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Real-time aqueous tritium monitor using liquid scintillation counting

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Abstract

The ability to continuously monitor low-level tritium releases in aqueous effluents is of particular interest to heavy water facilities such as those at the Savannah River Site (SRS) and Canadian CANDU reactors. SRS developed a real-time monitoring system based on flow-through liquid scintillation (LS) counting. Sensitivities of 16 pCi/ml and 1 pCi/ml result from five minute and daily averages of counting data respectively. This sensitivity is about 200 times better than similar methods using solid scintillants. The LS system features uncomplicated sample pretreatment, precise proportioning of the cocktail and sample water, on-line quench corrections, cocktail consumption as low as 0.15 ml/min, and response to changes in environmental tritium in less than 30 min. Field tests demonstrate that conditions necessary for stable analytical results are achieved.

1. Introduction

Inherent to heavy water reactor operation is the production of tritium in the moderator. The potential release of tritium to the environment through aqueous effluents has been a long standing concern at the Savannah River Site (SRS), at CANDU reactors, and at other tritium-handling facilities. Earlier attempts [1,2] to address the environmental monitoring needs by liquid scintillation were discontinued because difficulty of the problem restricted success. However, the potential for such releases became a reality in several unexpected environmental discharges in recent years at SRS and at the Pickering NGS reactor unit. Heat exchanger leaks went undetected for periods longer than previously anticipated in each case. The absence of a capability to continuously monitor for tritium in these effluents precluded taking prompt corrective action to mitigate the release.

The Savannah River Site (SRS) and the Pickering NGS have now successfully developed several tritium effluent water monitors (TEWM). The first SRS system uses solid scintillant (SS) beads [3], and is presently used at several SRS facilities. The TEWM reported here and the CANDU systems [4] apply flow-through liquid scintillation (LS) counting technologies. The LS TEWM meets goals to simplify sample pretreatment, provide quantification as well as detection, and rapid detection of tritium levels of several pCi/ml. This sensitivity is important if a purpose of the monitor is to detect small leaks before they result in more significant problems.

2. Description of the monitor

Fig. 1 provides a simplified overview of the fluid flow, sample water pretreatment, and counting subsystems that comprise the aqueous tritium monitor.

2.1. Sample pretreatment

Sample pretreatment for the LS monitor is accomplished by coarse and fine filtration steps followed by flash distillation. Water is pumped through a coarse screen filter at the environmental sampling point, and through a 10 μm cross-flow filter. The face of the sintered metal cross-flow filter is continuously washed by a 10 l/min flow rate; since only a few ml/min are drawn through for distillation, it can operate for extended periods without additional cleaning or replacement. A small continuous still, maintained at 170°C, immediately flashes water to steam. Distillation diminishes concentrations of species that may otherwise cause quenching and luminescence.

This pretreatment system for the liquid scintillant TEWM is considerably simpler than was required for the system that uses solid scintillation beads. This is possible for several reasons. First, while LS cells have little restriction to flow, minor fouling can cause high pressure differentials and almost total blockage of small passages between solid scintillant grains or beads. As small amounts of material coat the solid scintillant particles, many low-

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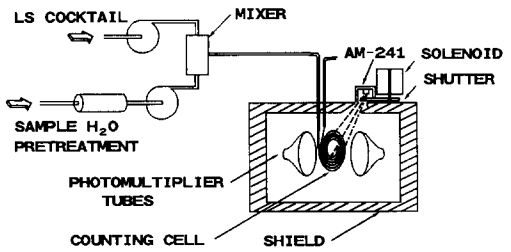

Fig. 1. Overview of the liquid scintillation tritium effluent water monitor.

energy tritium beta particles can not reach the scintillant; this can profoundly decrease SS counting efficiency. A liquid scintillant cell can tolerate some fouling without significantly degrading counting efficiencies since sample and scintillant are almost homogeneously mixed. Further, the flowing water/LS cocktail mixture helps clean the counting cell.

2.2. Pumping systems and time response

Good time response is achieved by rapidly delivering purified sample water to the counter while minimizing scintillant consumption. This is attained by pumping excess water from one system stage to the next where only a small fraction is drawn off for use in the next stage. Specifically, a centrifugal pump moves environmental water to be monitored at about 10 l/min from the sampling location to the instrument position where it passes across the surface of a cross-flow filter. Only 2 ml/min of sample water is drawn through the filter for further pretreatment by flash distillation; an additional 10 ml/min of filtered water is used to cool the distillation system. About 0.12 ml/min of the treated water is pumped from the bottom of an open 1 ml collection vessel for counting; the remainder of the treated water is allowed to overflow into another vessel for disposal. A 0.25 ml static mixer blends approximately 0.15 ml/min of LS cocktail with the sample water, and the counting mixture passes through a 2.5 ml flow cell.

A single, computer-controlled motor drives positive displacement pumps for sample water and environmentally safe LS cocktail to ensure constant proportioning of the liquids. Three pumps provide flow from filtration to distillation, from distillation to mixing cell and from cocktail to mixing cell. Use of a single gear reduced DC electric motor to drive the three pumps simplifies the computer monitoring and control of flow-rates. At the lowest speed, the instrument reaches full response to changes in environmental tritium concentration in less than 30 min, and cocktail consumption is less than 7 l/month. Flow-rates may be increased by up to a factor of six thereby allowing for practical compromises between scintillant cost and response time.

Excellent time response with low cocktail consumption is realized by minimizing dead volumes through careful attention to tubing lengths and diameters, mixing cell volume, etc. The small tubing diameters placed limits on the high end of the flow-rate range because the viscosity of Ultima Gold XR (TMCanberra/Packard Instruments) is relatively high. Other properties of this cocktail make it attractive for the flow-through liquid scintillation counting application. These properties include its excellent water loading, high counting efficiency, quench resistance, and good environmental safety. Other cocktails with lower viscosity but similar counting properties are now available if higher flow rates are necessary.

2.3. Counter

A 2.5 ml flow-through cell, shielded for background reduction and viewed by dual photomultiplier tubes (PMTs) is the core or the LS counting system. It is based on a Packard/Radiomatic Model A250 HPLC counter with flow cell formed by a coiled Teflon (TME.I. du Pont de Nemours & Co.) tube. As is standard with this system, amplified signals are stored by the multi-channel analyzer when PMT signals are coincident. If singles event rates are high due to luminescence or a light leak, high voltage to the PMTs is disabled. SRS-developed modifications, discussed below, make the HPLC instrument more suitable for environmental monitoring.

2.4. Counting efficiency

The tritium counting efficiency determined by addition of tritium standards is about 36% for the LS monitor. While this is not a high efficiency compared to modern discrete sample liquid scintillation counters, it is several orders of magnitude larger than the 0.18% efficiency [3] for a flow-though cell packed with plastic scintillation beads. The short range of the tritium beta in water (maximum) accounts for the difference in efficiencies between the solid and liquid scintillation cells. Since the tritium beta range is small relative to the average distance between solid scintillant beads, most tritium betas lose their energy in water before having an opportunity to interact with the solid scintillant. Addition of low-activity aqueous tritium standards are accomplished through simple valve operations. The standard is pumped until the count rates reach a plateau (Fig. 2), indicating that the cell is completely flushed with a fresh cocktail/standard mixture. The figure evinces very low sample retention by the coiled Teflon flow cell; count-rates quickly return to baseline when ordinary sample water is reintroduced.

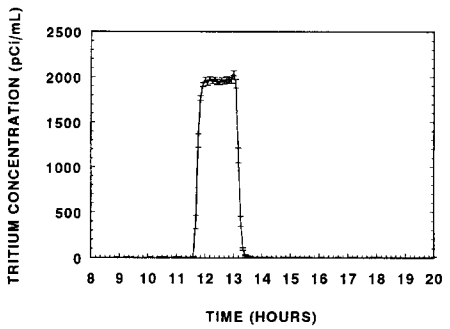

Fig. 2. Addition of a tritium check standard solution. The nominal concentration of the check standard was 1930 pCi/ml.

2.5. Background

The counting cell and PMT assembly are housed in a stainless steel lined, 2.54 cm-thick lead shield which reduces counting backgrounds to 16 counts/min in the tritium window.

2.6. Sensitivity

Tritium sensitivities [5] for the flow-through liquid scintillation monitor versus counting time are compared to those for the solid scintillant system in Fig. 3. Since both instruments accumulate short interval counting data in computer memory, both monitors can pool data to give average counting results over longer counting intervals. Sensitivities for 5 min, hourly and daily averages are better than 16, 5 and 1 pCi/ml respectively for the LS monitor. The significant sensitivity advantage of the liquid system is mostly due to its better counting efficiency.

2.7. Quench correction

Sample preparation steps generally result in small concentrations of oxygen and other chemicals being dissolved along with the sample/cocktail mixture. These trace constituents can provide alternate paths for scintillant de-excitation following an ionizing event. Competing de-excitation channels decrease the amount of light emitted and can lower counting efficiencies. Many discrete sample liquid scintillation counters provide methods for determining the extent of such quenching and correcting for its effects on counting efficiencies. In external source methods, the difference spectrum between that collected when the sample is exposed to a gamma-ray source and that collected by the source alone is used is used to determine the light output characteristics of the sample/cocktail mixture. Counting efficiency for the sample is determined by comparing this difference spectrum response to the response obtained on a series of known standards having different quenching levels.

An external, shuttered ^{241}Am source provides periodic, automatic, on-line quench corrections for the TEWM. Low energy gamma-rays from the source are easily attenuated with light weight shielding for the field monitor, a 3 mm-thick tungsten shutter assembly is opened to expose the counting cell to the 59.5 keV gamma-rays for several minutes. Though the period between quench checks is adjustable in software, one hour intervals were used in this work. While numerous methods have been used to determine a quench indicating parameter [6], a simple approach gave good results and was implemented. Least-square fitting methods determines the fractional channel number containing 99.5% of the integrated difference spectrum.

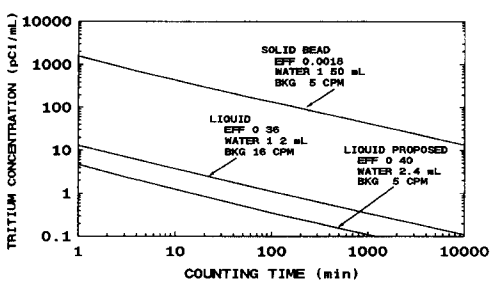

Fig. 3. Sensitivities of liquid and solid scintillant tritium effluent water monitors. The center curve is the minimum detectable concentration for the monitor described in this report.

2.8. Used LS cocktail

As this work began, it was believed that the generation of LS cocktail waste might limit acceptance of the method. We believed that the clear advantages offered by LS methods – in sensitivity, reproducibility of results, and pretreatment ease – warranted taking steps to overcome this perceived disadvantage. Our earlier report [7] describes development and application of Nafion membrane drying methods to regenerating LS cocktail containing tritiated water. The study found that the regenerated cocktails gave counting efficiencies that were as good as or better than fresh cocktail from the vendor. The method is specific to removal tritium. Other authors [1,2] discussed preliminary work using Nafion to selectively add water to cocktail for counting.

Though cocktails are not released to the environment, studies by an independent laboratory found the "environmentally safe" cocktail had very low toxicity and could be discharged with appropriate permits at low concentrations to the stream. As mentioned above, the present instrument greatly reduced cocktail consumption relative to HPLC instruments. This was accomplished with little loss in time response as flow-rates were reduced by making compensating reductions in dead volumes.

2.9. Logging and control

An IBM PC compatible computer stores and analyzes the counting data every 30 seconds. It pools these data to obtain the more sensitive five minute, hourly and daily averages reported above. It also reports detection of any non-tritium activities through analysis of higher energy regions in the beta spectra. Tritium and higher energy data are logged in every counting interval, and spectra are saved along with quench and efficiency results on an hourly basis. Revised control software enables continuous operation for environmental monitoring rather than short chromatographic runs.

The PC performs similar functions for aqueous tritium monitor subsystems. Operations of subsystems are followed by numerous transducers in order to better understand the first-generation LS monitor performance. Should any failures occur, they may be readily recognized and diagnosed. Mass-flow meters are incorporated in every branch of the flow paths. Temperature sensors monitor the still and condensor intake and exit water. A pulse counter helps determine DC motor speed, and the speed is controlled by a digital to analog device.

3. Field test results

Field tests demonstrated reliable operations on surface and well waters with minimal maintenance requirements. Early tests were conducted at a monitoring well near the Savannah River Technology Center. Surface water was monitored at an outfall that received cooling water from the inactive L-Reactor at SRS. Performance of the monitor was exceptionally stable throughout the combined five months of operation.

When development of the tritium monitor first began, the on-line quench correction was expected to play a pivotal role in the success of the monitor. Counting efficiencies determined in hourly checks of the quench indicating parameter remained nearly constant. The lack of significant quenching effects demonstrates that the selected pretreatment regimen is effective if not optimal. The quench test verified proper operation of the counting system on a regular basis.

Near-constant counting efficiencies, observed in periodic checks using low activity tritium standards, clearly indicate that necessary conditions for stable analytical results are achieved. Data from check calibrations, repeated in the field at approximate one week intervals, show the tritium counting efficiency remained constant at 0.36 ± 0.02 throughout the months of field testing. Reproducable direct efficiency measurements confirmed that the pumping and blending of water and cocktail remained constant through the test period and that the counting cell did not foul. The resistance to fouling is thought to be due to effective sample pretreatment and appropriate cell design.

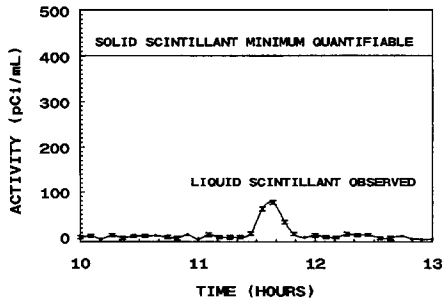

Fig. 4. Response to a low level tritium release. Tritium was easily observed by the liquid scintillation based monitor at L-Reactor outfall, but levels were below those that can be quantified by the solid scintillant system.

The monitoring well, near the Savannah River Technology Center, was the simpler field test case; the system ran for approximately three months without interruption other than for two electrical power outages. At the more difficult surface water location, cleaning or replacement were required for the filters at two week intervals and for the still approximately once a month. Minor changes to pretreatment were identified that could extend the service periods. System design enabled completing such change-outs in a few minutes.

The system was shut down for several days at a time while it was under development at the laboratory, while relocating it to new monitoring sites and following an electrical power interruption. When the system was restarted after each of these protracted outages, the high voltage would disable as though a light leak had occurred. PMT bias could be restored when the pumps were operated and lines were purged with fresh water and cocktail. It is believed that the excess light was produced by bioluminescence.

Ambient tritium background concentrations were normally low and stable. Fig. 4 displays a time series of 5-min averaged tritium results from a 3-hour period at the L-Lake location. Tritium levels at the location were slightly elevated as reactor heat exchanger maintenance was performed. However, the actual tritium release, determined from measured concentrations and flow-rates, was very small and below reportable quantities. These low levels were easily observed by the liquid scintillation based monitor, but were far below levels that can be quantified by the solid scintillant system.

4. Conclusions

Success of methods developed by several groups for continuously monitoring tritium in aqueous effluents was determined by careful application of known counting and pretreatment technologies. Adequate pretreatment of sam-

ple water is essential for reliable operation over extended periods. The different approaches to the counting systems are primarily due to differences in goals set for the monitors. Sensitivity of the liquid scintillation monitor is sufficent to detect and measure tritium at levels near the environmental background for surface water. This study addressed objections to applying liquid scintillation technology to such applications by minimizing cocktail consumption, regenerating cocktail for reuse, pretreating sample water to minimize quenching, and periodic testing for quenching. The present effort was also assisted by the relatively recent availability of quench-resistant cocktails that accept high water loadings.

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