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by

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ABSTRACT

The development of a low-level tritium monitor for aqueous effluents has explored several potential techniques. In one method, a water-immiscible liquid scintillation cocktail was ultrasonically mixed with an aqueous sample to form a water-cocktail dispersion which was analyzed by liquid scintillation spectrometry. The organic cocktail could then be reused after phase separation. Of the cocktails tested, the highest tritium detection efficiency (7%) was determined for a toluene-based cocktail. In another technique, the response of various solid scintillators (plastic beads, crushed inorganic salts, etc.) to tritium solutions was measured. A 2% tritium detection efficiency was observed for the most efficient solid scintillators tested. In a third method, a large surface area detector was constructed from thin fibers of plastic scintillator. This detector had a 0.1% intrinsic tritium detection efficiency. While sensitivities of ~25 kBq/L of tritium for a short count have been attained using several of these techniques, none can reach the environmental level of <1 kBq/L in aqueous solutions.

INTRODUCTION

There is presently no commercially available on-line monitor for tritium in aqueous solutions. The sources of tritiated water in the environment and the difficulties in developing a tritium monitor with real-time response have been reported (e.g., Reference 1).

A monitor capable of continuously measuring tritium in aqueous solutions could improve many operations that involve tritium as a product or as an impurity (e.g., heavy water purification, heavy water moderated reactors, etc.). Process control at such facilities is typically performed by batch sampling and laboratory analysis. The strategic location of tritium monitors throughout the process could improve the efficiency of the operation and alert personnel to process upsets. Installed on the effluent, a monitor could mitigate an unplanned tritium release and its consequences by stopping the effluent flow when high tritium concentrations were detected. The sensitivity requirements for each monitor would depend on the type of process and its location within the process. For example, an analysis of the discharge pathway from the heavy water purification facility at SRS indicates that an effluent monitor should be capable of detecting a

tritium concentration of 37 kBq/L within several minutes.

A real-time monitor for tritium in environmental streams could also be used to verify compliance with existing regulations. Compliance monitoring is now performed exclusively by proportional sampling and laboratory analyses. This practice has been acceptable due to the historically low tritium levels in the environment and to the low biological hazard associated with tritiated water. However, from a public perception point of view, it is desirable to have on-line monitoring for tritium in aqueous streams to verify that EPA Drinking Water Standards (0.74 kBq/L) (2) are not being exceeded, for example. The advantages of continuously monitoring radionuclide releases from commercial (3) or DOE facilities (4) in real time are obvious. The sensitivity levels for compliance monitoring are much lower than required for process control or breakthrough monitoring and should be well below the applicable standard.

The monitors should be field hardened to environmental or process conditions, operate unattended for long periods of time, be simple to calibrate and operate, be easy to maintain, and provide stable readings under steady state conditions. A semi-continuous tritium monitoring technique has been reported using water soluble cocktails in a suitable flow cell (5) but the cost of the cocktails for continuous operation would be high and their discharge to the environment questionable. Recycling the cocktail is under investigation (6). The concepts under evaluation in this study include the use of water immiscible liquid scintillation cocktails, plastic beads of solid scintillators or crushed inorganic scintillators, and thin fibers made from plastic scintillator material as possible real-time tritium detectors. The background, efficiency, sensitivity, precision, and accuracy of each detector system are presented along with the advantages and disadvantages of each technique.

WATER-IMMISCIBLE LIQUID SCINTILLATION COCKTAILS

Experiments were performed to evaluate water insoluble liquid scintillation cocktails as a means of detecting tritium in aqueous solutions. Conceptually, an aqueous sample is mixed with the water-immiscible cocktail and the semi-stable dispersion analyzed by standard liquid scintillation counting techniques. After counting, the suspension was separated, the aqueous phase was discarded, and the cocktail was subsequently reused. Various cocktail-water combinations were tested after ultrasonic mixing and the efficiency, suspension time, separation time, and recycle capability of each were determined.

Samples of four major types of liquid scintillation cocktails (toluene, xylene, mineral oil, and pseudocumene) were obtained from commercial vendors for testing. A small ultrasonic mixer with a frequency of 25 kHz and a power output of 20 watts, was

filled with water and used throughout these experiments. A Packard Model 2000LB liquid scintillation counter was used for counting the dispersions. Tritium beta spectra were recorded to evaluate changes in spectral shape as the dispersion began to separate into two phases. Special counting protocols were developed to acquire and store the spectra on computer compatible disks.

Various combinations of mixing times and ratios of aqueous to organic phase were tested in a systematic manner for each cocktail. These procedures were then repeated using the recycled cocktail, both before and after backwashing with deionized water. The optimum tritium detection efficiency occurred when 1 mL of a tritium spiked aqueous sample was mixed with 15 mL of cocktail.

The results of the tests showed that the toluene- and xylene-based cocktails had the highest tritium detection efficiency. The observed tritium counting efficiencies are given in Table I. In addition to low detection efficiency, the mineral oil and pseudocumene-based cocktails did not mix well, agglomerating and sticking to the walls of the vial. While the xylene-based cocktail had the highest counting efficiency, the toluene-based cocktail showed the better tendency to mix and yet quickly separate from the aqueous phase. The detailed procedure and results of the study have been presented (7). In summary, the average tritium counting efficiency for the tests with the xylene-based cocktail was 7.1 ± 2.3 percent (32% 2σ relative standard deviation (RSD)). Similar tests using the toluene-based cocktail yielded an average tritium counting efficiency of 2.8 ± 1.1 percent (39% 2σ RSD).

It was observed that after washing fresh cocktail or backwashing used cocktail, a white precipitate formed which did not tend to settle during phase separation. One or more of the components of the liquid scintillation cocktail mixture may be extracting as a result of repeated aqueous washing. This speculation may also explain some of the inconsistent results for counting efficiency. Changes in the volume ratios and mixing times did not improve the detection efficiency or the measurement precision. The external standard method of quench correction showed no correlation with the observed counting results. Additional experiments with different scintillators or different mixing methods are suggested.

SOLID SCINTILLATORS

Various solid scintillators have been tested for tritium response using a commercial instrument originally designed to detect labeled compounds separated by a high pressure liquid chromatograph (HPLC). The system was described in reference 1 along with the results of the experiments with the yttrium silicate inorganic scintillator provided with the system. The other solid scintillators tested to date are beads of

plastic scintillator in three size fractions (see Table II). The beads are manufactured by Bicron, Inc. from product BC-400. To test the beads, special FEP Teflon tubing was formed into a U-tube, the beads poured into the tube, and fixed in the bottom with glass wool plugs. The U-tube containing the beads was placed in a cell holder, connected to a liquid recirculation system, and placed in the instrument. The U-tube configuration was similar to that supplied by the vendor for the yttrium silicate cell with a 1 mL void volume. Two different sizes of FEP tubing were used for the bead tests (6.4 mm and 4.8 mm ID).

A solution recirculation system was assembled which included a HPLC pump capable of producing a controlled flow (1-2 mL/min) at high pressures. The aqueous solution was pumped from a storage reservoir, through the measurement cell, and back to the storage reservoir. Flow and pressure measurements were made during the system operation. Because Teflon tubing was used in the measurement cells, all tests were performed with an upper operating limit of 700 kPa differential pressure.

The electronic parameters, e.g., high voltages, lower and upper level discriminators, amplifier gains, coincidence resolving time, etc. were set per the manufacturer's recommendations for the yttrium silicate cells. These parameters remained constant throughout the testing program for all scintillators. Data were acquired by a computer based data acquisition system. The average count rates in the tritium and gross beta counting channels were output every hour while the real-time display of the data was updated every 10 minutes.

A typical test of each scintillator ran for 7-10 days. During the first few days, deionized water was circulated through the cell and data collected on the background count rate. For the next several days, the intake of the HPLC pump was switched to a tritium spiked aqueous solution with specific activity of 250-300 kBq/L. This solution was recirculated through the cell, sampled, and analyzed by standard liquid scintillation counting. The response of the system to the tritium solution was compared to the analysis result. The system was then flushed with deionized water for several days. A plot of the data recorded during a typical run is shown in Figure 1. Note that the data recorded in the gross-beta channel is independent of the tritium concentration.

Table II gives a comparison of the figure of merit (FOM) of the various solid scintillator/cell configurations as expressed as E^2/B where E is the detection efficiency (cpm/concentration) in percent and B is the background in cpm. Of the systems tested, the 0.4 mL cell filled with crushed Yt silicate had the highest FOM. This cell has a spiral geometry. The FOM for the 4.8 mm U-tube containing plastic scintillator beads in the size range 0.1- 0.25 mm was only 10%

lower than the 0.4 mL cell. While the yttrium silicate cells had higher detection efficiencies, they also had a higher backgrounds leading to comparable FOMs. In addition, the cells containing crushed scintillator had high differential pressure (400-600 kPa) which plugged more quickly when exposed to solutions containing particulates. The back pressure on the cells containing 0.1-0.25 mm beads was <70 kPa.

The sensitivity of each measurement cell was calculated as the minimum detectible activity (8). Using this formalism, the tritium counting efficiency, background, sample size, and count time were combined to evaluate each cell's ability to detect events which are statistically above background. The results are summarized in Table III for several arbitrary counting times. The counting times chosen indicate each cell's ability to detect a change in concentration over a short interval, an intermediate interval, and over an extended period. The results show that a release producing tritium concentrations > 25 kBq/L could be detected within ten minutes by cells containing small scintillator beads and cells containing Yt silicate. While this may be adequate for process control or breakthrough monitoring, none of the scintillator/cell configurations can reach the <1 kBq/L sensitivity goal for compliance monitoring even when the data are pooled over a period of one day. Additional experiments with smaller beads in smaller diameter cells are suggested.

PLASTIC SCINTILLATION FIBERS

A monitor capable of continuously measuring low tritium concentrations requires a detector with high tritium detection efficiency. A detector cell was constructed with 477 - 1.0 mm diameter X 50 mm long plastic scintillator fibers yielding an effective surface area of 750 cm². Since the maximum range of the tritium beta particle in water is about 6 microns, the effective interaction volume is only 0.5 mL even though the liquid volume of the cell is about 100 mL. The fibers, manufactured by Bicron, Inc., were equally spaced on 2 mm centers, and glued individually into two pre-drilled Lexan plates which served as the ends of the cell. All other cell components were made from Lexan and were coated with reflective paint on their interior surfaces. The flow of liquid is perpendicular to the fibers. The outside ends of the fibers protruding through the Lexan plates were polished and then optically coupled to a pair of Philips XP2202B photomultiplier tubes (PMT).

Standard fast-slow coincidence electronics were used in the post-detector amplification and timing systems. The PMT anode outputs were used in the timing circuit as the coincidence requirement ($2\tau = 5.8$ nsec) while the dynode outputs were summed for energy analysis. High gain demanded operating the PMTs at or near their maximum voltages (+2000 Volts).

Energy calibration was accomplished using gamma-ray point sources positioned outside the measurement cell. The resulting Compton spectra were analyzed by standard pulse height analysis techniques. Figure 2 displays three spectra taken with one of the PMTs and the results of the analysis of the highest energy component in each Compton spectrum. The gain of each PMT was matched by high voltage adjustment before the signals were summed for energy analysis. Beta spectra were then taken with and without tritium solutions circulating through the cell and the final single channel analyzer (SCA) window adjustments were made. The SCA signal was then fed to a linear gate which passed the energy pulse provided the coincidence requirement was met.

Figure 3 displays the monitor output when deionized water and tritium spiked water were circulated through the system. A recirculation system similar to that used during the testing of the other solid inorganic scintillators was used for these tests. The major difference was that this system circulated solutions at a nominal flow of 30 mL/min. The data shown in Figure 3 results in a bulk efficiency (cpm/concentration) of 0.1% for this detection cell. Because of the high background, the FOM for this system is significantly lower than that calculated for the other solid scintillators tested. A lower sensitivity limit of 100 kBq/L has been calculated from these data. The design of an improved cell is nearing completion. New high gain, low noise PMTs and preamplifiers will be tested to improve the system performance.

CONCLUSIONS

While additional experiments are underway to investigate the use of immiscible liquid scintillation cocktails as an on-line aqueous tritium effluent monitor, the most promising technique employs stationary solid scintillators as tritium detectors. These type detectors have application as process control and breakthrough monitors with the current technology. To explore solid scintillators as compliance monitors, calculations of the maximum tritium detection efficiency have been performed. Monte-Carlo methods were used to generate the maximum efficiency for an aqueous solution in contact with a detecting surface. The extremes of the calculations were established by the maximum beta range for tritium in water. This limit established an effective interaction volume for the sensor per unit area. Applying the Monte Carlo method outlined by Rucker et. al (9), an efficiency of $9.4 \pm 0.3\%$ per unit area was calculated assuming 100% intrinsic detection efficiency (i.e., all events reaching the scintillator are detected). This efficiency was compared to that observed for all solid scintillators tested. The result of this comparison is shown in Table IV. In the case of the inorganic scintillators, the cell void volume was assumed to be the interaction volume. In one experiment, four fibers (150 mm long) were placed in the U-tube cell and the response recorded as tritium solution

flowed through the cell. In this experiment, the scintillations were viewed perpendicular to the fiber length. It can be seen from the data in Table IV. that all the experimental efficiencies are less than the computed maximum. Part of this is due to the imprecise treatment of the low energy portion of the beta spectrum in the calculation while part is due to the low-energy threshold of scintillators.

The data suggest that a combination of large surface area scintillators with low specific volume, e.g., a large bundle of smaller diameter fibers, could produce a detector with sufficient tritium efficiency to operate as an environmental monitor. Other combinations of scintillators and cell configurations are being tested during the development of a tritium monitor for aqueous streams.

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**Table I. Liquid Scintillation Cocktails used During the
Testing with Measured Range of Tritium Detection Efficiencies**

Vendor/Trade Name	Cocktail Base	Efficiency Range	Eff. Ave.
=====			
Packard/Insta-Flor	Xylene	3-11%	7.1%
Packard/Perma-Flor	Toluene	1-5%	2.8%
Packard/Opti-Flor-O	Pseudocumene	<2%	1.2%
Bicron/BC-517	Mineral Oil	<1%	0.8%
=====			

Table II. A summary of the solid scintillators tested in this study. The Figure of Merit is the square of the tritium detection efficiency in percent divided by the background count rate in cpm.

Scintillator	Cell	Figure of Merit (E^2/B)X1000
Yttrium silicate	1.0 mL void	2.0
Yttrium silicate	0.4 mL void	5.5
0.1-0.25 mm beads	4.8 mm U-tube	4.9
0.1-0.25 mm beads	6.4 mm U-tube	1.06
0.25-0.5 mm beads	4.8 mm U-tube	3.4
0.25-0.5 mm beads	6.4 mm U-tube	4.2
0.5-1.0 mm beads	4.8 mm U-tube	0.23
0.5-1.0 mm beads	6.4 mm U-tube	0.37

Table III. The minimum detectible tritium concentrations (kBq/L) calculated for several counting intervals for each solid scintillator tested. See explanation in text.

Scintillator	<u>Minimum Detectible Concentration</u>		
	10 min	1 hour	1 day
Yt silicate (1.0 mL)	41	16	3.2
Yt silicate (0.4 mL)	25	10	2.0
0.1-0.25 mm beads(4.8)	27	10	2.1
0.1-0.25 mm beads(6.4)	57	22	4.5
0.25-0.5 mm beads(4.8)	32	13	2.5
0.25-0.5 mm beads(6.4)	29	11	2.3
0.5-1.0 mm beads(4.8)	124	48	9.6
0.5-1.9 mm beads(6.4)	97	38	7.5

Table IV. Comparison of observed detector efficiencies for the solid scintillators reported in this study. The interaction volume is the surface area of the detector times the maximum range of the tritium beta particle (6.6 μ m).

Scintillator	Area cm ²	Int. Volume cm ³	Efficiency (%)
Yt silicate (1.0 mL)	--	1.0	0.18
Yt silicate (0.4 mL)	--	0.4	0.73
0.1-0.25 mm beads(4.8)	187	0.123	1.69
0.1-0.25 mm beads(6.4)	327	0.215	0.51
0.25-0.5 mm beads(4.8)	98	0.065	2.65
0.25-0.5 mm beads(6.4)	172	0.113	1.82
0.5-1.0 mm beads(4.8)	43	0.028	1.66
0.5-1.9 mm beads(6.4)	76	0.050	1.16
4 fibers (1.0 ϕ x150mm)	4.8	0.003	4.64
477 fibers (1.0 ϕ x50mm)	749	0.493	0.22

LIST OF FIGURES

Figure 1. Hourly average count rate data obtained from a 4.8 mm Teflon U-tube filled with 0.1-0.25 mm plastic scintillator beads. Water spiked with tritium is introduced into the system and then subsequently flushed.

Figure 2. Compton spectra obtained from point sources located outside the cell. Analysis of the maximum energy component was used to establish energy calibration.

Figure 3. A plot of the count rate seen by the fiber detector when exposed to tritium spiked water in a recirculation experiment followed by a deionized water flush.

(Figures are DRAFT)

Figure 1. Hourly average count rate data obtained from a 4.8 mm Teflon U-tube filled with 0.1-0.25 mm plastic scintillator beads. Water spiked with tritium is introduced into the system and then subsequently flushed.

Standard Point Sources

in air

Figure 3. A plot of the count rate seen by the fiber detector when exposed to tritium spiked water in a recirculation experiment followed by a deionized water flush.

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