REAL-TIME FIBER OPTIC TRITIUM MONITORING IN FLUIDS

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ABSTRACT

Clean up of the tritium facilities are now on the critical path for the Decontamination and Decommissioning (D&D) of the DOE Miamisburg Environmental Management Project (MEMP) - commonly referred to as Mound Site. Significant inventories of tritiated oil exist at Mound. These inventories resulted from operating many glove boxes and fume hoods over the facility lifetime. Vacuum pumps were critical to the handling of tritium gas in these glove boxes and fume hoods, and required the use of oil in their operation. While in use, the oil became contaminated with tritium, which tends to replace the hydrogen in the oil hydrocarbons. Ridding the site of these large quantities of oil and also water with tritium concentrations presents a major challenge in meeting the MEMP goals.

The current baseline methods to evaluate tritiated oil and/or tritiated water require collecting a sample and sending it to a laboratory for liquid scintillation counting, or calorimetry. Laboratory scintillation counting has good detection capability and precision, however; is labor intensive and expensive. There is frequently long sampling-to-analysis turnaround time; and analysis inaccuracies can occur when sampling high activity oils and water, because of multiple sample dilutions sometimes necessary to make a sample countable. Information and data obtained from many technology searches and screenings indicated that a fiber optic detector and quantifying system might be able to provide faster (real time) measurements for tritium detection and concentration levels than either of the two current baseline methodologies.

Initial test results indicate this method of tritium measurement is not only feasible but also more accurate and faster than the current baseline methods. This real-time tritium detection of oil samples provides on-the-spot tritium concentration information, and permits segregation of various tritium concentration oils to be handled through Mound Waste Management in a much more expedient manner.

INTRODUCTION

The Mound site was selected by the U.S. Department of Energy (DOE), National Energy Technology Laboratory (NETL) to host a Large Scale Demonstration and Deployment Project (LSDDP). This is one of a series of such projects designed to demonstrate "safer, better, cheaper, and faster" technologies, to aid in the safe shutdown and decontamination and decommissioning of nuclear facilities at Mound and at other DOE sites. Clean up of the
operational tritium areas within the Mound complex are on the critical path for the Mound site closure project.

In the DOE complex, tritium is one of the most commonly occurring radionuclide contaminates. Tritium emits only a single spectrum of beta particles with a maximum energy of 18.6 keV and decays with a half-life of 12.3 years. The radiological properties that keep tritium from becoming an external radiation hazard to humans also make its detection and measurement very difficult. Tritium is a potential internal hazard to humans because it can replace hydrogen in biologically important molecules and, in the form of tritiated water, is rapidly and completely assimilated by the body through inhalation, ingestion, or absorption even through intact skin.

Tritium can easily replace hydrogen in chemical compounds, particularly those involving carbon, nitrogen, sulfur, oxygen, and some metals. Tritium can be readily adsorbed on surface layers of material such as oxide or water films. Tritium can diffuse into the interior of materials and it can diffuse through thin layers of material. During past tritium processing operations performed at Mound, vacuum pumps were used to evacuate glove boxes and other enclosed work areas where tritium was present and entrained in the air. As a part of the pumping action, the tritium became entrained in the pump oil, where it has remained either as a dissolved gas or in suspended water droplets. In some pump oil reservoirs, the water droplets may have coalesced and settled to the bottom. If such settling has occurred, the tritium might be concentrated there, and it may be desirable to sample the water in addition to the oil. Alternatively, it may be desirable to agitate the reservoirs to homogenize any settled materials in the oil prior to making measurements.

Hundreds of pump oil reservoirs in the range of 5 to 10 liters exist at Mound. Not all the reservoirs are highly contaminated with tritium, but those that are must be handled in accordance with established disposal procedures. The significant quantities of High Activity Tritium (HAT) contaminated oil represent a major waste stream and many resources will be needed to deal with them during Mound D&D activities. The needs for detection, characterization, handling and disposal of tritiated oil and water serve as a challenge to Mound to find and develop new detection technologies. Thus deployment of innovative technologies, into the baseline project, is not only an attractive idea, but also something that may be required if the projected cost and schedule are to be met.

One technology demonstration is testing, and evaluating the performance of specially prepared plastic optical fiber bundles coated with a scintillent material. The demonstration is looking at the feasibility of the system (fiber bundles coupled to a photomultiplier tube and counter) during the immersion of fiber bundles into several different oil and/or water samples.

The present approach to quantify tritium concentrations in oil or water is to collect a sample and send it to a laboratory for analysis, usually via liquid scintillation counting, or by calorimetry, depending on the tritium concentration level. The sensitivity of the calorimeter is ineffective below 10 to 50 curies per liter tritium concentration levels.

The objective of the demonstration was to determine if a fast and reliable detection method, based on scintillating optical fibers could be used to characterize the oil reservoirs for tritium
concentration. If so, the reservoirs could be sorted by degree of contamination, and significant time and money could be saved in treatment and disposal.

DESCRIPTION OF THE FIBER OPTIC TECHNOLOGY

The scintillating fiber bundle technology tested at Mound was originally developed by McDermott Technology, Inc. (MTI) under contract to DOE to measure extremely low tritium concentration in water. The project title was In-Situ Detector for Tritium Beta, contract no. DE-AC21-96MC33128. Details of the work are contained in an MTI Initial Phase final report, but are not included here. The objective of the MTI Initial Phase was to design a monitoring system capable of detecting and quantifying tritium in-situ in ground and surface waters, and in water from effluent lines prior to discharge into public waterways. The purpose was to measure tritium concentration at or below release levels to verify that the concentration was low enough to meet Environmental Protection Agency (EPA) drinking water standards. Initial Phase design work was successfully completed with the predicted capability to detect tritium levels below 20 nanocuries per liter. The designed system was based on the detection of the low energy beta radiation from the radioactive decay of tritium using a special form of scintillating optical fiber directly in contact with the water to be measured. To support the design, laboratory tests were performed in several areas. Different types of scintillating fiber were tested to determine which provided optimum system performance. The fibers contained a fluor material in a special cladding configuration, which optimizes the absorption of beta radiation. The tritium detection system consisted of an immersible sensor module containing the optical fiber and detection electronics as well as signal processing electronics. An umbilical cable was used to interconnect the components. The system design goals included optional permanent installation for routine water monitoring in wells, process and effluent lines or as a potential portable survey tool which could be moved from one location to another.

Not all the design goals were met in MTI’s initial work effort because of the large physical size of the immersible sensor required to achieve the very low-level tritium detection sensitivity that would be able to demonstrate compliance with EPA drinking water standards. As a result, the project did not progress into a subsequent phase, namely prototype construction and test.

For applications at Mound, the tritium concentration of interest in pump oil is above 500 microcuries per liter. This level is four orders of magnitude greater than in the previous work and is at the tritium concentration that MTI was able to measure in water. Thus, MTI was confident that fiber bundles based on the original design, and shown in Figure 1, could be used to perform the feasibility tests at Mound with a good opportunity for success.

DEMONSTRATION

The objective of the LSDDP demonstration was to use the fiber optic detector technology to determine the feasibility to:

1. Characterize tritium concentrations in contaminated oils and waters, and
2. Meet requirements for real-time measuring for the presence and concentration of the tritiated oils and waters in storage containers.
Two demonstration phases were to be conducted on various oil and water samples. The Phase I demonstration was performed on one tritium water standard and five tritiated oil samples. These samples ranged in activity from about 5 curies per liter down to 0.5 curies per liter and they were used to attempt to calibrate the system.

The Phase II Demonstration will be conducted using oil and water samples having greater tritium concentrations than those used in Phase I. A majority of the Phase II oil samples will be in the one to ten (10) curies per liter range, however, some could possibly be in the 30 to 50 curies per liter range or greater. If available, tritiated water samples collected from the Mound Tritium Emissions Reduction Facility (TERF) having high level tritium contamination in the several hundred to thousand curies per liter range will be tested in order to provide a meaningful comparison between oil and water.

In Phase I, an attempt to provide a calibration of the system, samples of known tritium activity were measured to determine a calibration curve for both the water and oil. The measurements

![Fig.1. Fiber Optic Probe Assembly](image)
were expected to be performed using three different tritium concentrations for water and five concentrations for oil.

Each tritiated water sample was to be measured three times using a new, unused fiber optic probe for each series. The three water samples used as calibration standards for tritium detector technology are listed below. The total level of tritium contained in all three samples is 111.0 mCi.

- 100 cc H₂O @ 10 mCi/liter (10 mCi/L x 0.1 L = 1.0 mCi)
- 100 cc H₂O @ 100 mCi/liter (100 mCi/L x 0.1 L = 10.0 mCi)
- 100 cc H₂O @ 1000 mCi/liter (1000 mCi/L x 0.1 L = 100.0 mCi)

Five tritiated oil samples of approximately 60cc each were also prepared. The samples were prepared by mixing proportional amounts of the tritiated and base oils to produce different tritium concentrations. These concentrations were 100%, 70%, 50%, 30%, and 10% of the original concentration of the tritiated oil sample. The oil samples were stirred to mix the two oils, but gently enough to avoid formation of air bubbles in the oil. After the samples are prepared, a small amount of each of the oil samples was analyzed to determine the tritium concentration and any other nuclides that are present. The oil samples were then capped to prevent spillage and evaporation and finally used to evaluate the tritium detector system/technology.

The following operational concerns were addressed during the tests. They include, but were not limited to, the following:

- Sensitivity to ambient light.
- Ability to decontaminate between measurements of different samples.
- Linearity.
- Repeatability.

The equipment listed is the basic hardware used to perform the measurements:

- Photomultiplier Tube (PMT) and Housing Adjustable.
- Stand for PMT Assembly.
- Eight 0.75 inch diameter x 10.5 inches long Stainless Steel Test Vials
- Single vial Holder.
- Multiple vial holder
- Sliding Vial-to-PMT cover.
- 18 Fiberoptic Tritium Probes 3/8 inch OD.
- Data Acquisition Computer.

A diagram showing the hardware (Measurement and Data Acquisition Components) is shown in Figure 2. The PMT housing is connected to the data acquisition system via two signal cables, and the data acquisition equipment can be located up to 20 feet away from the probe.
RESULTS

The demonstration included in situ measuring of samples of oil or water, in order to acquire results that are acceptable in accuracy and repeatability. The Phase I test included collecting data for repeatability, accuracy, and statistical analysis for the volumes of calibration oil and water. The Linearity of the detector response was also analyzed.

The first issue addressed, in a separate effect test performed prior to the start of Phase I, was the effect of petroleum liquids on the fiber and scintillant. Several scintillant-coated fiber samples were soaked in pump oil for two hours. The fluorescent intensity from the scintillator coating was characterized before and after soaking and no changes were observed. The conclusion was that the fibers could be used for tests at Mound with little risk that changes in fluor chemistry

Fig. 2. Measurement and Data Acquisition Components
might occur during the course of the feasibility tests. Since the initial test, fibers have been soaked in the oil samples over periods of days with no observable reduction in effectiveness.

The second issue of whether tritium in the oil would be measurable had to wait until the actual demonstration. During the previous work, MTI concluded that the mean free path of the low-energy tritium beta emission in water was on the order of 0.001 mm. The mean free path of the low energy beta in oil is not known. If it exceeded 0.001 mm., MTI was confident that the existing fiber bundles and photon counting electronics would be sensitive enough to detect tritium concentrations on the order of millicuries per liter. From simply considering the molecular weight of waste oil compared to water, it was expected that the mean free path of the tritium beta emission is greater in oil than in water, but this issue will be investigated as a part of the demonstration testing. The exact mean free path of tritium in oil is still not known, however, the results of the oil measurements show that tritium can be seen using the fiber optic probes. This is shown in Table I, the Oil Measurement Results.

<table>
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<th>Date</th>
<th>% Contamination</th>
<th>Calculated Activity Level (Ci)</th>
<th>Probe Number</th>
<th>Reading Repetitions</th>
<th>Recorded Net Ave. Signal, (CPS)</th>
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The original test plan was to first measure three tritiated water standards to obtain a calibration curve on which to compare future oil sample concentration levels. This did not prove possible as the first water standard measured read only 1.8 counts per second (cps) with a background reading of 1.3 cps. This 1 Ci standard was the highest tritium activity standard available and when this measurement was made there was serious doubt cast on the viability of the technology as a tritium measurement tool. The decision was made to postpone further water sample measurements and move directly to oil measures.
The first oil samples to be measured were undiluted. The tritium activity was determined, by using liquid scintillation counting (LSC), to be approximately 4.65 Ci and this value was used as the 100% datum point. Over the next several weeks data was collected from samples diluted as shown in Table 1 and a calibration curve for oil was generated from the data obtained as shown in Figure 3.

Over the course of the demonstration, many configurations of probes were used. The accuracy of each probe as well as repeatability between probes was monitored. The data show the accuracy of each probe is within ±10% of the median value obtained at each concentration level. The repeatability between probes also falls within ±10% of the mean value of all probes measured at a specific concentration. Data obtained from the LSC of the various oil concentrations show that the liquid scintillation counting is much more variable, in some cases ±100%, than the fiber optic method. The error bars generated for the calibration curve in Figure 3 are set for ±10% of count rate (cps) – X axis, and ±25% of the activity (Curies) – Y axis.

The use of a probe to be repeatably used over several oil concentrations was investigated. The data obtained revealed that the probe assemblies would drain within 10 minutes to levels near background and that when inserted into a second oil sample the count rate obtained was within the predetermined errors.

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**Fig. 3. Oil Calibration Curve**

\[
y = 0.3985 \times 0.5284^{x}
\]

\[
R^2 = 0.9937
\]
The data are higher than expected based on the tritiated water (HTO) sample. The oil signal also varies as the square of the tritium concentration, to a very good approximation. Based on previous MTI data, a linear response was expected.

One possible explanation comes from the fact that similar square-dependence behavior has been seen before in Mound LSC samples and have attributed it to the presence of tritium contributing in two ways to the production of a measured effect, in this case light production. The possible explanation here is the production of radical/ion species by the tritium beta radiation. The species would have significantly longer lifetimes in the viscous oil medium than in water, and would be more likely to be fluorescent in oil than water. Formed by tritium betas, and attaining a steady-state concentration dependent on tritium concentration and oil-specific parameters, they could be further excited to fluoresce by other betas. Hence the double (square) effect of tritium. This phenomenon could be called radiation-generated fluorescence of the oil.

If true, this "model" suggests that similar fiber optics, but undoped by fluorescent material, could also see a significant portion of the observed signal. This would work if much of the oil fluorescence was in the visible portion of the spectrum (vs. UV), to which the fiber transmittance and photomultiplier sensitivity are tuned.

The creation and lifetime of the radical/ion species is probably medium dependent. Testing various types of tritiated oil (mineral, polyphenyl, etc.) would be required to sort this out and will be put into the Phase II test plan.

CONCLUSIONS

The Phase I data shows there is still much investigation to be accomplished, however, the basic premise is valid. The scintillant coated fiber optic bundles will detect and quantify tritium in fluids. The accuracy and repeatability is excellent both with each fiber optic probe and between probes and much better than that of the baseline LSC method. The fibers can sustain repeated immersions in oil without degradation and the probes are reusable without significant wait times between uses.

The driving force for looking for other methods to characterize tritiated fluids at Mound was to find a more efficient method. The use of the fiber optic system has demonstrated it is a method that is more accurate and can be faster and safer than the current baseline.

It is the intent of the Phase II demonstration to determine the cost effectiveness of this technology when used on a large scale.

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