DETERMINATION OF TRITIUM IN URINE SAMPLES AND VALIDITY OF RESULTS

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INTRODUCTION

The In Vitro Analysis Group, of the Analytical Laboratories Department, at the Idaho National Engineering and Environmental Laboratory (INEEL), is responsible for analyzing bioassay samples from various facilities in order to determine possible uptake by INEEL personnel. At the INEEL, principle radionuclides of interests are: Plutonium (Pu), Uranium (U), Americium (Am), Strontium (Sr), Cesium (Cs), and Tritium (H-3). Alpha and Gamma spectroscopy are used for detecting the alpha and gamma emitting radionuclides while liquid scintillation and gross Alpha/Beta gas proportional counting is used for detecting beta-emitting radionuclides.

For the determination of Tritium in a urine sample, an aliquot of the urine sample is placed in a liquid scintillation vial, a scintillator is added to the vial, and the mixture is counted in a liquid scintillation counter. A known blank and quality control sample with known activity is also analyzed along with these samples. Quality control sample results are compared with true added activity to verify the validity of sample results. Final results of H-3 in microcurie per mL are reported after subtracting blank results.

BACKGROUND

The In Vitro data is reported with both the estimated random and total uncertainties at one sigma level. Small negatives and other results less than or equal to the total uncertainty including zero are interpreted as not detected. For results greater than two times, but less than three times the total uncertainty, detection is questionable. The decision level, that quantity of analyte at or above which a decision is made that the analyte is definitely present, is three times the total uncertainty. Results greater than three times the total uncertainty indicates detection, i.e., are true positives. Recently, non-routine urine bioassay analyses were performed in order to determine H-3 uptake by personnel working on a special project at one of the facilities at the INEEL. Several results were reported as a positive detect and/or questionable. The two issues raised regarding the "positive detects" of Tritium were the other possible sources of Tritium and validity of results in urine samples. A detailed series of experiments were performed in order to answer these questions.

OTHER POSSIBLE SOURCES OF TRITIUM

Concerns were raised that detection of H-3 in urine samples could be due to other factors. e.g. our analytical process, high H-3 drinking water at the facility where a special project was going on, the cocktail we used and the blank urine (free of Tritium) used for the final calculations. Other radionuclides present in similar region as Tritium, 0 to 18 KeV are, Pu-241 at 21 KeV, and Pb-210 at 16 KeV. Possibility of these radionuclides was also considered.

1) Analytical Process: The In Vitro Analysis Group uses the industry wide accepted practice of directly pipetting three mL of urine sample in 15 mL of the Ecoscint cocktail into a 20 mL plastic vial. The vial is counted on a Packard-1900CA liquid scintillation instrument for 60 minutes. The calculation program, subtracts blank counts from sample counts, takes efficiency of the sample, quenching process, t_o of the sample, volume taken and decay correction into consideration then gives us final results in microcurie/mL. The practice has weathered technical inquiry over the years and has been found as an acceptable method supported by several published literatures. The In-Vitro laboratory is one of the first DOELAP certified laboratories.

2) High H-3 water at the facility: Several questions were considered to explore this issue. e.g. how much water individuals drink which is high in H-3? What is the excretion rate of the H-3 for that particular individual considering 10 days biological half-life of H-3? Analyzing samples of non-lab personnel drinking same water proved that they had no detection of H-3 in their urine. These results proved that because an individual drinks high H-3 water does not mean their urine sample will be positive in H-3. Excretion of Tritium in urine depends on individual's water intake, physical exercise, and metabolism.

3) Use of the cocktail: The amount of radiation in the pure scintillation fluid is practically the same (or just slightly greater, corresponding to 18mL vs. 15mL) as the cocktail containing blank sample. This would indicate that the majority of the blank counts are due to background, which is also represented in the scintillation fluid. (Ecoscint manufacture claimed that "Scintillation fluids are manufactured using organic chemicals derived from petroleum and contain very small concentrations of radioisotopes which are always going to be there, no matter how hard we work in the industry to strive for zero background"). The essential point is that organic scintillation fluid does not contribute to positive H-3 results.

4) Other Beta emitters: Other radionuclides present in a similar region as Tritium, 0 to 18 KeV are, Pu-241 at 21 KeV, and Pb-210 at 16 KeV. The possibility of "other sources" of beta activity in several samples was investigated. If present, these sources could lead to false positives when reporting Tritium results. Several samples were boiled down to approximately 3-mL volumes and held at the volume using water from the same facility. The known Tritium count values from these waters were then backed out of the calculated results. Table 1 on page-3 shows the results of this work in microcurie/mL.

Final result after subtracting blank + added water counts from samples:

Sample Id	Facility-1water	Facility-2 water
	Results	Results
01A089	-7.4E-6	-3.8E-6
01A090	-1.7E-5	-3.2E-6
01B003	-1.3E-5	-1.4E-5
01B006	-6.4E-6	-2.7E-5

Table 1: microcurie/mL results of boildown/Tritium removal experiment

The negative results shown in table-1 indicate that no other beta emitters were present in significant quantities such that a false positive would be reported since other nuclides would have stayed in the samples at this temperature.

VALIDITY OF REPORTED DATA

Examination of to-date reported data was undertaken in order to establish the following criteria:
(1) What is the critical limit or critical activity for positive detection for this method?
(2) What is the minimum detectable activity for this method?
(3) What is the numerical relationship of the reported Tritium data to (1) and (2) above?

In order to establish the critical limit and critical activity, there must be some known and simple background/blank that can be used. An empty vial and known Tritium-free urine blank was counted on a Packard-1900CA liquid Scintillation instrument in order to determine a baseline count rate. This value was then divided by the counter efficiency, decay constant for Tritium, volume, and count time, in order to convert the count rate to microcuries/mL.

Following the nationally accepted Curie equations, a decision can be made regarding whether samples contain activity above this critical level. If the net activity (gross-blank) exceeds the critical level, then there is some real activity present, i.e., the sample shows a *positive detect.* In the absence of statistical fluctuations and other instrumental variations, the critical limit could be set at zero, and any net positive counts could be interpreted as evidence of real counts or activity. With the statistical fluctuations that are inevitable in any counting measurement, however, there will be many instances of net positive measured activity even for samples with no *true* activity. One must therefore choose a high enough critical limit in order to minimize the likelihood of reporting such false positives, while, at the same time, keeping it low enough to reduce the possibility of missing real activity when some is actually present (false negatives). In the Curie formalism, the critical limit is calculated by multiplying the square root of the blank times 2.33. The minimum detectable activity is then calculated in order to establish an activity value such as those false negatives, are highly unlikely. Setting the allowable false negative rate at 5% and following the Curie convention leads to a simple equation which multiplies the square root of the blank by 4.65, adds 2.71, and divides this sum by sample and nuclear constants to convert to activity units.

Table-2 on page-4 shows the sample IDs, the reported results, 1 and 3-sigma uncertainty, MDA, efficiency, and the critical limit in counts and in units of microcuries/mL. Finally, a quick comparison between the reported values and the critical and detection limits is shown.

Figure 1 on this page shows the comparison of the reported values to both the critical and minimum detectable activities for this group of samples.

Table-2

Sample Names	Reported Values	Tot. Uncert.	3-sigma	Effic.	MDA	Critical Limit in counts	Critical Limit in uCi/mL
01A089	2.03E-06	5.00E-07	1.29E-06	0.33	1.57E-06	9.47	7.30E-07
01A090	1.30E-06	4.00E-07	1.03E-06	0.35	1.43E-06	9.47	6.89E-07
01A143	3.00E-06	7.00E-07	1.81E-06	0.23	2.18E-06	9.47	1.05E-06
01B003	2.60E-06	6.00E-07	1.55E-06	0.25	2.01E-06	9.47	9.64E-07
01B006	4.00E-06	5.00E-07	1.29E-06	0.32	1.57E-06	9.47	7.53E-07
01L015	2.30E-06	6.00E-07	1.55E-06	0.26	1.93E-06	9.47	9.27E-07
00L077	2.10E-06	8.00E-07	2.06E-06	0.24	2.08E-06	9.36	9.98E-07
00L113	2.70E-06	6.00E-07	1.55E-06	0.25	2.05E-06	9.50	9.86E-07
01A042	1.80E-06	5.00E-07	1.29E-06	0.30	1.66E-06	9.32	7.97E-07
01A043	1.50E-06	5.00E-07	1.29E-06	0.29	1.72E-06	9.32	8.24E-07
01A044	1.30E-06	5.00E-07	1.29E-06	0.28	1.78E-06	9.32	8.54E-07
01A069	1.30E-06	8.00E-07	2.06E-06	0.19	2.64E-06	9.47	1.27E-06
01B079	2.16E-06	5.09E-07	1.31E-06	0.28	1.66E-06	8.06	7.94E-07
01B099	4.04E-06	6.35E-07	1.64E-06	0.24	1.94E-06	8.06	9.26E-07
01B100	4.01E-06	6.20E-07	1.60E-06	0.22	2.11E-06	8.06	1.01E-06
Facility-1	1.56E-06	1.67E-07	4.31E-07	0.37	1.35E-06	9.36	6.48E-07
Facility-2	1.20E-05	3.15E-07	8.13E-07	0.37	1.35E-06	9.36	6.48E-07
Cocktail	3.90E-07	3.90E-07	1.01E-06	0.44	1.06E-06	8.50	5.19E-07

Table 2: In vitro Laboratory Tritium Data with uncertainties, critical and detection limit values

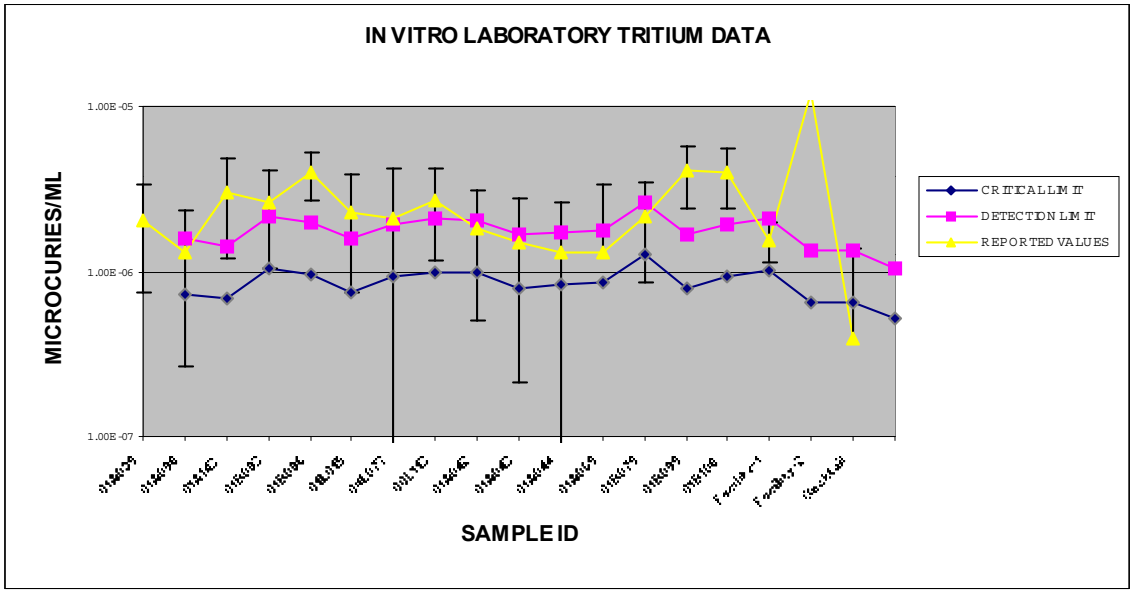

Figure-1. Comparison of reported data, critical and detection limit activity values

Table-2 and Figure-1 on page-4 both point out that the reported values are statistical positive detects well above the critical limits in almost all analyses. The lower bounds of the error bars are at the 99 % confidence limit points and these values are also generally above the critical limit values.

Table-3 below, shows a statistical comparison between the reported Tritium values, the lower 95% confidence limit, the lower 99% confidence limit value, and the critical limit for detection.

TEST	DIFFERNCE SIGNIFICANT?	P VALUE	ALPHA
REPORTED VS. CRIT LIMIT	YES	.0028	.05
LOWER 95% VS. CRIT LIMIT	NO	.167	.05
LOWER 99% VS CRIT LIMIT	NO	.413	.05

Table 3: Statistical comparison of critical limit to reported and uncertainty values

Table-3 shows that there is only a slight (<1%) chance of falsely concluding that the reported numbers are positive detects. At 95% lower limit for this data set, there is a 16.7% chance of making this error while at the 99% limit there is a 41 % chance. This evidence strongly supports the conclusion of positive detects for most of these data.

SUMMARY:

Analysis of the reported to date Tritium results indicates some samples have slightly statistically significant positive results. The source of the Tritium in these samples is subject to speculation only.

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