincidence systems consist of two detectors, a primary and a secondary detector, where the primary detector (the Liquid Scintillation Counter) is surrounded be the secondary detector (sometimes referred to as Guard Counters), or an array of detectors. Counts are only recorded from the primary detector if there is no corresponding event in the second detector with a defined time window (again, typically a few nanoseconds).

The use of anti-coincidence is used frequently in particle physics studies, particularly related to Weakly Interacting Massive Particles (WIMPs) [96], though there are some older works adopting the technique for tritium detection such as Huber *et al.* (1967) [97], Aoyama *et al.* (1987) and Aoyama *et al.* (1989) [98], [99]. In the older works, the use of anti-coincidence methods is commonly used as

tandem proportional gas counters, but not exclusively so. Huber *et al.* (1967) developed a low-level counter with a plastic scintillation anti-coincidence shield capable of 1.7 counts per minute background count-rate [97].

In addition to coincidence methods, Vaidya et al (1998) developed a simple circuit that separates counts originating from low-every beta decay from those of non-quenchable background [100]. Electric pulses generated by beta decay have a fast component followed by a delayed pulse, whereas non-quenchable background have a similar fast component followed by a series of low-intensity after-pulses. Utilising an OPA678 operational amplifier, the authors were able to differentiate between the two pulse shapes through the integration of the delayed portion of the pulse shape. Application of the circuit led to a 55% decrease in background count.

As shown above, however, the performance of the technique can be greatly increased. Trace levels of tritium can be detected readily in water, MDA of less than 0.6×10^{-3} Bq ml^{-1} for a 500-minute count and even commercially available LSC systems showing detection efficiencies of aqueous tritium above 60 % [101].

Industrial Standards

As a result of the sensitivity of LSC, its technological maturity and ubiquity in industry, two international standards for the detection of tritium in drinking water are based on the technique: ISO-9698 and NEMI 7500-^{3}H B [102], [103]. ISO-9698 allows for a minimal detection activity of >1 Bq L^{-1} given appropriate technical conditions and up to 10^6 Bq L^{-1} without sample dilution. NEMI 7500-^{3}H B, has a detection sensitivity of 74 kBq L^{-1} for a ±6 % and 37 Bq L^{-1} for an uncertainty of ±10 % at the 95 % confidence interval. The two standards have been shown to give the same results when their respective recommendations are followed [104].

Imaging of Aqueous Tritium Samples

Imaging Plates

The use of imaging plates is widespread in the field of radiography [105]–[107]. They offer a sensitive, potentially reusable, and passive method of detection ionising radiation [108]. Unlike liquid scintillation techniques, imaging plates rely on photo-stimulated luminescence to determine the presence of radiation. Photo-stimulated luminescence is the process in which energy is released from a phosphor following stimulation by electromagnetic radiation (visible light, X-ray, gamma ray). The technique requires two-stage illumination, first by the radiation of interest (in the case of ^{3}H, beta particles), the second to 'read' the image (this is typically a visible-wavelength laser). In addition to

general radiography, the technique has been used in the analysis of materials used in the construction of fusion facilities, due to the presence of tritium in the reactions.
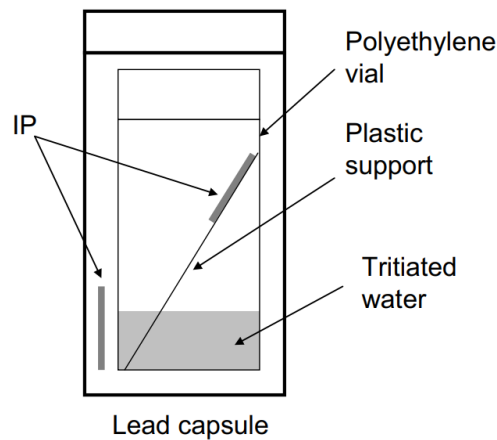

Figure 8. Schematic of the experimental setup used by Hatano et al. (2011) [109].

The imaging plate technique has also been used in the context of aqueous tritium analysis. Hatano *et al.* (2011) exposed commercially available Eu-doped BaFBr imaging plates from Fujifilm (BAS-IP MS) to room temperature water vapor containing HTO at a concentration of 16 to 400 k Bq cm^{-3} to YYY [109]. The imaging plates were approximately 10 × 20 mm in size and mounted inside a lead capsule using experimental setup shown in Figure 8. Within the capsule, tritiated water vapour evaporates from the aqueous sample below the plate and interacts with the imagining plate causing photo-stimulated luminescence.

Typically, phosphors used for imaging plate analysis are hygroscopic and so plates include an additional protection layer to prevent degradation of the phosphor from excessive water absorption. Normally this layer is removed when conducting imaging plate analysis of beta containing solutions [109]. However, to avoid overly rapid absorption of tritiated water in the phosphor Hatano et al. (2011) retained a 9 µm layer of polyethylene terephthalate (PET) was utilised over the imaging plate. The results from this study indicate that the feasibility of measuring tritium concentration in water with imaging plates. Specifically, that the intensity of the photo-stimulated luminescence was proportional to both the concentration of tritium in solution and the time the plate was exposed to the water vapour see Figure 9.
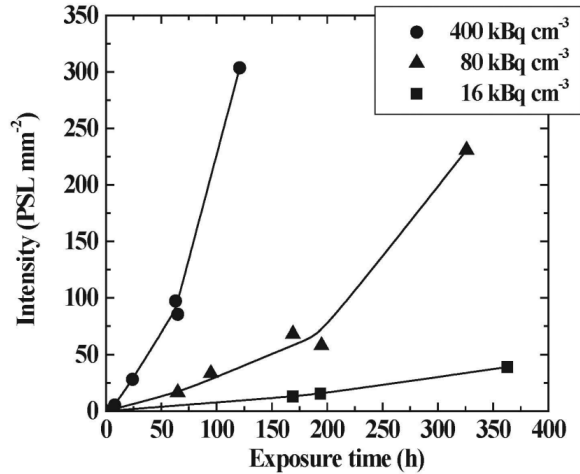
Figure 9. The change in luminescence of Fujifilm (BAS-IR) imaging plates with exposure time to aqueous tritium, Hatano et al (2011).

Further work by Hatano et al (2012) then describes an extension of this where a Fujifilm (BAS-IR) imaging plate was used without the protective 9 µm PET layer, used in their previous work to protect the imaging plate. This work measured ^{3}H concentration (4-400 kBq mL^{-1}) in water samples, with the use of a Fujifilm FLA-7000 laser scanner. Like their previous work, the results showed the linear proportionality of ^{3}H concentration to the intensity of the photo-stimulated luminescence, see Figure 10. Non-linear proportionality was observed for time of exposure of the imaging plate to the ^{3}H to the intensity of observed photo-stimulated luminescence, as result of increasing ^{3}H concentration in the phosphor over time.
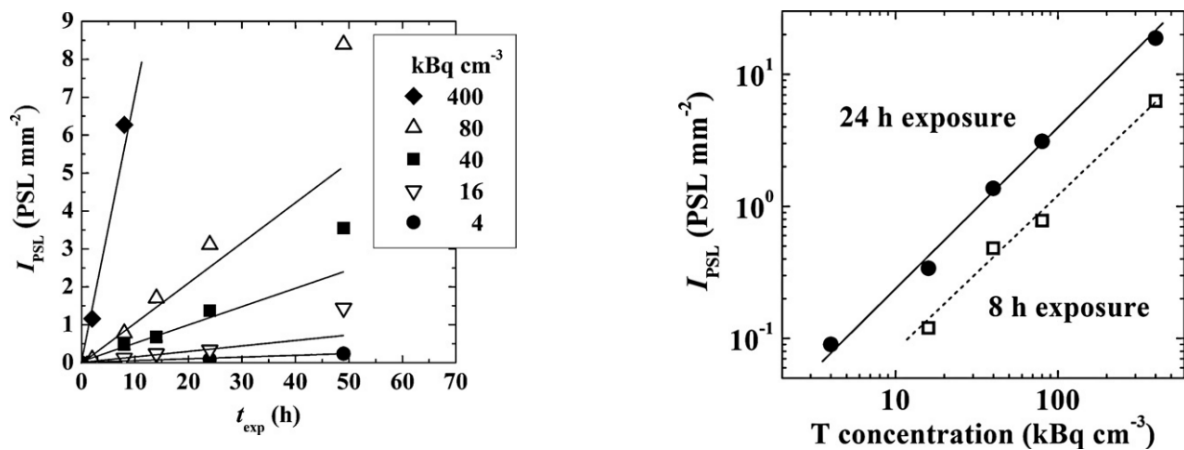

Figure 10. Relationships between exposure time and PSL intensity (left) and the relationship between tritium concentration and imaging intensity (right), Hatano et al. (2012).

The authors noted that removing the PET layer from the imaging plate allowed the technique to measure lower concentration of ^{3}H in a shorter exposure time than their previous work. Without the PET layer, exposure times of 10-20 hours are required to get sufficient photo-stimulated luminescence on ^{3}H concentrations 80 kBq mL^{-3}. This is a result of the ^{3}H migrating into the phosphor more rapidly.

Unlike scintillation techniques where there is a clear measure of efficiency (the ratio of the detected count to the activity of the sample), it is difficult to establish the efficiency of the imaging plate method and to make the comparison to more conventional detection methods.

In both the works of Hatano *et al.* (2011) and (2012) [109] [110], the imaging plate is supported in the detection arrangement by a plastic support so that it does not come into contact with the HTO solution and as such only comes into contact from the HTO water vapour. The ^{3}H adsorbed on the phosphor was shown to be desorbed by keeping the imaging plate exposed to air at room temperature for 200 hours, allowing the imaging plate to be reused. This was achieved if the total exposure of the plate was sufficiently short (circa <24 hours). For longer periods of tritium exposure, the residual contamination becomes to engrained to remove through passive exposure to air. As such, this imaging plate technique has an important advantage over traditional LSC, in that it creates significantly less radioactive waste.

Melt-On Scintillation Imaging

Irikura *et al.* 2017 describe a new approach to imaging radioactivity distributions by using a melt-on scintillator (Meltilex) to the previously discussed imaging plate [111]. Diluted 10 ml samples of [^{3}H]thymidine, (36 kBq ml^{-3} - 37 MBq ml^{-3}) were added to glass fibre filter discs. The filters were then air dried and the melt-on scintillator was placed on top and subsequently heated to 90°C. Following this, scintillation images were obtained with a LAS4000mini CCD imager (GE Healthcare Life Sciences) over a 30-minute duration exposure. Imaging plates, like those reported by Hatano *et al.*, were used as a comparison to the melt-on scintillators, using a TR2040E plate (GE Healthcare Life Sciences) and measured with a FLA-9000 (GE Healthcare Life Sciences).

In calibration experiments, the authors contacted a series of glass fibre plates and imaging plates with calibrated references levels of tritiated water. The outcome of the scintillation imaging is shown in Figure 11. The intensity of the images followed a linear trend with activity present. Both the scintillation and the imaging plate methods exhibit broad linear proportionality between intensity and radioactivity, as shown in the comparison between the measured intensity and deposited radioactivity, Figure 12. The authors note, and as can be seen in Figure 12, that the sensitivity of the melt-on scintillation imaging technique is lower than imaging plates.
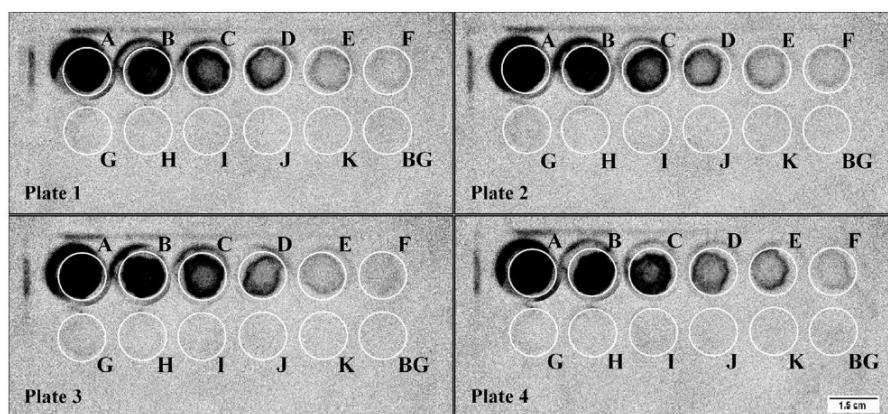
Figure 11. Scintillation images of ^3H radioactivity on a glass fibre using a melt-on scintillator, taken from Irikura et al. (2018) [111].
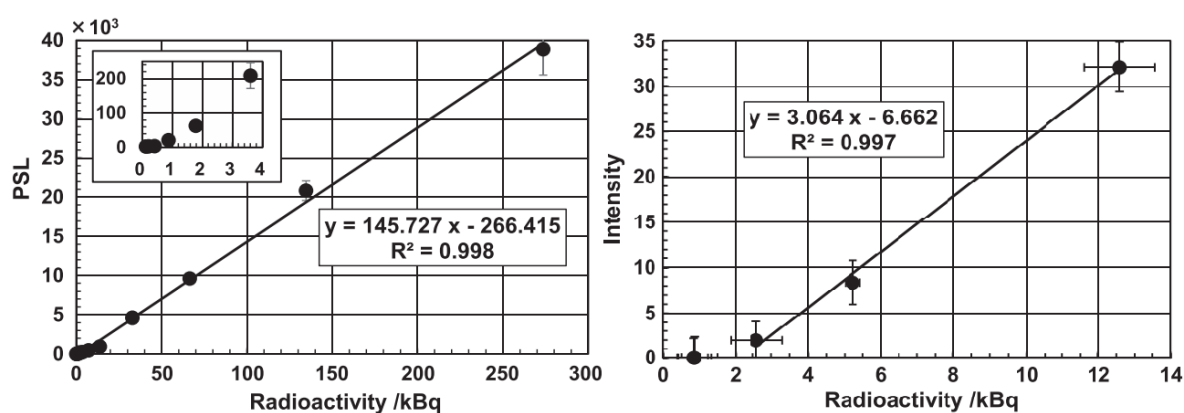

Figure 12. Plots of the relationship between recorded PSL and scintillation intensity and the sample activity for imaging plates (left) and melt-on scintillators (right) [111].

The comparison with imaging plate technology aside, the linear relationship between intensity and activity allowed the scintillation images to be used as a calibration for analysing unknown tritiated sources. The authors also note that repeated measurements show the scintillation imaging to be repeatable to a good degree of precision, with a coefficient of variation in the data of > 1%. Nonetheless, when using the method to analyse tritium uptake during cell proliferation (the biological process of cell division) , the scintillation imaging method was shown to overestimate the radioactivity present compared to a LSC analysis.

When viewed in the context of the other techniques reviewed here, imaging plates and melt-on scintillators have only been in used with tritium samples of activity several orders of magnitude higher, in the kBq ml^{-1} range compared to sensitivities of sub-1 Bq g^{-1} for most of the other techniques described here. Furthermore, no values of efficiency have been reported in the studies of HTO detection using imaging plates, discussed above. However, studies of interactions of 8-20 keV x-rays with imaging plates has shown quantum efficiency values between 80-100% [112], [113], though these

values are only indicative. This does indicate that the technique could be very efficient should it be investigated further.

Plastic Scintillators

Plastic scintillators are detection media where a primary fluorescent emitter is suspended in a solid polymer matrix. They typically have a high fluorescent light output and fast response times; they are also physically robust and can be made into any form relatively easily [27]. Despite this, plastic scintillators have not been widely used for the radiometric detection of ^{3}H because not enough of the emitted low energy beta particles penetrate sufficiently far enough into the material to cause statistically significant scintillation. Attempts have been made to use PS in the detection by maximising the surface area of the scintillator exposed to the ^{3}H solution by taking advantage of the durability and malleability of the material.

The potential long-term drawback of organic scintillators in the detection of tritium is contamination. Due to organic scintillators containing polymers, there is a risk of tritium atoms exchanging with hydrogen in the scintillation volume. This could cause long term contamination of the scintillation which would cause increase in background counts.

Rathnakaran et $al.$ (2000) described the development of a plastic scintillator-based detector for the measurement of coolant water from a pressurised heavy water reactor [114]. The detector consisted of 6 plastic scintillator films (5 μm thick, 500 cm^2 area each) stacked into a flow cell with a total surface area exposed to the sample volume of 3000 cm^2. The specific scintillator type used was not described. The packing of the plastic scintillator films created a pseudo-sponge like volume with high porosity. The scintillation volume was coupled to two EMI-9635 PMTs, located at either end of the detection volume. The detector was able to achieve a detection sensitivity of 37 kBq L^{-1} under a flow rate of 100 mL min^{-1}.

In earlier work by Singh et $al.$ (1995) a precursor to the above aqueous ^{3}H detector was proposed to allow for the detection of gaseous phase ^{3}H, with four different sized detectors tested (6.3, 11.5, 19, 27 cm^3, respectively), again no description of the scintillator itself was provided [115]. This detector type showed a maximum detection efficiency of 65% when the smallest volume detector was tested. As neither the detector efficiency nor volume is reported in Rathnakaran et $al.$ (2000), for the purposes of comparison in Table 3, the values of efficiency from Singh et $al.$ (1995) are used. This is because despite efficiency not being discussed in Rathnakaran et $al.$ (2000), the detectors described in both works appear fundamentally the same, however one would expect aqueous ^{3}H to reduce the efficiency given its self-attenuation effects [116]. The works of Singh and Rathnakaran are at least 20 years old and there appears to be no further work or progress toward a commercial technology.

The principle of surrounding the radioactive source with the scintillation material has been implemented by etching plastic scintillators. In the work of Uda *et al.* (2010), a 35 × 35 mm NE102A (OKEN/NE Technology) plastic scintillator tile was etched with a spiral groove (22 cm length, 1 mm width, 0.5 mm depth) of volume approximately 0.11 ml, a schematic is shown in Figure 13 [117]. Even with the groove etched into scintillator, the range of the low-energy beta particles is so short that only disintegrations close to the surface of the plastic will cause a scintillation reaction.
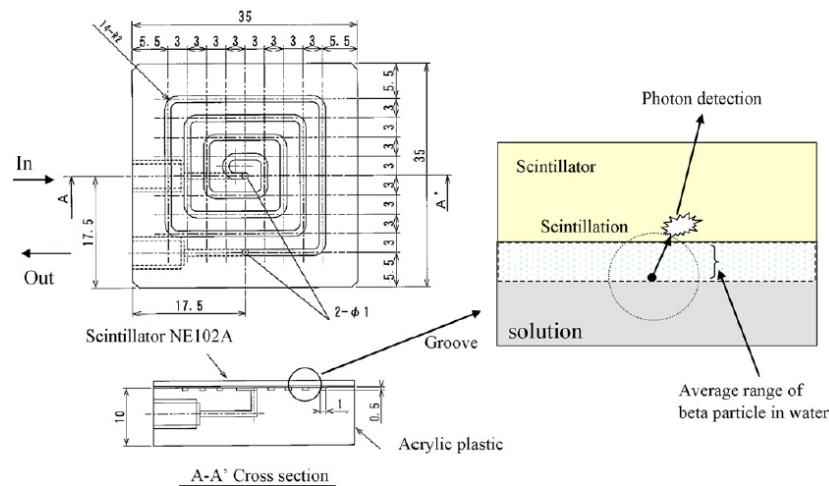

Figure 13. The configuration of the plastic scintillator and beta particle detection scheme, taken from Uda et al. (2010) [117]*.*

The results of Uda *et al.* (2010) suggest that the efficiency of the grooved-plastic scintillator was approximately 0.32%, mainly because of the low-energy beta radiation not reaching the bulk of the scintillator. This is well below the 9% efficiency the authors recorded for liquid scintillation counting of HTO – and far below that of recorded elsewhere. Their work estimates that the MDA is 190 Bq for the apparatus, or 1430 Bq cm^{-3} if the volume of the groove is considered.

Uda *et al.* (2010) presented options to improve the efficiency of their detector. These included increasing the groove length, which they estimate could lower the MDA to 72 Bq cm^{-3} from a 20-fold increase in the groove length.

they estimate that by increasing the groove volume by a factor of 20 would lower the MDA to 72 Bq cm^{-3}. This is close to the legal limit for liquid effluent in Japan, which is 60 Bq cm^{-3}. They reference the typical MDA of typical low-background liquid scintillator being approximately 0.5 Bq L^{-1}.

A series of work on plastics scintillators sheets for the detection of tritium and other low-energy beta emitters was reported by Furuta *et al.* [118], [119]. The authors using 0.5-mm thick BC-400 PS sheets, with liquid samples micro-pipetted onto the surface of one and then sandwiched in between. The sheets were coupled to PMTs connected in coincidence, see Figure 14. The technique was

demonstrated to detect low levels of ^{3}H-methionine (0.04 Bq mL^{-1}) over 10-hour counting durations. However, tritiated water was impossible to measure as the samples were typically air dried prior to counting which will necessarily remove HTO and thus tritium related activity.
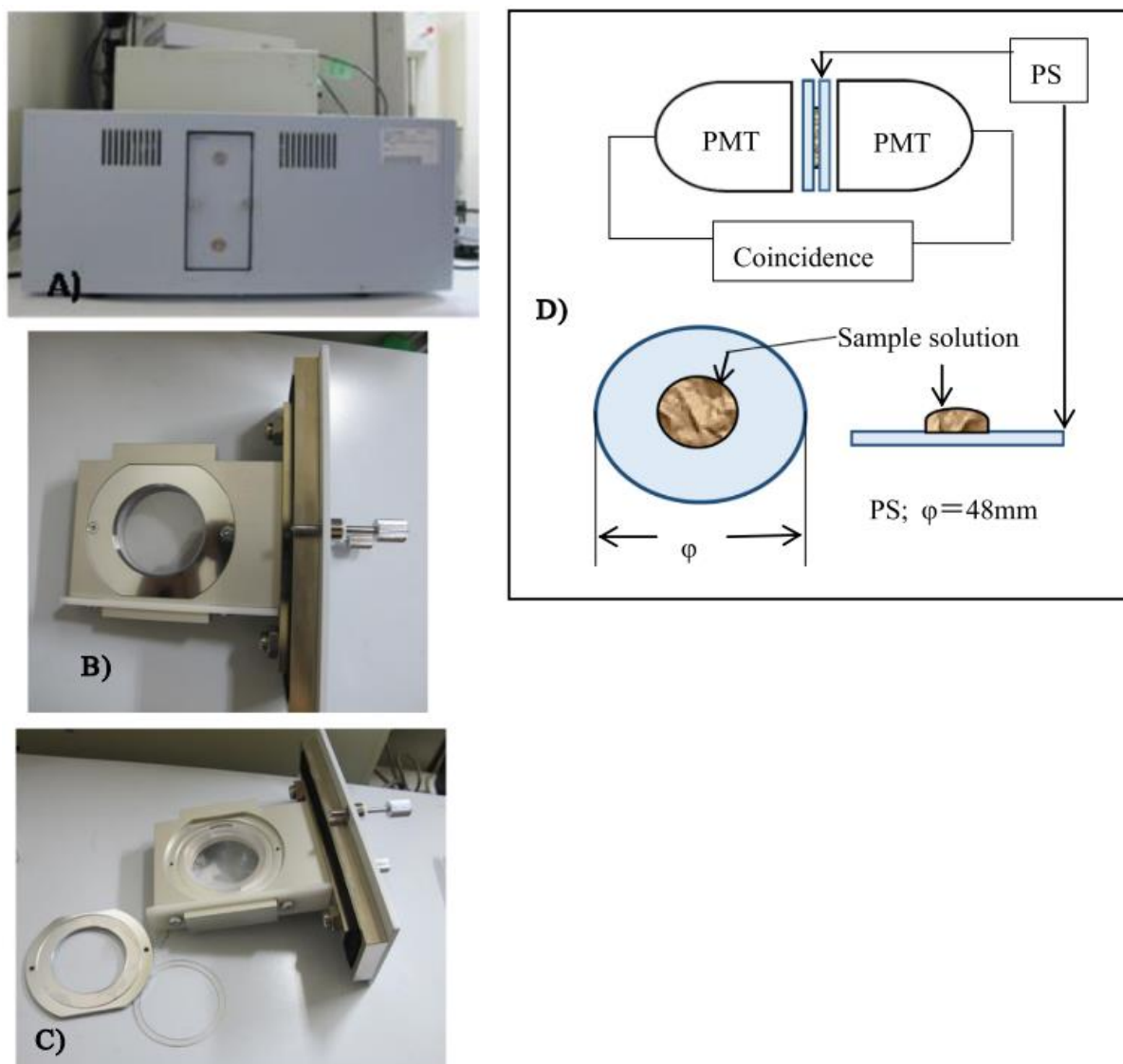

Figure 14. A) Detector enclosure containing detector cell, HV power supply and coincidence module, B) side elevation of the scintillator holding cell., C) sample holder with the plastic scintillation sheet and window removed, D) a schematic of the setup and location of sample solution on the PS sheet. [119]

Azevedo *et al.* (2018) reported the design and simulation of a real-time monitor for analysing tritium content in water using plastic scintillators [120]. The system uses 340 unclad BCF-10 scintillating fibres (of 2 mm width) inside a Teflon^{TM} tube (43 mm internal diameter) connected to two photosensors in coincidence where tritiated water surrounds the fibres. The prototype of the simulated detector is shown in Figure 15, where the PMTs are located at either end of the scintillation cell.
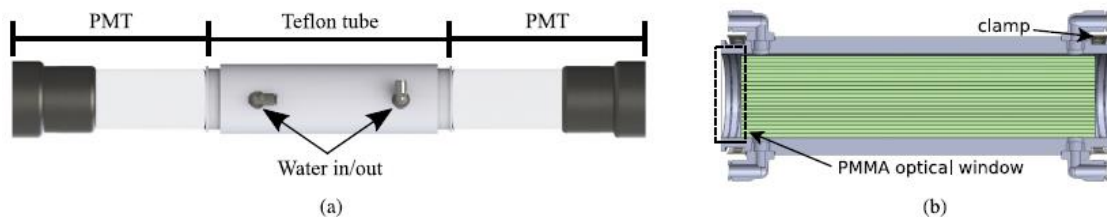
Figure 15. A schematic layout of the prototype real-time water monitor based on 340 scintillating fibres. A) shows the full module showing the PMTs positioning at opposite ends of the scintillation module, B) cross-section of the scintillation module, showing the fibres and the transparent PMMA windows [121]*.*

The proposed detector was studied using Monte Carlo simulations and reported in Azevedo *et al.* (2020). The effect of fibre length was examined, comparing 18 cm and 1 m fibres, with the results suggesting that the shorter fibres had a 25% higher count rate than the longer 1 m fibres. The length of the counting time was studied with datasets of 1-minute and 60-minute integration times simulated. Results show that using a counting time of 1 minute (that the authors consider to be quasi real-time) was insufficient to be able to discern between samples of low activity, e.g., in the range 100-500 Bq L^{-1} due to high statistical uncertainty, with either the 18 cm or 1 m fibres [121]. In contrast, a 60-minute integration time provided robust data with sufficient resolution to distinguish between activities. The shorter fibre length showed a 25% increase in counting rate over the longer, 1-metre fibre. This was attributed to the increased photon absorption of the longer fibres, where the photons fail to reach the PMT before absorption. The authors report a detection efficiency of 5% for the simulated detector. The detector shows promise as a means of detecting low-activity, tritiated water with simulations predicting a sensitivity to meet the World Health Organisation and European Union drinking water standards but at the time of writing no physical device has been reported.

Liquid Scintillation Counting Using Plastic Scintillating Particles

Hoftstetter (1995) reported the development of a second-generation continuous monitoring system for aqueous effluent containing ^{3}H at the Savannah River Site using beads of unspecified size and type of plastic scintillator coupled with coincidence electronics [122]. The apparatus consisted of a water filtration and purification system (to remove solid particulates and dissolved impurities) followed inline by a Berthold LB-501A. The purification stage is required to reduce interference effects from the bioluminescence and chemiluminescence. Flow rates through the purification system were reported to be 100 mL min^{-1} and 3 mL min^{-1} through the radiation detector itself. The sensitivity of the real-time system was reported to be 25 kBq L^{-1}.

A similar approach was used by Taracon *et al.* (2002), placing plastic scintillator beads of BC-400 in polyvinyl toluene inside BC-408 plastic scintillator vials to measure solutions containing 37.2 Bq g^{-1}. Bead size was estimated to be in the range of 250 – 500 µm, with the shape of the vial being equivalent

to that of 7 ml polyethylene [123]. The plastic scintillator-containing-vials were placed inside a Tri-Carb 2000 CA/LL for linear amplification measurements and a Quantulus detector for logarithmic amplification. The authors report a very low efficiency for the tritium energy range, i.e., 0.27% and 0.33% for the respective linear and logarithmic amplification procedures. They estimated, using the logarithmic amplification technique, a theoretical limit of detection for the system of approximately 5 Bq g^{-1}.

Santiago *et al.* (2013) reported the development of a range of polystyrene-based microspheres for the potential replacement of liquid scintillation solutions [124]. The authors synthesised seven different polystyrene-based microbeads with a mean bead size of 130 μm. Samples of 1.5 g of plastic scintillation beads and 0.75 ml of radioactive solutions placed 6 mL polyethylene vials, placed in a 1220 QUANTULUS counter using logarithmic amplification. The authors reported a higher efficiency than that of Taraon *et al.*, with the highest efficiency for ^{3}H reported at 1.19%, however the ^{3}H solution concentration was higher, at 600 Bq g^{-1}. This was achieved using a scintillator synthesised from 10 g of polystyrene, 0.2 g of PPO and 0.005 g of POPOP in 100 mL of dichloromethane. The efficiency values reported, for ^{3}H and the other nuclides studied, were above those obtained using commercially available plastic scintillation microbeads.

Furuta and Ito (2018) describe a modified approach to liquid scintillation counting for measuring tritiated water content in expelled air. The experimental method takes expired air and mixes it with 72.5 g of cooled (5°C) EJ-200 plastic scintillation pellets stored in a 100 mL Teflon^{TM} vial [125]. The condensed liquid vapour/pellet mixture is counted using the low background AccuFLEX LSC-LB7 LS counter that uses the 5 PMT coincidence counting system. The technique employed demonstrated a detectable concertation of 100 Bq L^{-1}. However, the authors note improvements in the can be made to increase the efficiency, recorded at 5%, in the collection of the air sample and the cleaning procedures. The results indicate the described method is adequate for the safety management of radiation workers.

One of the proposed advantages of the Furuta and Ito (2018) approach of reusable PS beads over standard LS techniques is that it minimises the production of radioactive wastes as no cocktail is mixed. This is advantageous over LS techniques as it produces less contaminated waste and could reduce costs. This is also referred to as a benefit of the technique in other works discussed [124], [126]. The scintillation pellets can be cleaned and reused following washing with pure water. The cleaning method described showed a 100% decrease in count following the pellets exposure to a 250 μL HTO sample, of concentration of 452 kBq mL^{-1}, in a 5 L volume air sample bag.

Inorganic Scintillators

Use of scintillation detectors utilising inorganic crystals is comparatively rare in ^{3}H detection. This is perhaps primarily due to the mechanical inflexibility of the crystals as materials. Unlike plastic scintillators, inorganic crystals lack malleability and durability, and can be incredibly brittle. As such, they cannot be formed in complex shapes or etched, as in the case of the Uda *et al.* (2010) plastic scintillator described above. However, recent advances in the materials sciences combined with inorganic crystals have enabled the crystals to be used in aqueous tritium detectors.

Some common inorganic scintillators, such as sodium iodide (NaI(Tl)), as well as having a high atomic number, are hydroscopic and would absorb tritiated water into the crystal structure if they were brought into direct contact. As a result, their use has not been reported widely in the literature for tritiated water analysis. Curtis (1972) reported the use of NaI(Tl) crystals for the detection bremsstrahlung radiation from tritiated water samples, but this is the only reported use of sodium iodide. The most widely adopted inorganic scintillator used for tritium detection is calcium fluoride doped with europium (CaF$_2$(Eu)), as it is non-hydroscopic, and non-reactive. Furthermore, it has a low atomic number which generates a relatively low proportion of backscatter which is ideal for detecting low-energy beta particles [127]. More details on the relevant physical and optical properties of CaF$_2$(Eu) are given in Table 2.

The first reported use of the CaF$_2$(Eu) for tritium detection was by Colmenares *et al.* (1974). In their work, the authors describe the development of an in-line tritium gas detector. As a gaseous detector, it is outside the bounds of this review, but the results of Colmenares *et al.* suggest that the material was a suitable medium for the detection of low-energy beta particles.

Table 2. Physical and Optical Properties of CaF2(Eu) [128]*.*

Density (g cm^{-3})	3.18
Solubility at 20°C (g 100 ml^{-1})	0.0016
Refractive Index	1.47
Peak Wavelength of Emission (nm)	435
Light Yield (photons $_\gamma$keV^{-1})	19,000
Light Output Relative to NaI(Tl) (%)	50 %
Adsorption Coefficient (cm^{-1})	0.3

CaF$_2$:Eu Cells

The use of CaF$_2$(Eu) in a flow cell was first reported by Kawano et al (2011) [129]. The initial design reported was to be a real-time radioactive water effluent monitor. For the detection medium, granular CaF$_2$(Eu) was packed inside a 44 mm long, 3 mm internal diameter Teflon^{TM} PFA (perfluoroalkoxy) tube. The grain size was one of three diameters: 50, 100, and 300 μm. Two PMTs were connected to the tube in coincidence. The setup was tested with aqueous tritium solutions ranging from 10 – 100 Bq ml^{-1}. The work showed that the detector performed best with the smallest diameter CaF$_2$ grains, obtaining a sensitivity of 10 Bq ml^{-1}. However, this was achieved with a 10,000 second counting duration, making it far from real-time. Subsequent work by the authors included the use of lead shielding around the flow-cell setup to reduce the effects of background counts. Results showed a 51.3% reduction in detected background count. This is a significant reduction in background and one that would decrease the MDA of the flow-cell [130].

Similar work was reported by Alton *et al.* (2018) of a *in situ* monitoring device for the analysis of groundwater samples, with a specific interest in ^{3}H [131]. Initial simulations compared the detection efficiency of single layer (12 μm thickness) CaF$_2$:Eu crystals and stacked-sphere geometries of the same inorganic scintillator (radius 3.5 μm), referred to as *heterogeneous scintillator*. The simulated detectors were exposed to tritiated water, with results showing a 20% increase in detection efficiency of the heterogeneous scintillator over the single crystal.

Experimental validation of the simulated data was conducted using a single, 5-mm thick CaF$_2$:Eu crystal and a heterogeneous scintillator, created by crushing a single CaF$_2$:Eu crystal with a pestle and mortar, to form scintillator particles with a mean and maximum size of 1.1 and 8.8 μm, respectively. Both the single crystal and the heterogenous scintillator were mounted to 6 × 6 mm silicon-based photomultiplier (SiPM). The detectors were exposed to static 20 mL volumes of 1.5 MBq L^{-1} tritiated water. Similar to the simulated work, the experimental results showed a similar increase in efficiency for the heterogeneous scintillator over the single crystal.

The authors also analyse the optimal flow conditions and particle size for the flow sensor. They note that a smaller heterogeneous scintillator particle size improves the counting efficiency of a potential flow cell. However, by decreasing the particle size, the flow-cell takes longer to completely fill, if at all, and as such could under-count the radioactivity present. Therefore, the authors note that it is possible to determine an ideal particle size, such that the detection efficiency and flowrate are optimised. At present only the detection mechanisms have been developed for the system and the functioning flow-cell is not completed.

A recent simulation study of a static cell design based on CaF_2(Eu) sheets was reported by Song *et al.* (2021) [132]. The overall design of the cell is simpler to that of the CaF_2(Eu) flow-cell proposed by Kawano *et al.* (2011), with a detector cell sandwiched between two PMTs connected in coincidence. The difference to the earlier works is that the cell is composed of CaF_2(Eu) sheets, rather than being in granular form.
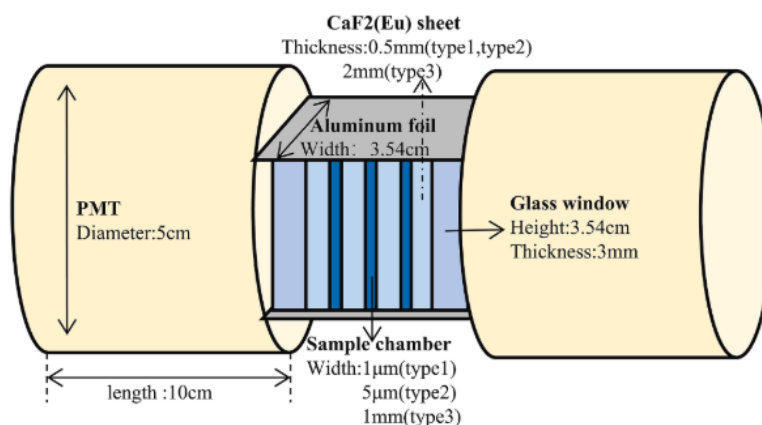

Figure 16. The geometry of the counter with three sample chambers in Monte Carlo simulation of the CaF₂(Eu) cell [132].

Through their simulations, the authors modelled a variety of scintillator thickness and chamber sizes, and a number of chambers. Within these parameters, the volume of the cell ranged from approximately 0.5-28 ml. Their results show that the optimal chamber size was 3 μm, beyond this width there is negligible increase in the energy deposited within the scintillators, and that thinner crystals had the highest detection efficiency (< 2 mm). The overall performance of the cell is consistent with the work of Kawano *et al.* with the best reported MDA 2.95 Bq ml^{-1} and a photon collection efficiency of 25%.

Electrochemical-Assisted Radiometric Tritium Detection.

Work conducted by Berhane *et al.* (2017) combines the electrochemical reaction between ^{3}H and palladium in tandem with a scintillator and PMT setup to produce a novel tritium detector. Palladium is unique among metals at being able to absorb hydrogen into its crystal matrix [133]. Commercial H_2 sensors rely on changes in capacitance or resistance in the system as a result of hydrogen atoms entering the Pd matrix to quantify hydrogen concentration in a solution [134].

The ^{3}H detector expands on the H-Pd interaction, using a Pd layer (either non-porous or nano-porous) directly to coat a CaF_2(Eu) scintillator crystal [135]. To apply the Pd layers to the CaF_2(Eu) crystals, an electrodeposition technique was used from a $(NH_4)_2PdCl_4$ solution. For nano-porous Pd films, the crystals were pre-coated with a layer of hexagonally close-packed (HCP) polystyrene spheres (diameter 0.2 – 1.0 μm). The HCP polystyrene spheres are subsequently dissolved away following the

Pd coating. For non-porous films, the crystals were template-free, i.e., blank. The coated scintillator, either non or nano-porous, was then mounted onto a Hamamatsu H7828-01 PMT and connected to Black Star-Apollo 100 Universal Counter-Timer.

The nano-porous layer in particular allows for a significantly greater Pd surface area than the non-porous layer, thereby facilitating greater ^{3}H uptake. Having the porous Pd allows ^{3}H to be brought within 100 nanometres of the scintillation media, optimising the potential for low-energy beta particles to cause scintillation in the calcium fluoride.
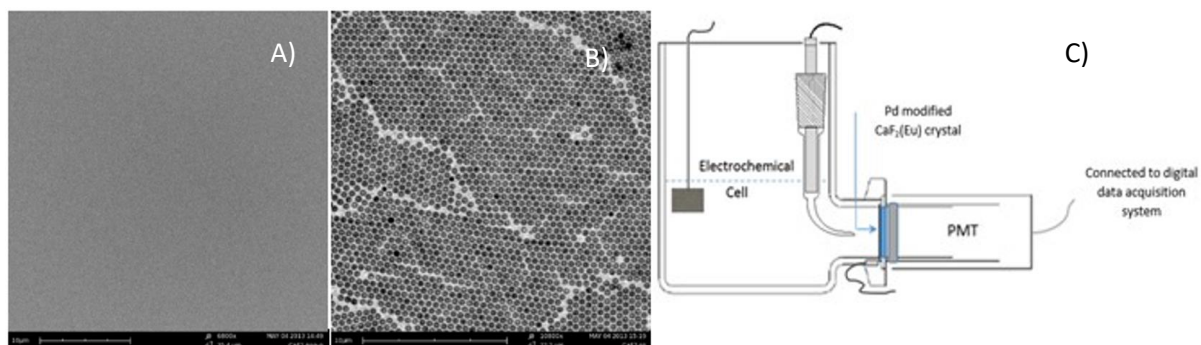

Figure 17. Scanning electron microscope (SEM) image of A) non-porous Pd layer, B) nano-porous Pd layer where the pore diameter is 500 nm, C) an experimental schematic of the NANODOT ^{3}H detection technique [135].

The Pd-layer detector has been tested with various ^{3}H solutions, both calibration samples and groundwater samples. Initial calibration samples were 10 MBq L^{-1}, which is several orders of magnitude higher than samples used in the other tritium analysis techniques described above and those found in groundwater samples. The technique has been shown to retain ^{3}H in the Pd layer even if the electrochemical cell, where the active samples are contained during the electrochemical loading, is flushed with de-ionsied water.

Based a sample volume of 30 mL connected to the Pd layer, the absolute efficiency of the detector is estimated to be 0.01% which is one of the lowest reported in this review. This is, however, an estimated efficiency based on the volume in which the sample is loaded. A higher efficiency might be determined if the total mass of ^{3}H in the Pd layer was determined rather than using the resident volume of the sample.

Additionally, the technique relies on the use of a dark box arrangement to house the experimental apparatus during radiometric counting. The exposure of the PMT to ambient light has a demonstrable influence on the response to ambient light and therefore background count. This is a fundamental aspect to capture the low intensity of light produced in the scintillator, and something that is not discussed in other works.

Techniques to Reduce Counting Durations

Although more peripheral to the central scope of this work, the treatments that are used to speed up the radiometric analysis of aqueous tritium samples by concentrating or enriching the tritium content in a sample are worthy of consideration. Even using ultra-low background liquid scintillation counters, with background counts of <1 cpm, it is still difficult to detect the presence of ^{3}H in environmental samples ($\approx$0.5 Bq L^{-1}). Therefore, techniques have been developed that enrich the tritium content in the samples to more measurable ^{3}H concentrations.

The most common enrichment technique is electrolysis, pioneered for the enrichment of tritium in water samples by Kaufman and Libby (1954). The electrolysis process causes the water sample to dissociate into its constituent molecules of H$_2$ and O$_2$ (see Equations 7-9), these evolve as gases thereby reducing the overall liquid volume in the sample. The process enriches the tritium content due to the mass differences between the isotopes of hydrogen (^{1}H, ^{2}H, and ^{3}H). The lighter isotopes have lower dissociation energies, therefore the protium and deuterium isotopes dissociate under electrolysis more rapidly in comparison to the heavier tritium. Electrolytic enrichment techniques have been described by Takahashi *et al.* (1968) [136], Taylor (1981) [137], Sauzay and Schell (1972) [138], Cook *et al.* (1998) [139], and Wallova *et al.* (2020) amongst many others [140]. The reduction in overall volume leads to an enrichment of the HTO molecule, referred to as the enrichment factor.

$$2H_2O(aq) \rightarrow 2H_2(g) + O_2(g) \qquad \text{Eq. 7}$$

$$2\,H^+(aq) + 2e^- \rightarrow H_2(g) \qquad \text{Eq. 8}$$

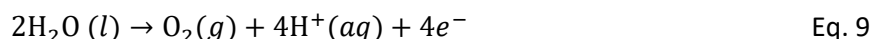$$2H_2O\,(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad \text{Eq. 9}$$

Figure 18. A front view of the 10-cell tritium enrichment system described in Kumar et al. (2016)

Electrolytic enrichment is a typical three-stage process consisting of: primary distillation, electrolytic enrichment, and secondary distillation. The primary distillation phase attempts to remove dissolved salts (e.g., Cl^-, SO_4^{2-}, Na^+, K^+, etc.) in the samples that may interfere with the electrolysis process. For the enrichment stage 1.5 g of high purity sodium peroxide (Na_2O_2), is added to the cell to make the samples conductive. The electrolysis is typically temperature controlled over several days. The final stage, secondary distillation removes the sodium peroxide electrolyte, and again takes several days.

The enrichment factor depends on a variety of experimental factors: e.g., time, amount of charge passed, the initial mass of tritium in the sample, etc. The duration of enrichment is typically on the order of several days. Enrichment factors for standard treatments range from 6-100 [140], [141]. The need to achieve specific enrichment factors can be dictated by other experimental limitations, such as the sensitivity of the counting system being used to analyse the enriched sample, or time constraints of the project.

Having an accurate measure of the enrichment factor is critical in determining the activity of samples, as the enriched solutions will be analysed, and the pre-enrichment solution activity is back calculated. Two common methods to determine the enrichment factor are the Spike Proxy Method and the Deuterium Method, with the latter reported to be the more accurate [142]. Several other works have been published presenting mathematical and statistical treatments to understand the enrichment factor so that more precise activity calculations can be made [143], [144]. The need to do this remains one of the fundamental issues with the radiometric analysis of low-activity tritium samples.

The principal disadvantages of tritium enrichment are:

1) the enrichment process is restricted by the size of the enrichment cells;

2) the electrolysis stage can take over a week to achieve maximum tritium enrichment;

3) the post-electrolysis distillation, neutralising the alkalinity in the solution is tedious and time consuming;

4) to determine the concentration of tritium in the original sample from the data obtained from the enriched sample, very accurate tritium enrichment factors must be known;

5) The additional calculation step increases the statistical uncertainty in the final value;

6) The process is very energy intensive and therefore there are additional costs associated with electrolysis including the cost of the electricity.

The above factors are further compounded by the need to repeat procedures on multiple samples which tests the reproducibility of the system. Despite these disadvantages, tritium enrichment can

achieve enrichment factors of up to 100 and even 1000 times have been reported [145], [141], i.e., the detectable tritium concentration appears to be 100 times the pre-electrolysis level, with volume reduction up to 25 times the original volume.

In addition to the enrichment derived issues, discrepancies in repeated procedures can be caused by contamination lingering in equipment from earlier runs or imprecise experimental protocols, such as with respect to maintaining the electrochemical parameters. If done correctly, the residual error can be very low, as shown by Morgenstern and Taylor (2009), who developed an electrolytic technique to prepare environmental samples for LSC analysis [146]. Their work also emphasises the work done by the IAEA to maintain consistency across laboratories by performing regular inter-lab. comparisons. Results of the comparisons still shows even the best performing laboratories can have residual error in the measurements of over 8 tritium units (TU), approximately 16 Bq L^{-1}, see Figure 19 [146].
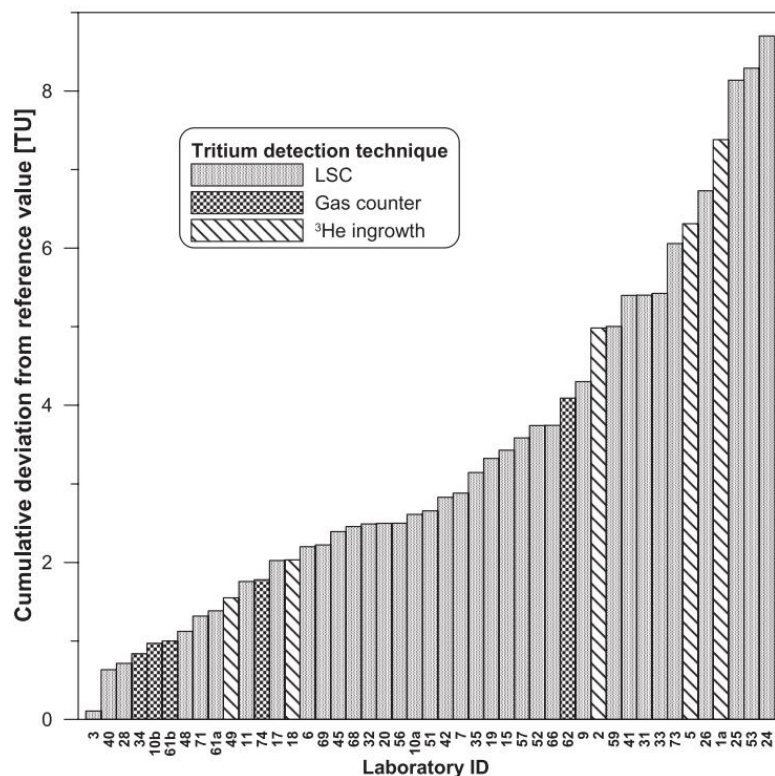

Figure 19. Cumulative deviations from reference tritium standards in the 7th IAEA Intercomparison of Low-Level Tritium Measurements in Water. Only showing the best performing two-thirds of the dataset [146].

In addition to increasing the ^{3}H content through electrolytic concentration, there are steps to reduce the effects of quenching in the LSC samples. To reduce the effects of chemical quenching, a range of purification techniques have been reported. Distillation is the most common technique utilised, this also includes atmospheric, multi-vial [147], membrane [148], azeotropic distillation ([149], in combination with ion exchange treatments [150], [151], or sub-boiling distillation [152]. Most of these techniques are labour intensive and time consuming to achieve the volumes of solution necessary for

LS counting (~50 ml). Li *et al.* (2020) reported a technique recently that reduces the time taken to achieve sample purification using a reverse osmosis (RO) film [153]. The RO technique showed comparative sample purification performance to standard distillation methods in 25% of the time (standard distillation takes approx. 3 hours).

Discussion and Benchmarking

All the ^{3}H detection techniques described in this review are based on the beta decay causing luminescence in a detection media, and the majority are based on scintillation with the one exception being the use of imaging plates, based on photoluminescence. Given the fundamental differences to the other techniques described, imaging plate techniques are the hardest to assess in terms of potential use or commercialisation. The process does show promise as aqueous tritium has been imaged and the activity calculated in a relatively short time frame (30 minutes in the case of Irikura *et al.* (2017) [111]), but in-depth comparisons with the other techniques is not possible here as the papers do not discuss detector efficiency. As can be seen from Table 3, the activities used in the research are far above the WHO and EU drinking water limits for HTO, so from that point of view alone it is the least sensitive method here, however the work is relatively recent and there is much scope for further improvement.

Of the other techniques, liquid scintillation counting is by far the most mature of the technologies described in this review and forms the basis of recognised international standards for detecting ^{3}H in drinking waters. In the case of LSC, it optimises the interaction between the low-energy β^- particles and scintillant by combining them in a cocktail. Typical performance for LSC techniques in the analysis of environmental samples demonstrates a MDA of the order of 1×10^{-4} Bq g^{-1} for a counting duration of around 3-5 hours and detection efficiency of 60% [154], [87]. However this may require the enrichment of the samples to an enrichment factor of 20, which takes up to 6 days to achieve [154]. In their review of the measures taken to reduce background count in the detection of environmental radionuclides, Douglas *et al.* (2015) state that given the sensitivity of current LSC systems, the electrolytic enrichment step could be omitted. A primary reason for omitting this step, aside from it reducing the counting times, is due to the need for accurate conversion factors to determine the pre-enrichment concentration and the time consuming nature of the process [154].

The example of LSC shown in the list of the best performing detection techniques for each of the different categories, see Table 3, is from the work of Erchinger *et al.* (2015) who described the development of an ultra-low background LS counter [92]. The results appear to be the best performance reported for low-activity radiometric ^{3}H detection to date, with amongst the highest reported detection efficiency and the lowest estimated MDA (6×10^{-4} Bq g^{-1}). This was achieved

without the need for sample enrichment due to the sensitivity of the counter, using Quantulus LSC, and bespoke background reduction shielding. Though this is the best performing technique, the performance of off-the-shelf liquid scintillation counters is similar, as Erchinger *et al.* (2015) achieved their sensitivity primarily by significant reduction of background interference. The MDA is two orders of magnitude better than the other detectors in this review but, given the advanced technical maturity of liquid scintillation compared to the other techniques (the development of LSC pre-dates all the other techniques by at least thirty years), it is to be expected.

The principal drawback of liquid scintillation techniques, and the use of highly specialised ultra-low background liquid scintillator counters, is that it is not readily deployable for real-time *in situ* measurements of groundwater samples. Samples may have to undergo days of pre-treatment before analysis in the counter, which may require specialist laboratories as in the case of the detector developed by Erchinger *et al.* (2015). Samples also must be prepared before counting, which may include distillation, enrichment, and then mixed with the scintillation cocktail, which are difficult processes to automate.

For scientific and research purposes, the static, ultra-low background counting facilities will continue to be necessary and the sensitivity will undoubtedly be improved upon. Despite this, there remains a need for real-time *in situ* assessment of aqueous samples for tritium content. Five of the examples presented in Table 3 are based on the on-line flow cell concepts, where ^{3}H-contaminated samples could be analysed with autonomous sample preparation. Of the five examples, only one system has been commercialised by LabLogic Ltd. (the Wilma Online Radiation Monitor system). The Wilma system has purported to have an MDA that is amongst the best performing of all those listed in Table 3. with an MDA levels of 0.0814 Bq g^{-1} for a 60-minute count [65]. This is still one of the best performing systems compared to other techniques listed in Table 3 and, as stated, the only commercially available, on-line system.

Other than the Wilma system, none of the potential on-line flow cells appear to be near a commercially available system. However, systems under development show promise. The MDA reported by Azevedo *et al.* (2020) for their scintillating fibre detector was 0.03 Bq g^{-1}, the simulated detector was also estimated to have a modest detection efficiency of 5% [121]. Of the reported detectors in Table 3, this is the second-best MDA and the only detection technique other than LSC-based techniques to have an MDA lower than both the WHO and EU ^{3}H drinking water limits [121]. Whether these will be validated experimentally is yet to be reported. Even if the experimental MDA is not as low as the simulated one reported, the principal benefit is the faster expected preparation and analysis times, which is the defining purpose of the systems. Though if competitive levels of detection

sensitivity are required, the proposed systems still fall some way short of the best performing LSC system.

One of the major impediments to *in situ* real-time analysis is that tritium is rarely found in isolation in the environment, but rather as part of a mixture of contamination, particularly in such mixtures found around nuclear sites due to water-borne migration in the ground. Common radionuclides that are found along with tritium include longer-lived fission products, e.g. strontium (^{90}Sr, half-life 28.8 years) and caesium (^{137}Cs, 30 years), which yield mid-energy beta and gamma-ray emissions [17], [18]. Even though these isotopes may often arise in lower concentrations than ^{3}H, because of the difficulty of detecting tritium, they present significant radiological interference which could easily overwhelm detection of the tritium emission. However, tritium can also serve as a migratory precursor of these longer-lived, higher-radiotoxicity agents. As such, any real-time detection method needs either an in-built method of sample preparation, a hyper-sensitivity to very-low energy beta particles, or MCA capability by which different contaminant nuclides might be discerned.

The Electrochemical-Assisted Radiometric Tritium Detection method, reported by Berhane *et al.* (2017) has the potential to treat samples prior to counting, as the technique uses an electrochemical process to isolate tritium from the groundwater samples in a palladium layer on the surface of the CaF$_2$(Eu) scintillator. Following this the sample can be flushed out of the cell leaving only the tritium in the vicinity of the detector that would be counted. However, at the time of publication no results have been published that demonstrate the capability of the technique for tritium detection in multi-isotope aqueous solutions. The other CaF$_2$(Eu)-based, flow-cell systems do not report on the use of mixed isotope sources in their work either, and hence either rely on the specificity of the scintillator to the tritium β$^-$ emission or would require a sample pre-treatment step to remove contamination, e.g., ion exchange. Furthermore, none report the use of MCA.

Furthermore, unlike modern LSC systems, almost all the CaF$_2$(Eu)-based detectors reviewed here do not refer to energy spectra, but rather to a pulse or count rate that is proportional to the intensity of the incident radiation. Whilst most of the systems use PMTs, allowing for the potential use of coincidence counting systems to reduce the impact of spurious counts [121], [155], it is not reported that they collect spectral information. As such, any radiation present in a sample, tritium or otherwise would contribute to the count rate, further emphasising the need for a pre-treatment of the sample.

The granular CaF$_2$(Eu) detector proposed by Alton *et al.* (2017) uses a silicon photomultiplier (SiPM). In their work they present simulated energy spectra of the beta particles detected. However, in their follow-up paper where simulation results are verified experimentally, only count-rate data of beta

particles is presented. In addition, the authors do not state that their proposed detector is suitable for use in multi-isotope solutions.

A second main disadvantage of LSC is the production of secondary radioactive wastes. The technique requires the mixing of ^{3}H-containing solutions with a liquid scintillation cocktail, commonly in 40:60 or 50:50 ratio. As such, the liquid radioactive waste volume is doubled and the sample vials, containing the mixture, become contaminated as well creating solid radioactive wastes. Even online LSC systems, such as the Wilma On-line Water Radiation Monitor, require mixing of scintillant and samples, though this is performed semi-autonomously.

The development of the imaging plate sensors [109], plastic scintillation (both solid-crystal and pelletised) [117], [125], electrochemical-assisted radiometric detection [135], all refer to the flushing and reuse of the ^{3}H sensors, thereby reducing the amount of waste produced. These works show that the sensors or detectors can be reused – up to certain level of contamination in some circumstances – and do not require the use of additional materials such as scintillation cocktails. The works also demonstrate systems that have reasonable performance measures in terms of detection efficiency, though still orders of magnitude less sensitive than the best LSC techniques. They do offer a shorter measurement time compared to traditional LSC methods. However, it is unclear as to how much of a reduction in wastes these techniques might realise, compared to techniques available currently.

It is interesting the note, that there have been few specific efforts to reduce the effects of background counts described in the non-LSC techniques listed above. As documented, the use of both passive and active background count suppression methods is adopted widely in both commercial and research LSC apparatus. A majority of the CaF_2(Eu) scintillator setups have adopted the use of two PMTs, which are used in coincidence to reduce spurious counts, but other than that there is little else in terms of reported background count discrimination techniques [115], [117], [119], [120], [132]. Only the work of Kawano *et al.* (2014) studied the effect of background reduction using 5 cm thick lead shielding to improve counting sensitivity. Their results showed a significant reduction (53.8%) in background count which contributed to a 35% reduction in the MDA over a 10,000 second counting period. Combining these results and the difficulty in detecting tritium in the first instance, it is surprising that there is not more reported work on reducing background counts. Perhaps this is because the techniques are not at a sufficiently mature stage to consider such measures.

Given the difficulty in detecting tritium in aqueous media and the resulting lack of commercialised competition to liquid scintillation counting, it is likely that LSC will remain the primary means of analysing aqueous for tritium content for some time. However, the need for a more responsive and more environmentally friendly method of radiometric analysis remains.

In April 2021, TEPCO (the Japanese utility company responsible for cleaning up the Fukushima site) announced that they plan to dispose of the 1.25 million m^3 (containing 870 TBq of ^{3}H) of tritiated water (HTO) to the Pacific Ocean. The announcement came with government assurances of public safety that the water is below 1500 Bq L^{-1} (1.5 Bq g^{-1}) [156]. The debate and opposition to the release are at the heart of the ambiguity and efficacy of the Linear no threshold model discussed at the start of this review. Public fears and apprehension may be well placed when it comes to the operational record of TEPCO, but the likely impact of the release at the levels published would pose very minimal environmental and public harm. Public assurance on the safety of the low-activity HTO have even extended to developing a cartoon mascot, Little Mr Tritium, see Figure 20, which has since been abandoned.

Figure 20. Little Mr Tritium, a cartoon mascot developed by the Japanese government as a means of public assurance on the safety of low-activity HTO [157].

More tangible assurance is perhaps possible via clear communication and regular publication of the tritium levels in the discharged water and surrounding environment. The adoption of responsive and rapid real-time radiometric analysis without manual sample preparation would go some way to achieving this, not just through providing the data to assure the public but also saving time, money, and reducing waste. But, as apparent in this review, few if any techniques are yet viable and most have a long way to go to achieve the international recognition of liquid scintillation counting.

Conclusion

This review outlined the status of the techniques employed or being developed to detect tritium in aqueous media. Of the techniques reviewed, liquid scintillation counting is the best performing and industry benchmark, with a minimal detectable activity of the order 1×10^{-4} Bq g^{-1} and a detection efficiency of 60% achievable by most off-the-shelf counters. The lowest apparent MDA was 6×10^{-4} Bq L^{-1} for a 195-minute counting time recorded by Erchinger *et al.* (2015) using ultra-low background LSC. Given its performance, LSC forms the basis of recognised international standards for detecting ^{3}H in drinking water.

A significant drawback of LSC is that the preparation of samples is time consuming, especially if the samples undergo enrichment. Sample preparation can also double the volume of radioactive waste generated that requires disposal. Additionally, LSC is also not readily deployable for *in situ* measurements.

The other techniques for detecting aqueous ^{3}H described here have sought to alleviate these issues, particularly as many are reusable with minimal waste generation. There are several techniques based on a flow-cell arrangement, using solid organic and inorganic scintillators, with the underlying design philosophy that the detectors are to be used in real-time and *in situ*. These all seek to maximise the surface area where the tritium solution contacts the scintillator, imrproving the geometric efficiency. The Wilma Online Radiation Monitoring System (LabLogic Ltd., UK) is the only LSC flow-cell design that has been commercialised for real-time use, with a respectable MDA of 0.0814 Bq g^{-1} over a 60-minute counting time.

One of the additional complications to detecting tritium is that it is almost always found in the environment as part of a mixed radionuclide solution. Despite this, only one technique incorporates a sample pre-treatment step that removes other radioactive contamination (e.g. ^{90}Sr, ^{137}Cs) which can overwhelm the weaker ^{3}H signal. This is based on a CaF$_2$(Eu) counter that incorporates a palladium layer for electrochemical sequestration of tritium from mixed radioactive solutions. Like many of the other designs reviewed, either based on scintillators or imaging plate, the CaF$_2$(Eu) does not provide spectral information, just count rate. Despite this, several of the techniques in the literature show evidence of meeting key performance parameters, such as the WHO and EU tritiated drinking water limits 10,000 and 100 Bq L^{-1}, respectfully.

In addition to the detection methods themselves, significant improvements in the limit of detection can be made by reducing the influence of background radiation. Few studies have focussed on this issue, but studies that have have seen minimal detectable activities reduce by 35%.

Combining the newer technologies, isolation of tritium from contaminants and improved background suppression systems could see the ubiquitous liquid scintillation counter replaced as the industry standard for aqueous ^{3}H detection. But the difficulty in detecting tritium in aqueous media remains, as does the resulting lack of commercialised competition to liquid scintillation counting. As such, it is likely that LSC will be the industry benchmark for the near future at least.

Table 3. Overview of the radiometric detection systems reviewed in this work and their best reported performance.

Detection Technique	Paper Reference	Reported Counting Durations / Flow Rate	Reported ^{3}H Max. Efficiency	Estimated MDA	MDA < WHO ^{3}H Limit	MDA < EU ^{3}H Limit
Liquid Scintillation Counting (Best Performing)	Erchinger *et al.* 2015, Douglas et al 2016.	195 minutes	102 %	6×10^{-4} Bq g^{-1}	✓	✓
Liquid Scintillation Flow-Cell	Sigg *et al.* 1994	5 minutes	36 %	0.59 Bq g^{-1}	✓	-
LabLogic Wilma On-line LSC	LabLogic	60 minutes	15 %	0.081 Bq g^{-1}	✓	✓
Imaging Plate[1]	Hatano *et al.* 2011	3-50 Hours	N/A	4×10^{3} Bq g^{-1}	-	-
Imaging Plate Melt-On Scintillator[1]	Irikura *et al.* 2017	30 minutes	N/A	3.6×10^{3} Bq g^{-1}	-	-
Plastic Scintillation Sheets	Singh *et al.* 1995	100 mL min^{-1}	65%	37×10^{3} Bq g^{-1}	-	-
Grooved Plastic Scintillation	Uda *et al.* 2010	10 minutes	0.32 %	1.72×10^{3} Bq g^{-1}	-	-
Fibre optic tube	Azevedo *et al.* 2020	1 hour	5 %	0.03 Bq g^{-1}	✓	✓
Plastic Scintillator Pellets - Static	Furuta and Ito 2018	1 hour	5 %	0.23 Bq g^{-1}	✓	-
Plastic Scintillator Pellets – Flow Cell	Hoftstetter 1995	3 mL min^{-1}	3 %	0.8 Bq g^{-1}	✓	-
CaF$_2$:EU Heterogeneous Scintillator Pellets.	Kawano *et al.* 2014	10,000 sec		2.43 Bq g^{-1}	✓	-

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[1] This technique is based on Photostimulated Luminescence and a comparative efficiency value with scintillation techniques is not reported in the manuscripts and difficult to estimate, and as such subsequent MDA calculations are not possible.

CaF$_2$:EU Heterogeneous Scintillator Pellets.	Alton *et al.* 2018	10 minutes	0.84 %[2]	10.31 Bq g^{-1}	-	-
CaF$_2$:Eu Scintillator Sheets	Song *et al.* 2021	60 minutes	25 %	2.95 Bq ml^{-1}	✓	-
Electrochemical-Assisted Radiometric Tritium Detection.	Berhane *et al.* 2017	1-5 hours	0.002%[5]	50.58 Bq g^{-1}	-	-

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[2] Efficiency reported estimation based on the total disintegrations per second in the sample volume and the net counts per second recorded in the detector.

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