

Development of Aqueous Tritium Effluent Monitor

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ABSTRACT

A variety of techniques are being evaluated and tested in an attempt to develop a real-time monitor for low-level tritium in aqueous streams. One system being tested is a commercially available HPLC radioactivity monitor. This system uses crushed yttrium silicate as the scintillator and employs standard fast coincidence electronics to measure tritium. Laboratory tests of this unit indicate that the monitor can sense tritium at concentrations above 600 pCi/cc using a two minute counting interval. Pooling the count rate data over a longer interval, e.g., 24 hr results in a detection limit of ≈ 20 pCi/cc under constant background conditions. Unfortunately, the cells are easily plugged with debris even under laboratory conditions.

To overcome this problem, a prototype system using unclad fibers of plastic scintillator as the detection medium was designed and is being tested in the laboratory. Approximately 500 1-mm in diam fibers were assembled into a flow cell, with two 51-mm in diam photomultipliers (PMTs) coupled to the ends of the fiber bundles, to detect the scintillations. Fast coincidence, pulse shaping electronics are used to minimize the single photon and dark current backgrounds. The tritium counting efficiency, background, and sensitivity will be determined in the laboratory followed by field reliability testing.

The results of laboratory tests and a comparison of other types of scintillators (liquids, plastic beads and fibers, crushed inorganic, etc.) are presented. The sample preconditioning requirements (e.g., filtration, ion exchange, etc.) and known interferences (e.g., chemical and biological luminescence, natural radioactivity, etc.) for continuous monitoring of tritium in surface waters are discussed.

INTRODUCTION

Tritium is one of the most significant radioactive isotopes released to the environment by the nuclear industry. It is produced in light water reactors by ternary fission, in heavy water reactors by neutron capture in the moderator, in tritium production facilities at our defense facilities, in fallout from nuclear weapons testing, and as a byproduct of nuclear fusion development. The releases are predominantly in the form of tritiated water (HTO), its most active

biologically form. While tritium is produced by cosmic ray protons in the atmosphere, the manmade quantities dwarf the natural levels.^{1,2}

The measurement of tritium is difficult due to its low energy beta emissions (maximum energy = 18.6 keV) and long half life (12.33 years).³ Most monitoring methods for tritium have relied on grab sampling and laboratory analysis by liquid scintillation counting methods. The main interferences in the laboratory analysis are due to color and chemical quenching in the sample. These laboratory analysis techniques have been summarized in a variety of publications.⁴ Real-time monitoring for tritium in the environment is not presently performed. Liquid scintillation techniques do not adapt readily to the measurement of tritium in flowing streams. A semicontinuous flow system has been tested using rapid mixing of the sample with the scintillation cocktail followed by injection into the counting chamber for a short count and then out to waste. The entire process is then repeated at short intervals to provide near real-time monitoring.⁵

The use of solid scintillators for tritiated water measurements in flowing streams has also been reported.⁵ While these detectors are less sensitive than liquid scintillation techniques, they offer three main advantages: the use of solid scintillators permit continuous monitoring, are not affected by chemical and color quenching, and are less expensive to operate (the cost of liquid scintillation cocktail is high and disposal of the contaminated cocktail is difficult).

Background

Management at the Department of Energy Savannah River Site (SRS) requested the development of an on-line monitor to detect tritium in various aqueous effluent streams. The Environmental Technology Section of the Savannah River Laboratory is conducting laboratory and field testing of various systems; they are looking for environmental levels of tritium with response time suitable for corrective action. After reviewing various flow-through scintillation systems, counting cells loaded with solid scintillators were recommended over water/liquid scintillation cocktail mixtures since: no potentially mixed waste was generated, an improved response time was achieved, the sensitivity was sufficient, and the operation was much simpler.

The specific objective was to develop a monitoring system capable of detecting tritium at a concentration of 2000 pCi/cc within 2 min, detect changes at the 2 pCi/cc level over a 24 hr interval, and to measure concentrations within 10% at the normal reactor discharge levels over a 24 hr period. The continuous monitor was not necessarily intended to replace the existing tritium grab samplers, with subsequent laboratory analyses as a means of quantifying a release. The primary purpose was to detect an abnormal release and provide early warning for emergency response.

To efficiently detect tritium, one needs a detector with high surface area as the most probable beta energy is about 5.7 keV; this corresponds to an average

range of only 6 μm in water. Most of the beta energy is lost in the water before reaching the scintillator, and relatively few photons are produced when there is an interaction. Maximizing the surface area increases the probability of a light producing event, while minimizing the detector volume reduces the background from cosmic rays and other beta emitters. Efficient light collection is mandatory.

Beads of plastic scintillator have been suggested as a tritium detector, but have large spacings relative to the short beta range. Only tritium in a thin sheath over the surface of the beads would be detected, resulting in a low counting efficiency and low sensitivity. Large sheets of plastic scintillator⁶ and thin fibers coated with anthracene⁷ have also been evaluated for tritium sensitivity. Crushed scintillators offer the highest surface to volume ratio and even with the decreased light collection efficiency, provides a sensitive tritium detection method.

EXPERIMENTAL

A commercially available tritium detection system was purchased for evaluation at SRS. The system was originally designed to detect tritium labeled compounds as they are eluted from a high-pressure liquid chromatography column.* The detector consisted of a Teflon measurement cell filled with crushed yttrium silicate solid scintillator interposed between two PMTs. Special pulse shaping and timing electronics are provided to minimize the background and maximize the counting efficiency for tritium. A computer-based data acquisition and analysis system is also provided as part of the system. Several solid scintillation materials are offered by the vendor for use as the tritium detector: cerium-activated lithium glass, calcium fluoride, yttrium glass, and yttrium silicate. The latter was chosen due to its high light output.⁸ The inorganic scintillator was crushed and then suitable grain sizes were selected to optimize the counting efficiency while minimizing back pressure.

A recirculation system was set up in the laboratory to circulate aqueous solutions containing tritium and various contaminants. The detector system uses a HPLC pump capable of reaching system pressures of 100 psi at well-controlled flow rates. Due to the burst pressure of the Teflon cell, the system pressures were carefully monitored and did not exceed this value during the testing. Several cells of differing void volumes and scintillator loadings were evaluated. A simple diagram of the monitoring system is shown in Figure 1. Backgrounds were taken by circulating demineralized water through the system. The efficiency of the system was determined using demineralized water spiked with various quantities of tritium and by comparing the monitor output with the concentrations determined from aliquots (analyzed by standard liquid scintillation counting techniques in our laboratory). System stability and

*Distributed by Berthold Analytical, Nashua, NH 03063

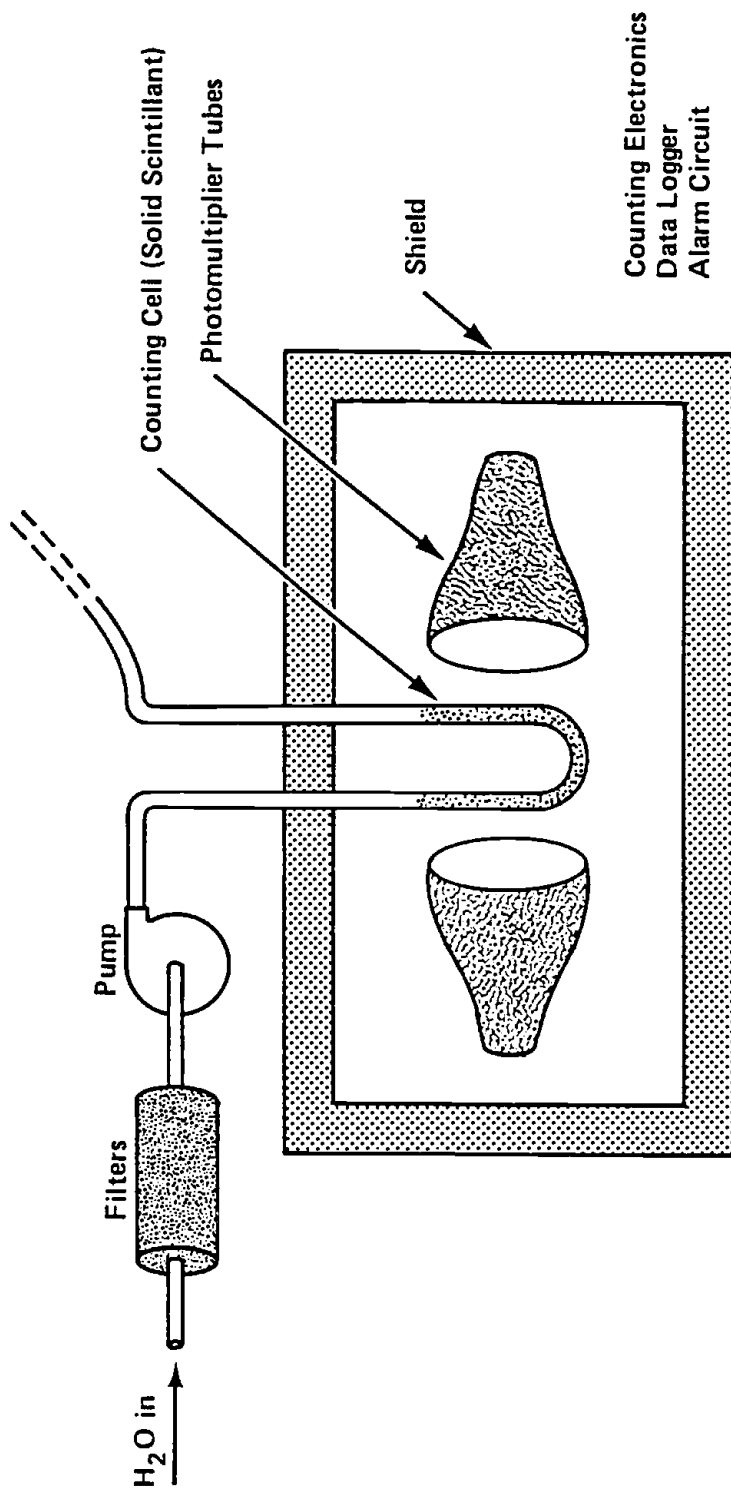


Figure 1. Simplified diagram of a continuous aqueous effluent tritium monitor using crushed scintillator.

Table 1. Performance Characteristics of Cells Containing Crushed Yttrium Silicate Inorganic Scintillator

Cell Void Volume (cc)	Background (cpm)	Efficiency (%)
0.4	12.5	1.77
0.5	14	0.4
1.0	18	0.35

reproducibility were determined by recirculating aqueous solutions through the system for extended periods (30 to 40 days).

The output of the tritium monitoring system was recorded using the computer-based data acquisition and analysis system. Two counting channels were set up on the system, the low-energy channel, set to encompass the tritium beta spectrum, and the high-energy channel, set to detect events above the tritium beta spectrum endpoint. Data were output at three different counting intervals, a short time interval (usually 10 min), an intermediate time interval (usually 10 hr), and a long time interval (usually 24 hr). The times were selected as typical for a field installation of the monitor, consistent with the overall goals of the project.

Three different counting cells were tested with three different cell configurations, each containing crushed yttrium silicate scintillator mesh sized to 35 microns. The largest cell had a void volume of 1 mL and was configured in a simple U-tube geometry using 7 mm OD \times 1 mm wall tubing. The smallest cell was a compact spiral of 5 mm OD scintillator filled tubing and with a void volume of 0.4 mL. The intermediate cell was a single loop of 6 mm tubing with a void volume of 0.5 mL. In all cases, the cells were placed between the two photomultipliers and maintained at a fixed distance relative to each other. The cells were sealed from stray light and the entire assembly placed inside a lead background shield.

The results of the testing of these cells are summarized in Table 1. The backgrounds are the minimum attainable for each cell. It was observed that the background would increase monotonically over a period of several weeks. A cell wash procedure restored the background to its minimum value.

DISCUSSION

Sensitivity

The sensitivity for measuring tritium is a function of the efficiency, the background, and the counting time. The detection limits were calculated using the methodology given by Currie.⁹ For completeness, the formalism used to evaluate the data are summarized below.

The minimum detectable concentration (pCi/cc) is defined as that concen-

Table 2. Minimum Detectable and Quantifiable Concentrations of Tritium for Cells Tested

Void (cc)	MDC (2 min) ^a (pCi/cc)	MDC (24 hr) (pCi/cc)	MQC (24 hr) ^b (pCi/cc)
0.4	600	20	60
0.5	2300	73	230
1.0	1450	48	150

^aMinimum detectable concentration for 2 min count (see text).

^bMinimum quantifiable concentration for 24 hr count (see text).

tration which has 95% probability of being above a threshold that is exceeded by only 5% of the background counts. It is given by:

$$\text{MDC} = \text{DL} / (V * t * \epsilon * 2.22)$$

where DL (counts) is the detection limit, V (cc) is the void volume of water in the active region of the cell, t (min) is the count time, ϵ (c/d) is the counting efficiency in the tritium channel, and 2.22 (dpm/pCi) is the rate conversion factor. The detection limit is given by:

$$\text{DL} = 2.71 + 3.29 * \text{sqrt}(B)$$

where the total background counts (B) is given by the product of the background count rate and the count time.

The minimum quantifiable concentration, as defined by Currie, is that concentration that will permit the quantification at a precision of 10% one sigma relative standard deviation as computed by the following:

$$\text{MQC} = \text{QL} / (V * t * \epsilon * 2.22)$$

where QL is the quantification limit (counts) as defined as

$$\text{QL} = 50 * [1 + \text{sqrt}[1 + (B / 25)]].$$

Using the data obtained from the cells tested in our laboratory and the above formalisms, the MDC and MQC for these cells for a short counting interval of 2 min and a long counting time of 24 hr can be calculated. The results are shown in Table 2. In all cases, it is obvious that the detection of a 2000 pCi/cc concentration is possible in a short period of time. At a 2 mL/min flow rate through the cells, careful engineering is required to minimize the holdup of the solution from the sampling point to the counting cell. It is also obvious that none of the cells meet the criteria for detecting or quantifying a release at the 2 to 10 pCi/cc concentration. A combination of a larger cell, with higher efficiency and lower backgrounds, is required. Figure 2 shows how the sensitivities could improve with reasonable advances in the cell and system design. A counting cell with a void volume of 3 mL a 7% counting efficiency, and a background of only 15 cpm would satisfy our requirements. The vendors claim that such improvements are possible, but to date, none have been attained.¹⁰

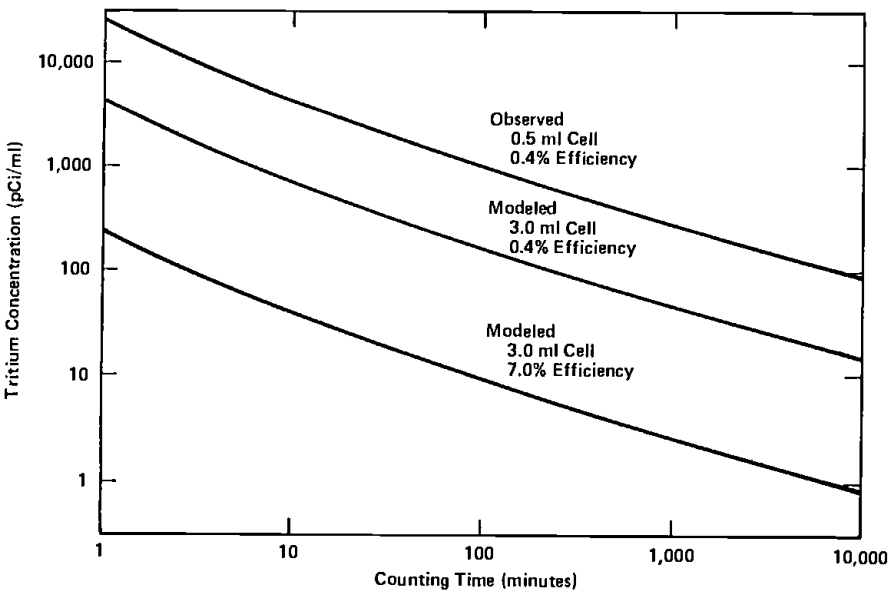
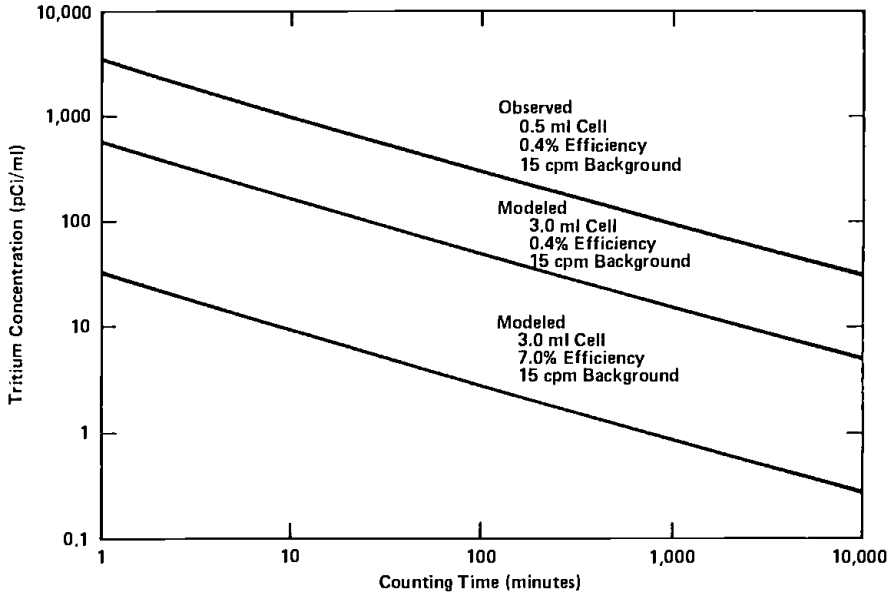


Figure 2. Minimum detectable and quantifiable activities for continuous aqueous effluent tritium monitor.

Stability

The variation of the efficiency or background of the detector will have a significant effect on the overall performance of the monitor. As stated previously, the background was observed to change by a factor of two over a several week period. This may be caused by the buildup of material on the surface of the scintillant or the presence of contaminants in the light-emitting water. Bioluminescence is a known interference with scintillation counting techniques.¹¹

To test the long term performance in a laboratory environment, and validate the calculated sensitivities, a 3-week-long experiment was performed using the 0.4 mL cell. First the background was established by recirculating demineralized water through the system, periodically cleaning with NaOCl or dilute nitric acid. This was continued until a constant background was attained (12.5 ± 0.8 cpm). After adequate background stability had been reached, a small quantity of tritium was introduced into the water recirculation system, and the monitor response noted. The initial aliquot increased the concentration of tritium to about 140 pCi/cc; an aliquot was removed for laboratory analysis. The monitor count rate increased by about 20% in the tritium counting channel while the high-energy beta channel showed no change in count rate (see Figure 3 for the hourly observations). After a suitable recirculation time (at least 24 hr) another aliquot of tritium standard was spiked into the system, and the response was measured. This cycle was continued until the concentration in the recirculation system reached ≈ 1000 pCi/cc. At this point the monitor was recording a system count rate of twice the background in the tritium counting channel and no change in the gross beta-counting channel. By removing aliquots of each solution for laboratory analysis, the efficiency of the monitor at each concentration could be calculated (see Figure 4 for a plot of the efficiency as a function of concentration). It was found that over the concentration range tested, the efficiency ($\epsilon = 0.0177 \pm 1\sigma$ R.S.D.) appears to be independent of tritium concentration (correlation coefficient = -0.073).

At this point in the experiment, the system was flushed with repeated washings of fresh demineralized water, and the detector response returned to background suggesting no memory effects. To begin testing aqueous solutions typical of surface streams, a sample of secondary cooling water from one of the reactors was obtained for testing and analysis. The cooling water is taken from the streams in the SRS area, passed through the reactor primary heat exchanger, and then discharged into a cooling pond before it is released back into the surface streams. A composite sample of the water discharged from one of the reactors was circulated through the monitor in an attempt to determine the tritium concentration. The calculated tritium concentration, from the increase in count rate observed by the monitor, was 200 pCi/cc, while laboratory analysis of an aliquot showed a tritium concentration of only 50 pCi/cc. The sample was highly quenched. The monitor response to the reactor effluent is shown on the right hand side of Figure 3. It is noteworthy that the gross beta

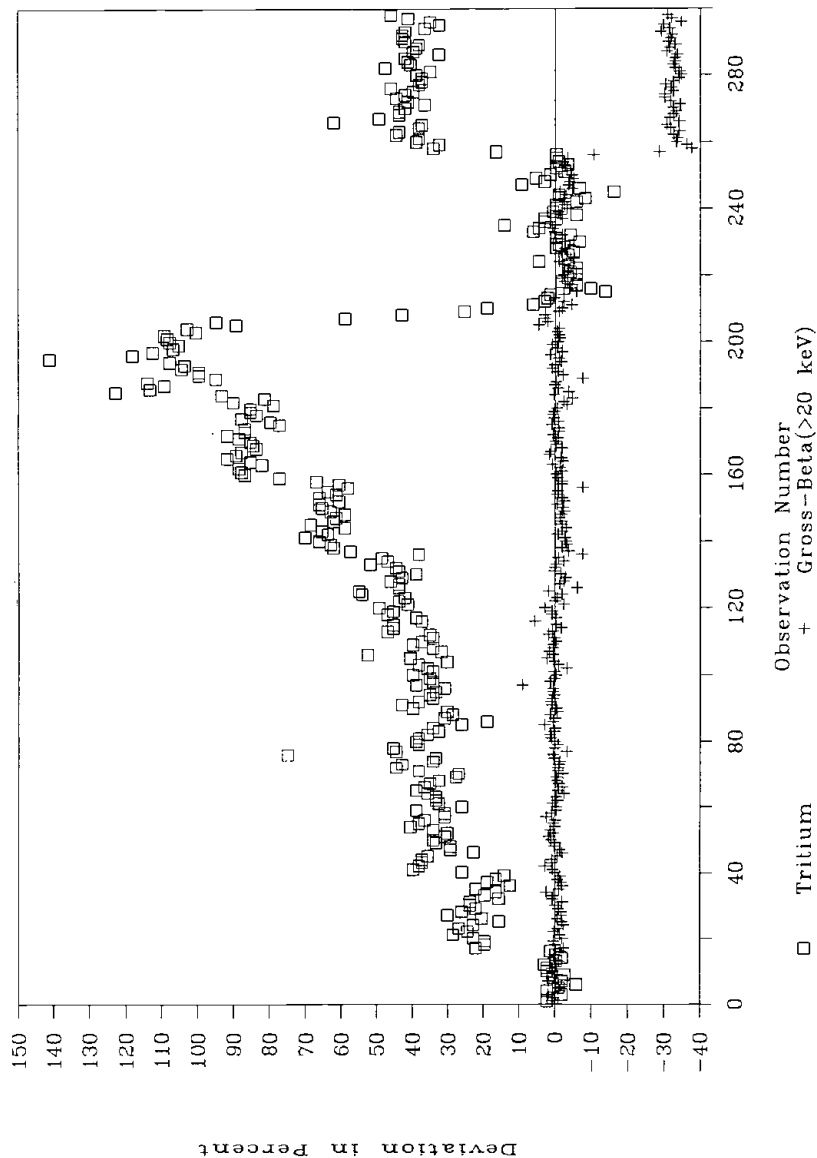


Figure 3. Monitor response to aqueous solutions containing tritium.

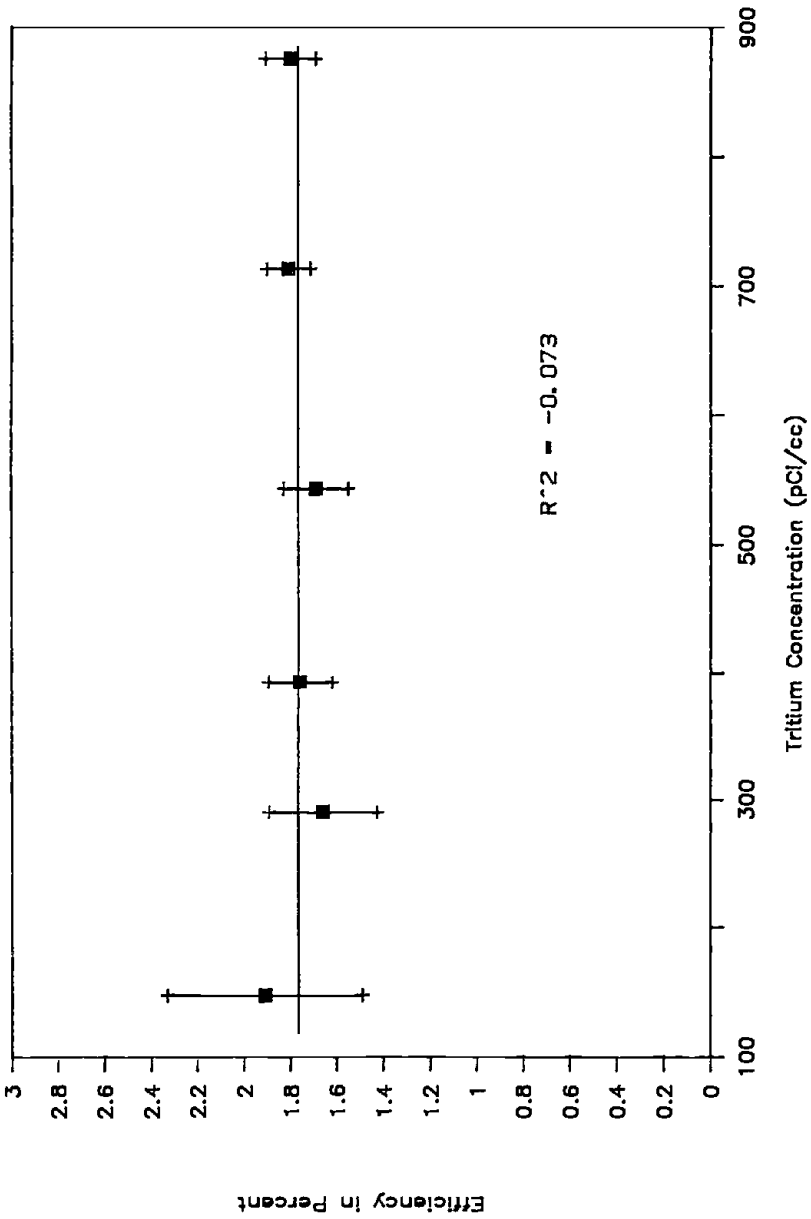


Figure 4. Variation of tritium counting efficiency with concentrations tested.

channel count rate decreased by $\approx 35\%$ during the experiment with reactor effluent. During this run, the differential pressure rose from 20 psi (its equilibrium value during the demineralized water tests) to 100 psi after about 2 days of run time. The explanation of this phenomenon can be attributed to the microorganisms in the sample. Bioluminescence is occurring in the tritium channel, resulting in an apparent increase in count rate. Meanwhile the microorganisms are creating a slime on the scintillator which reduces the light output in the gross beta channel. Plugging of the scintillator is consistent with this speculation.

Care will have to be taken to precondition the solution prior to reaching the measurement cell. Sterilization of the sample stream using biocides, ultraviolet light, ultrafiltration, etc. is mandatory if solid scintillators are to be used in the monitor. Other conditioning steps that will be required include the filtration of debris to prevent cell plugging, the removal of organics (e.g., by activated charcoal) that might produce light, and the removal of inorganic impurities (e.g., by ion exchange). These technologies are available using standard swimming pool water purification processes.

DEVELOPMENT OF ALTERNATE SENSORS

Since the plugging of tritium measurement cells containing crushed inorganic scintillators was apparently weak environmental applications, development of alternate sensors is underway at SRS. To minimize the plugging problem, the spacing between the light detecting media should be made larger for less restriction to flow. To provide a sensitive tritium monitor, a large surface area with efficient light detection is required. Borrowing on the design of the anthracene coated fiber detector⁷ and recent developments on the fabrication of plastic scintillator fibers, a flow cell was constructed with overall dimensions of 51-mm in diam by 51-mm in length, containing ≈ 500 fibers of 1-mm diam plastic scintillator* spaced on 2-mm centers. The ends of the fibers are cemented into a pair of light pipes which are, in turn, optically coupled to a pair of PMTs. The aqueous sample flows perpendicular to the fibers and the light is transmitted down the fibers to the PMTs. The high index of refraction of the plastic scintillator (1.58),¹² relative to that of typical aqueous solutions (1.3), should limit the loss of scattered light. The plastic scintillator is nearly transparent to the light produced by the tritium interactions (bulk light attenuation length = 250 cm^{12}), so detectors containing long lengths of fibers could be used.

The fabrication of the detector is underway and will be tested in the laboratory when the construction is complete. Pulse shaping and fast coincidence electronics will be used to discriminate single photon events and dark current noise. The background of the cell should depend only on the amount of scintillator and the lead shielding from cosmic rays. A comparison of the

*Manufactured by Bicon Inc., Newberry, OH 44065

Table 3. Comparison of Measured and Expected Responses for Various Types of Solid Scintillator Detectors

Scintillator	Background (cpm)	Volume (cc)	Efficiency (c/d)	MDC (10 min) (pCi/cc)
Crushed	12.5	0.4	0.0177	251
Crushed	14	0.5	0.004	938
Crushed	18	1.0	0.0035	603
Plates (Ref. 6)	40	1.8 ^b	0.006	286
Anthr. (Ref. 7)	30	0.28 ^b	0.016	600
1mm fibers	42	1.0 ^b	0.0104 ^c	304
0.5mm fibers	18.5 ^a	0.9 ^b	0.0104 ^c	228
0.25mm fibers	6.8 ^a	0.65 ^b	0.0104 ^c	199
0.1mm fibers ^d	4.1 ^a	0.029 ^b	0.0104 ^c	3551
0.25mm fibers ^d	4.3 ^a	0.012 ^b	0.0104 ^c	8761
0.5mm fibers ^d	3.9 ^a	0.0057 ^b	0.0104 ^c	17671
1.0mm fibers ^d	3.9 ^a	0.0053 ^b	0.0104 ^c	19005

^aBased on mass of scintillator relative to mass of plates and background observed in Ref. 6.

^bBased on active surface area and 6 μ m range of ³H beta.

^cBased on 65% light output of anthracene.

^dAssumes 50% void volume in U-cell 8.5-cm long.

expected response to that of already tested systems is shown in Table 3. The basis for the comparison is the intrinsic light production of the scintillator, the surface area of the active material, and an estimate of the light collection efficiency.

The data presented in Table 3 show that the detectors using plastic scintillator fibers offer the best chance of reaching the lower detection sensitivities, even with the conservative background estimates. If modern pulse shaping and timing electronics and photomultipliers can improve the signal to background ratio, the MDC can be reduced even further. Additional shielding may also increase the sensitivity for making tritium measurements. All these enhancements will be evaluated by further laboratory and field testing.

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