Liquid Scintillation Measurement Assurance Improvements for Tritium Counting (U)

by

G. D. Levi
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

J. P. Clark

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LSC ANALYSES OF TRITIUM SAMPLES (U)

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LIQUID SCINTILLATION MEASUREMENT ASSURANCE IMPROVEMENTS FOR TRITIUM COUNTING (U)

G. D. Levi, Jr. and J. P. Clark
Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

ABSTRACT

Liquid Scintillation Counting (LSC) for Tritium is done on 600 to 800 samples daily as part of a contamination control program at the Savannah River Site's Tritium Facilities. The tritium results from the LSCs are used: to release items as radiologically clean; to establish radiological control measures for workers; and to characterize waste. The following is a list of the sample matrices that are analyzed for tritium: filter paper smears, aqueous, oil, oily rags, ethylene glycol, ethyl alcohol, freon and mercury. Routine and special causes of variation in standards, counting equipment, environment, operators, counting times, samples, activity levels, etc. produce uncertainty in the LSC measurements. A comprehensive analytical process measurement assurance program such as JTIPMAP™ has been implemented. The process measurement assurance program is being used to quantify and control many of the sources of variation and provide accurate estimates of the overall measurement uncertainty associated with the LSC measurements. The paper will describe LSC operations, process improvements, quality control and quality assurance programs along with future improvements associated with the implementation of the process measurement assurance program.

INTRODUCTION

The Tritium Facilities at the Savannah River Site process tritium for the Department of Energy complex. The process of producing tritium at the Savannah River Site consisted of irradiating lithium-aluminum (LiAl) target rods with neutrons within a heavy water nuclear reactor. Upon completion of the neutron irradiation, the LiAl rods were removed from the reactor and transported to the Tritium Facilities where the hydrogen gas isotope tritium was extracted. Extracted tritium gas was packaged into reservoirs for the nuclear weapons stockpile. The Tritium Facilities current mission is to replenish the reservoirs from the nuclear weapons stockpile.

As part of the Tritium Facilities contamination control and waste characterization programs, liquid scintillation counting techniques are used to analyze for removable tritium contamination. The contamination control program consists of wiping the surface area of an object with Whatman™ 50 filter paper and analyzing it by liquid scintillation counting. The used Whatman™ 50 filter papers are known as smears.

Currently, 600 to 800 smears are analyzed daily for tritium by Liquid Scintillation Counters (LSCs). Radiological Control Operations (RCO) use the tritium results to release items as
radiologically clean, to establish levels of radiological control in work areas, and to monitor for tritium contamination outside radiological control work areas.

To protect workers from airborne tritium, room air is bubbled through a water or ethylene glycol solution. The tritium results from the water or ethylene glycol solutions are used to establish levels of radiological control.

With the increased emphasis on the proper disposal of radioactive waste, the analysis capability requirements for tritium have diversified because of waste characterization programs. Waste characterization samples now consist of smears, oils, oily rags, ethylene glycol and mercury.

As the requirements for differing tritium analysis capabilities increase along with the importance of the results generated, the establishment of a comprehensive analytical measurement assurance program is essential to assure the proper technical oversight of results generated by the LSCs.

DISCUSSION

Liquid Scintillation Counter Operations

In the Tritium Facilities, the LSCs are used to measure beta particles from decaying radioactive hydrogen atoms (tritium). The beta particles from tritium can not penetrate dense materials like sample vial walls so the detection device must be placed in contact with the beta particles. In liquid scintillation counting, the detection device is the scintillation cocktail solution. The components of a scintillation cocktail solution are listed in Table 1.

<table>
<thead>
<tr>
<th>Liquid Scintillation Cocktail Components</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solvent:</strong></td>
</tr>
<tr>
<td><strong>Emulsifier:</strong></td>
</tr>
<tr>
<td><strong>Fluor:</strong></td>
</tr>
</tbody>
</table>

Table 1. Normal Scintillation Vial Components.

The beta particles from a sample are brought in contact with the scintillation cocktail solution which excites the fluor molecules within the scintillation cocktail. Fig. 1 demonstrates the interaction between a beta particle and the scintillation cocktail molecules. As the fluor molecules return to the ground state, the energy is released as emitted light photons at a spectrum wavelength of approximately 370 nanometers (nm).
Fig. 2 illustrates the probability of the beta particle interacting with a scintillator molecule to produce photons is 100 percent. The amount of light photons being emitted from the scintillation cocktail solution is proportional to the energy of the beta particle. The light photons are emitted from the scintillation cocktail solution in all directions.

The vial of scintillation solution is inserted into a chamber consisting of an internal reflective material and two photomultiplier tubes (PMTs). The PMTs are located 180° on either side of the chamber. The light photons from the scintillation cocktail solution are directed into the PMTs where they are converted into a measurable electrical pulse. The amplitude of the pulse is determined as a voltage and is proportional to the amount of light photons that interact with the face of the PMT.

Fig. 3 illustrates the pulse height at the output of the PMTs are proportional to the energy of the beta particle.

Fig. 4 demonstrates the pulses from the PMTs entering the coincidence gate. Only when the coincidence circuit detects a pulse from both PMTs within 10 to 30 nanoseconds will the counter register an event. The pulses that are processed by the coincidence gate are sent to an analog-to-digital converter where they are digitized. The digitized pulses are stored in a multichannel analyzer (MCA) channel corresponding to the particle energy. The MCA accumulates counts (pulses) representing the spectrum of the tritium beta particles. The spectrum energy region for the tritium beta particles is 0 - 18.6 Kev. From the data stored within the MCA, the energies from the tritium beta particles along with a rate are used to determine the counts per minute (cpm).

Anything added to a scintillation cocktail solution such as water, oil or smears can reduce the efficiency of the scintillation
process. This reduction in counting efficiency is called quench. Fig. 5 illustrates the three major forms of quench: chemical, color and self-absorption. Chemical quench occurs when a chemical agent interferes with the transfer of kinetic energy between the radioactive sample and the solvent and the fluor molecules. Color quench occurs when the color in the vial like red, green and yellow absorbs the blue light that is emitted by the fluor molecule. Self-absorption quench occurs when a beta particle remains undetected because of entrapment in a non-scintillating media.

![Diagram of three major forms of quench: chemical, color, and self-absorption.]

Calibration

The LSCs are calibrated with 10 standards containing the same tritium activity but varying amounts of quenching agent. The calibration standards are certified against a National Institute of Standards and Technology (NIST) tritium standard. The overall uncertainty associated with the calibration standards is estimated to be less than $\pm 3.5\%$ at the 99% confidence level. Of the overall uncertainty, the random error is $\pm 3\%$ and the systematic error is $\pm 0.5\%$.

Fig. 6 illustrates the LSC propagating a calibration equation from the measured efficiency and quench number. The LSC derives the measured efficiency for a standard by dividing the
standard's cpm by its known tritium activity. The LSC derives the quench number for a standard by the Compton spectrum. The Compton spectrum is generated by bringing a gamma emitting isotope near a standard or sample vial that is within the chamber. The gamma energy causes the electrons to interact with the vial contents to generate light in a similar manner as beta particles. Once a sample's quench number is derived by the LSC, the efficiency can be calculated from the calibration equation. The sample's tritium activity in disintegrations per minute (dpm) is derived by dividing the sample's cpm by the calculated efficiency.

Performing Smears

Radiological Control Operations establishes and monitors Radiological Control Areas for transferable tritium contamination by performing smears. The radiological control area classifications are listed in Table 2. A smear is performed by wiping the surface area of an object to cover 100 cm². The smear is inserted into a vial that contains scintillation cocktail and distilled water. The vial is counted by a LSC to determine the tritium activity. The tritium activity from the smear is reported in dpm per cubic centimeter (dpm/100 cm²).

<table>
<thead>
<tr>
<th>Area</th>
<th>Activity Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiologically clean Area</td>
<td>&lt;150 dpm/100 cm²</td>
</tr>
<tr>
<td>Radiological Buffer Area</td>
<td>150 dpm/100 cm² to 10,000 dpm/100 cm²</td>
</tr>
<tr>
<td>Contamination Area</td>
<td>10,000 dpm/100 cm² to 1,000,000 dpm/100 cm²</td>
</tr>
<tr>
<td>High Contamination Area</td>
<td>&gt;1,000,000 dpm/100 cm²</td>
</tr>
</tbody>
</table>

Table 2. Radiological Control Area Classifications

Lab Operations for Smears

Approximately 600 to 800 smear samples are analyzed every 24 hour period for tritium activity. The Tritium Facilities Laboratory (TFL) utilizes three LSCs for performing smear analyses. Each smear is counted to a preset time of 30 seconds. The count time was established to meet the customer's requirement for a short turnaround time on smear analyses.

The counting statistic error for smear sample is the largest source of instrument measurement uncertainty. The counting statistic error for a smear sample with 150 dpm of tritium activity is approximately 22% at the 95% confidence level. The sampling error for smears is approximately 3 times greater than all other instrument errors combined. Thus, smears serve as a screening method for detecting tritium contamination.

At the current smear sample load, each LSC analyzes, in a 24 hour period, approximately 5 hours of samples. Even though additional LSCs have been added since the initial method start-up, the preset count time has not been increased due to the overriding factor that the customer still requires a short turnaround time on smear analyses.
Process Improvements

After evaluating the smear vial preparation procedure, a process improvement plan was formulated. The main objective of the plan was to reduce the quantity of scintillation cocktail required per vial and to reduce technician time in preparing vials.

The initial composition of the smear scintillation vial was:

- Standard size scintillation vial (~25 milliliters - mL)
- 20 mL scintillation cocktail (Optifluor)
- 3 mL water

Each scintillation vial was processed individually by hand dispensing the cocktail and water into the vial. Then the vial caps were screwed on by hand. The vials were grouped into sets of 100 and shaken until the scintillation cocktail solution and distilled water were mixed thoroughly. The preparation time for 1000 scintillation vials took two technicians approximately 2 hours.

To reduce the quantity of scintillation cocktail and the technician time required to prepare scintillation vials for smear samples, the scintillation vial size and composition were changed to:

- Mini size scintillation vial (~7 mL)
- 5 mL scintillation cocktail
- 1 mL water

The annual percent reduction in scintillation cocktail consumed and in liquid and solid waste generation from changing vial sizes and solution volumes are given in Table 3. The reduction in material cost are listed in Table 4. The annual cost savings in materials will be approximately $85,000/year.

<table>
<thead>
<tr>
<th></th>
<th>Standard Size Vial</th>
<th>Mini Vial Size</th>
<th>% Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scintillation Cocktail Consumption</td>
<td>5,800 L/year</td>
<td>1,460 L/year</td>
<td>75%</td>
</tr>
<tr>
<td>Liquid Waste Generation</td>
<td>6,721 L/year</td>
<td>1,752 L/year</td>
<td>74%</td>
</tr>
<tr>
<td>Solid Waste Generation</td>
<td>834 ft/year</td>
<td>359 ft/year</td>
<td>56%</td>
</tr>
</tbody>
</table>

Table 3. Percent reduction from process improvements.

<table>
<thead>
<tr>
<th></th>
<th>Standard Size Vial</th>
<th>Mini Vial Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cocktail Cost/Year</td>
<td>$88,000</td>
<td>$22,000</td>
</tr>
<tr>
<td>Vial Cost/Year</td>
<td>$26,000</td>
<td>$19,000</td>
</tr>
<tr>
<td>Solid Waste Cost/Year</td>
<td>$21,000</td>
<td>$ 9,000</td>
</tr>
<tr>
<td>Total Cost/Year</td>
<td>$135,000</td>
<td>$50,000</td>
</tr>
</tbody>
</table>

Table 4. Annual Cost Saving In Materials.

To ensure that measurement quality for smear samples was not jeopardized when the vial size and cocktail quantity was reduced, RCO performed duplicate smears in all of the radiological controlled areas for two weeks. The LSC results from the duplicate smears did not indicate significant difference between the different vial sizes and cocktail quantities.
Brandel Auto Dispensers were brought on line to eliminate the manual dispensing of the scintillation cocktail and the distilled water. A Brandel Auto Dispenser is capable of filling 96 mini vials in a 10 second filling cycle. The scintillation cocktail and distilled water are prepared by blending a batch solution. A batch consists of 5 liters (L) of scintillation cocktail and 0.750 L of distilled water mixed thoroughly together. To eliminate the procedure of having to screw on each scintillation vial cap, a pop-on cap scintillation vial was initiated. The total time that it takes two technicians to fill 1000 vials is now 30 minutes. The annual vial preparation cost for two technicians is listed in Table 5. By reducing the technician time, the annual savings will be $76,000/year.

<table>
<thead>
<tr>
<th></th>
<th>Initial Vial Preparation</th>
<th>New Vial Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two Technicians</td>
<td>$102,000/Year</td>
<td>$26,000/Year</td>
</tr>
</tbody>
</table>

Table 5. Annual Vial Preparation Cost For Two Technicians.

The additional benefit of batching the scintillation cocktail and distilled water is the elimination of customer concerns about the quality of the vials.

- During the shaking of the scintillation vial and distilled water together, a vial cap would come loose and drain its contents onto the other vials.
- Two phase separation of vial contents occurred when too much water was pipetted into the scintillation cocktail. The overloading of the cocktail's emulsifier led to a milky white vial appearance.

If RCO does not recognize that a vial was not prepared properly and places a smear into the vial, the smear is rejected by the lab. Smears rejected by the lab do not promote positive customer satisfaction as sample data may be compromised.

**Sample Diversity**

In the Tritium Facilities, there is a wide diversity of other sample matrices that require liquid scintillation counting.

For RCO to monitor and establish proper personnel protective measures against airborne tritium, room air is bubbled through 10 mL of water or ethylene glycol. When the room air is monitored for less than 10 minutes, a water matrix is used and when the room air is monitored for greater than 10 minutes, an ethylene glycol matrix is used. The sample vial is prepared using the following:

- Standard size scintillation vial (~25 mL)
- 20 mL scintillation cocktail
- 1 mL bubbler sample

The bubbler sample is analyzed by LSC for a preset count time of 15 minutes. The sample is bracketed by two Quality Control (QC) standards at a tritium activity of approximately 50 dpm. The bubbler results are converted from dpm to microcuries (μCi) and then reported to RCO. RCO converts the bubbler results to pCi/cc depending on the air flow rate passed through the solution.
Characterizing waste streams for isotopic composition and activity is required before the waste processor will accept waste from the Tritium Facilities. Waste characterization samples consist of oils, oily rags, smears and mercury. The vial preparation for these samples varies dependent upon the tritium activity within the sample. Some of the waste characterization samples have required double dilutions to reduce the tritium activity to a level that is measurable by liquid scintillation counting. For oil and mercury samples, the sample aliquot is limited due to sample degradation of the scintillation cocktail solution. For the majority of sample matrices, the sample vial is prepared using the following:

- Standard size scintillation vial (~25 mL)
- 20 mL scintillation cocktail
- 0.05 mL to 1 mL sample (depending on sample quench and/or tritium activity)

The waste characterization sample is analyzed by the LSC for a preset count time of 15 minutes or until a counting statistic error of 0.5% at the 95% confidence level is obtained. The sample is bracketed by two Quality Control standards with the appropriate tritium activity.

**Quality Control Program Measurement Improvements**

Upon the author's arrival in the TFL, the required tritium analysis capabilities by liquid scintillation counting were for smear and environmental outfall water stream samples. The Quality Control program consisted of analyzing a tritiated standard at a tritium activity of approximately 1000 dpm daily and comparing the observed value to a theoretical value. No control limits had been established for the QC standard. The QC standard being used was contaminated with scintillation cocktail, therefore the QC standard had a milky white appearance.

The steps taken to establish a more representative quality control program were:

- Preparation of a new tritiated standard for smear and aqueous samples that duplicate process samples.
- Rework the procedure section for QC standard vial preparation.

To simulate a smear sample, the QC smear standard was prepared using the following:

- Standard size scintillation vial (~25 mL)
- 20 mL scintillation cocktail
- 3 mL tritiated standard

The QC smear standard was established at a tritium activity of 150 dpm. This QC smear activity was chosen because RCO classifies any smear <150 dpm/100 cm² as free from tritium contamination.

An aqueous outfall QC standard was prepared to simulate the outfall samples using the following:

- Standard size scintillation vial (~25 mL)
- 20 mL scintillation cocktail
- 1 mL tritiated standard
The QC aqueous standard was established at a tritium activity of 20 picocuries (pCi)/mL. This activity was chosen because it is the activity level that the customer requires for tracking environmental outfall water streams.

With all new sample matrices there is an attempt to prepare a corresponding QC standard in such a manner to best simulate the scintillation vial preparation for the sample. QC standard mean values along with the random uncertainties for the LSCs are listed in Table 6.

<table>
<thead>
<tr>
<th>LSC Serial #</th>
<th>Smear QC</th>
<th>Aqueous QC</th>
<th>Oil QC</th>
</tr>
</thead>
<tbody>
<tr>
<td>7012299</td>
<td>--</td>
<td>20 pCi/mL ± 3 pCi/mL</td>
<td>--</td>
</tr>
<tr>
<td>7065009</td>
<td>136 dpm ± 34 dpm</td>
<td>20 pCi/mL ± 3 pCi/mL</td>
<td>90 dpm ± 6 dpm</td>
</tr>
<tr>
<td>7067580</td>
<td>139 dpm ± 32 dpm</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>7067809</td>
<td>133 dpm ± 34 dpm</td>
<td>--</td>
<td>92 dpm ± 6 dpm</td>
</tr>
</tbody>
</table>

Table 6. QC standard mean values and the random uncertainties at one standard deviation.

**Quality Assurance Program**

The QC standards that are used to simulate sample matrices contain low quantities of tritium activity, therefore counting statistic error plays a large part in the measurement uncertainty. The large measurement uncertainty of the QC standards can mask changes in instrument performance that may lead to systematic errors.

To better control the performance of the LSCs, two sealed tritiated quench standards with a tritium activity of approximately 500,000 dpm are analyzed daily. With the large tritium activity, the counting statistic error is insignificant when compared to the overall instrument performance.

A statistical control program is used to assure the LSCs perform within established statistical control limits set at the 99.7% confidence level. The program also provides a control chart for visual observation of instrument performance over the previous 90 days. The Quality Assurance (QA) standard mean values along with random uncertainties are listed in Table 7.

<table>
<thead>
<tr>
<th>LSC</th>
<th>QA Standard #1</th>
<th>QA Standard #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>7012299</td>
<td>506000 dpm ± 7000 dpm</td>
<td>508000 dpm ± 8000 dpm</td>
</tr>
<tr>
<td>7065009</td>
<td>500000 dpm ± 3000 dpm</td>
<td>505000 dpm ± 3000 dpm</td>
</tr>
<tr>
<td>7067580</td>
<td>498000 dpm ± 3000 dpm</td>
<td>503000 dpm ± 2000 dpm</td>
</tr>
<tr>
<td>7067809</td>
<td>498000 dpm ± 2000 dpm</td>
<td>500000 dpm ± 3000 dpm</td>
</tr>
</tbody>
</table>

Table 7. QA standard mean values and the random uncertainties at one standard deviation.

**Future Improvements**

Future process control improvements will initiate a process measurement assurance program such as JTIPMAP™ to assist in the process control of the quench curve calibrations and the quality control standards. All LSCs will be quench curve calibrated with the same set of quench
standards. A separate set of quench standards will be used as independent verifiers to validate the quench curve calibration as acceptable.

The data entered into the process measurement assurance program software will be evaluated to determine how a quench calibration affects the LSC systematic and random errors. Once a better understanding of the overall measurement uncertainty is understood for each LSC, the customer will be educated on how instrument measurement uncertainty affects the sample results and whether the total measurement uncertainty is acceptable.

The QC tritiated standards will be diluted from a vendor's NIST stock solution by TFL personnel. With TFL personnel preparing the QC tritiated standard, special precautions in standard prep and storage can be taken to assure the quality of the control standards. The performance of the quality control standard will also be statistically evaluated by the process measurement assurance program software.

The ultimate goal is to implement a process measurement assurance program, to obtain the appropriate controls to assure the quality of the results that are reported to our customers and to explain to our customers what the overall measurement uncertainties are for their samples.

REFERENCES