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A REVIEW OF TRITIUM-IN-WATER MONITORS

Un examen des moniteurs de tritium dans l'eau

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RÉSUMÉ

On examine la situation actuelle des moniteurs de tritium dans l'eau. On soutient que le défaut principal des moniteurs existants de tritium dans l'eau est l'imperfection du prélèvement d'échantillons. La plupart des détecteurs à scintillateur liquide et solide sont suffisamment sensibles pour les applications de détection en temps réel. Bien que d'autres techniques de détection de tritium dans l'eau soient possibles, elles présentent toutes les mêmes problèmes de prélèvement d'échantillons et sont soit non sensibles soit coûteuses soit compliquées soit inapplicables pour la détection en temps réel.

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ABSTRACT

The current status of tritium-in-water monitors is reviewed. It is argued that the main short-coming of existing tritium-in-water monitors is imperfections in the sample delivery. Most of the liquid and solid scintillation detectors are adequately sensitive for real time monitoring applications. Although other techniques for detecting tritium-in-water are possible they all suffer from the same sample delivery problems and are either insensitive, costly, complicated or not applicable for real time monitoring.

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INTRODUCTION

Tritium-in-water monitoring around heavy water moderated and cooled nuclear reactors is necessary for the control of tritium releases to the environment and as an early indication of heavy water leaks. It is desirable that these measurements be performed continuously with an online monitor. The required sensitivity and time response will depend upon the purpose of the monitoring and the particular facility (the DRL, flow rates, dilution, etc). However, it is often desired to measure down to several tens of kBq/L. For comparison, the maximum acceptable concentration for tritium in Canadian drinking water is 40 kBq/L [1].

Currently, most tritium-in-water monitoring is by grab sampling or some type of on-line scintillation counter. Neither of these methods is entirely satisfactory. This report gives the results of a review of the recent literature on this topic to determine if more development work in this area is appropriate at this time.

STATUS

The most direct and straightforward method of measuring the tritium concentration in water is to take a grab sample of the water and measure its tritium concentration using liquid scintillation counting techniques. The method is very sensitive but is costly in terms of manpower and does not give results in real time. In spite of these disadvantages this method is still widely used and is adequate where the required sample rate is not high.

Various approaches to real time tritium-in-water monitoring have been described. The two most common are automated batch sampling systems based on liquid scintillation counting and continuous systems using a scintillator flow cell.

Liquid Scintillation Counting

An automated batch sampling system has been described by Ting and Sullivan [2]. Their system consisted of a flow system that mixed liquid scintillator and a sample of the water supplied to it. The sampled water and the liquid scintillator were metered into a vial and counted in a standard liquid scintillation counter. The batch sample rate was 10 per hour. Failure of the tubing in the multichannel peristaltic circulating pump limited the length of continuous operation. Perhaps this problem could have been overcome with the selection of other material. Satisfactory performance has been obtained with teflon or stainless steel in pumps used with scintillation cocktail [3][4]. For flow rates of a few mL/min, gravity feed through capillary tubes has also been shown to be suitable for continuous sampling [5].

Osborne developed an automated urine analyser [3] that, on demand, metered a quantity of liquid scintillator with urine into a counting system. This system could be modified to periodically take a batch sample of water and measure its tritium activity.

Huntzinger [6] has also built a tritium-in-water monitor which mixes tritiated water with liquid scintillator. This monitor uses a "cross-flow" filter to obtain a clean sample before mixing with the scintillation cocktail.

A major problem encountered with automated liquid scintillation counting is to ensure that the water and scintillator cocktail is properly mixed. This problem is common to various low energy beta emitter detection techniques utilizing liquid scintillation cocktails. Some successful mixing techniques include: agitation by air while tumbling through a mixing cell [7][3], magnetic stirring [4][5], and sonication [8][9]. All the above require suitable metering systems for the water sample and the scintillator and are sensitive to the mixing ratio of the two components. The sample and scintillator flows must be kept constant and their mixing must be complete.

Scintillation Flow Cells

Several continuous tritium-in-water monitors have been developed using flow cells containing solid scintillator. Anthracene coated plexiglass [10], scintillator plate [11], thin scintillator sheets [12], scintillator sponge [13], scintillator film [14], doped quartz balls [15], and plastic scintillator beads [16] have been used.

In flow cells, the scintillator is usually made to be as thin as is practical. Because of the very short range of the tritium betas, there is no advantage to thick scintillators. Thick scintillators will increase the response to most interfering species although energy discrimination will help somewhat. But energy discrimination is not as helpful as might be expected. Many of the radiation interactions are with the water rather than the scintillator. The low energy electrons produced can not be differentiated from a tritium beta.

Purging the water sample by bubbling a clean, that is, nonradioactive, gas through it is an effective method of reducing the concentration of radioactive gases dissolved in the sample. Appropriate filtration can reduce the effects of radioactive particulates. Lead shielding can reduce the effect of external gamma fields.

Most of the monitors described are adequately sensitive to measure tritiated water concentrations of a few tens of kBq/L in laboratory conditions. However these monitors often fail in the field. Effluents requiring monitoring are often dirty and filtration down to at least 5-10 micron pore size is necessary [7]. Even at this size, some dirt (silt, charcoal particles, slime and algae) in the sample water can pass through the filters and foul the surface of the scintillator. This decreases the amount of light seen by the photomultipliers and decreases the cell efficiency. The clogging of the in-line filters can seriously affect the response time. The use of smaller pore size filters increases the frequency of necessary replacement.

In addition to dirt, the sample often contains other interfering substances. These include, in addition to radioactive materials, luminescent materials,

chemiluminescent materials, and any contamination that may reduce the sensitivity of the flow cell through discolouring of the scintillator plates or reduced light transmission to the photomultipliers.

Chlorine, which is often used to prevent bacterial growth in water systems, interferes with the measurement of tritium through chemiluminescence. The chlorine can be removed from the water with activated charcoal filters. This, however, can cause a carbon dust problem.

Other Detection Methods

Other techniques for detecting tritium have been reported. See, for example reference [19]. These methods include mass spectrometry, gas chromatography, calorimetry, Bremsstrahlung, electron multipliers, thermally stimulated exoelectron emission, film, and infrared spectroscopy. In general, these methods are either not adequately sensitive, too expensive, too complex, or not applicable to real time monitoring. They will not be discussed further.

A method of differentiating among interfering alpha, gamma and beta emitters is by the use of phoswich detectors. Phoswich detectors consist of two sandwiched scintillators of different fluorescent materials, with different time responses. By pulse shape analysis, the distribution of the energy between the two scintillators can be determined. This provides information on the nature of the radiation. This method has been suggested [17], but not specifically tested, for the detection of tritium. In principle the method could significantly reduce the response from gamma radiation and higher energy betas.

Kiel [18] has reported on the use of a semiconductor detector (silicon guard-ring photodiode) for low energy particle detection. The diode used was manufactured as a photodiode and not specifically made for nuclear counting. With this detector a tritium beta spectrum was obtained at a counting efficiency of about 50%. NCRP [19] has reported that with current state of the art detectors (1976) tritium in water concentrations of the order of 40 kBq/cm³ can be measured with a detector having a surface area of 10 mm². This is with a diode that is not optimized for tritium detection and with a very small surface area. Webb and Jones [20] have investigated an avalanche diode with about twice the area of the previously mentioned detector. Although they have not specifically looked at tritium betas, they reported a peak resolution of 1.65 keV f.w.h.m. for the Fe-55 X-ray of 5.9 keV. However, Johnson et al. [21] report only a 1% detection efficiency for tritium with an avalanche detector. No recent work has been found using semiconductor detectors for low concentration tritium measurements.

Mass spectrometry, by measuring the ³He concentration buildup in a sealed sample, can detect tritium in water concentrations lower than by liquid scintillation counting [22]. But the sample preparation is in the order of 0.5 man-hours per sample for a 20 minute spectrometer counting period; the

cost of the mass spectrometer equipment is about 3-4 times the cost of a liquid scintillation counter. Because of the storage time required for the ^3He concentration to rise, this method cannot be used for real time monitoring.

DISCUSSION OF IMPROVEMENTS

For those situations where real time results are required, scintillator flow cell detectors appear to be the best simple method of monitoring tritium in water. The major problem with these detectors is in supplying a clean sample to a clean detector cell. With proper filtration and water conditioning existing tritium-in-water monitors should be suitable for continuous real time measurements in a heavy water power station environment. There does not appear to be any fundamental limitation to supplying a clean sample. A strict maintenance and testing schedule would be required to ensure that the sensitivity and time response of the instruments are maintained.

Various methods for supplying an appropriate clean sample to the flow cell can be considered. The use of a radiant still has been suggested by Osborne, [23] but a prototype monitor was never built. Decours and Guerin [16] have used a modified commercial still on their prototype "TRIDYN" detector. The overall response time of the monitor was of the order one hour. They conclude that some improvement in the response time should be achievable by using a still with a higher throughput.

Experience at Atomic Energy of Canada Limited by Osborne [7] in collecting HTO with bubblers has shown that bubbling clean air through water will produce water vapour that is relatively clean. Huntzinger [6] has found in an experimental bubbler system, in which a clean and dry gas was passed through a representative waste water stream, that the collected water vapor was free of contaminants. This was true even when the starting water solution contained chemicals such as potassium permanganate, food coloring, light motor oil and detergents. The major difficulty in this approach is the large number of flow meters, humidity meters, level sensors and flow controllers required to control the sample, purge, and liquid scintillator flows.

The use of resin columns was investigated by Decours and Gerin [16]. Their system consisted of a 30 micron filter and a 5 micron filter, followed by a cation column, an anion column and a final cation resin column. A final activated charcoal filter, with a 5 micron pore size, was added. This filtration system, although effective in keeping the detector clean, was abandoned because of the long response time and cost of replacing the resin columns. At a flow rate of 6 L/h the response time was about 2 hours and the filters only lasted one week.

The use of semi-permeable membranes, Nafion in particular, may offer some possibilities for tritium-in-water monitoring. There are at least two different ways that Nafion could be used: 1) to mix water with liquid scintillator and 2) to provide a clean water sample.

Nafion may be used to mix liquid scintillator and water. For example, a monitor could be based on circulating liquid scintillator through a closed loop; collecting a water sample by diffusion through the Nafion; measuring it in a conventional scintillation counter; and removing the water before recirculating the liquid scintillator to collect water again. The removal of the water prior to the next pass through the Nafion is necessary so that the scintillator does not pick up water indefinitely. Alternatively, an open loop system could be used but this would be much more expensive to operate because of the liquid scintillation cocktail usage.

Nafion could also be used in conjunction with water and a solid scintillator. In this case, the Nafion would separate the sample flow from the water flowing through the flow cell. If the water were in a closed loop, the tritium concentrations would equalize on both sides of the Nafion independent of the permeation rate through the Nafion. The permeation rate would, of course, affect the monitor's time response. Besides delivering a clean sample to the flow cell, this scheme would allow the water chemistry of the sample side to be adjusted so as to prevent the growth of slimes, molds and algae.

The use of NAFION has also been suggested by Huntzinger [6] to measure water vapour in air bubbled through a waste water stream. Liquid scintillator was passed through Nafion tubing and the vapour stream from the bubblers passed over the exterior of the tubing. The vapour diffused directly into the scintillator and the activity measured in a flow through counter. Various tubing sizes were tried but the largest concentration ratio of sample water to liquid scintillator that was achieved was 0.0078. This ratio was disappointingly low and this approach was abandoned. In our experiments [25] we have achieved a much higher water loading in the scintillator.

Another untested method passes a clean flow, a calibration flow, and a sample flow through a detector in sequence. The clean flow could be reverse flushed in order to help maintain a clean detector. Such a system could feature automatic zero and background corrections; it could give some indication of the condition of the detection cell and it could be automatically corrected by a microcomputer. Labserco, has experimented with a system of this general type. It has not been described in the literature nor has it seen actual field service.

Systems with two flow cells, that can be alternately switched in or out, may reduce the down time and facilitate the routine cleaning of the detection cells. Reverse flushing of the cell not in use with an appropriate cleaner is also a possibility.

In a recent report, Huntzinger [6] has developed a tritium-in-water monitor using a "cross-flow" or "tangential" flow filter to reduce the clogging of the sampling system. In this design a macerator and an ultraviolet sterilizer was utilized to condition the sample flow before being introduced to the cross-flow filter. The fast moving flow continually washes over the cross-flow filter medium removing debris that would otherwise clog the filter. The resulting clean sample is introduced through a passive mixing cell and continuous flow liquid scintillator detector. This system, although the filtration was more efficient and self cleaning, still required

the filter to be replaced approximately every ten days. The obvious benefits of this design are the fact that the filter water volume is reduced and the filter can be inspected visually. Although the described monitor used liquid scintillator there are no apparent reasons why a flow cell with plastic scintillator cannot be used.

CONCLUSIONS

Existing real time tritium-in-water monitors are of sufficient sensitivity. The main problems centre around sample delivery and maintenance. Current systems based on flow cells with solid scintillators can provide satisfactory performance if a strict maintenance schedule is followed. For example, a recent report by A.N. Singh [13] indicates that their instrument has a maintenance requirement comparable to that experienced by Ontario Hydro and Chalk River [24] and Livermore [6]. The inline filters have to be changed every week, the activated charcoal and mixed resin filters every month and the detection cell is changed when the sensitivity drops below 80% (about every 6 months).

There are various options for possible improvements. Most of these are the application of good engineering practice to a defined problem. There is no indication radically new concepts are required. Indeed, most other solutions are likely to involve the same sort of sample delivery problems.

The Nafion based solutions appear to offer the promise of improved sample delivery. They warrant further investigation.

None of the other detection methods appear to offer significant advantages that would warrant further development at this time. Scintillation counting still appears to be the most appropriate detection method.

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