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LONG TERM UNCERTAINTY METHOD USED TO EVALUATE ICSI TRITIUM LABORATORY'S PROFICIENCY TEST RESULTS

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Abstract:

Results obtained for proficiency tests during 2000-2017 period are used to verify and validate measurements method of tritium specific activity in aqueous samples. The long-term uncertainty method (LTUM) was applied to Tritium Laboratory results in order to identify the constant and proportional bias effects, stability of the laboratory routine procedure, and total error of the measurements.

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1. INTRODUCTION

Tritium Laboratory of the National Institute for Cryogenics and Isotopic Technologies ICSI implemented and maintains quality assurance (QA) system since years 2000, being the first Romanian laboratory accredited by Romanian Accreditation Body (RENAR) for tritium activity concentration measurement. The QA system respects the requirements of ISO 17025 (SR EN ISO/IEC 17025, 2018), and one of the important demand is to verify the competence of the laboratory to adequately operate a standard method. Numerous guidelines have been published on the fitness for purpose of the analytical method (Weitzel et al., 2007; Magnusson & Örnemark, 2014). Usually these guidelines focus on "in-house" laboratory validation or verification against certified reference materials of the main measurement parameters: selectivity, linearity, accuracy, precision, sensitivity, ruggedness, and limit of detection. Of primary interest is the establishment of uncertainty budget also. This intra-laboratory verification has an important drawback, it will never give information about the differences between calculated and actual uncertainty. This type of information can be gained if the laboratory participates to intercomparison exercises.

Tritium activity concentration measurement in aqueous samples using liquid scintillation method is an ISO standard method (ISO 9698, 1998) since 1998, during this period undergoing different revisions, the last version being in 2019 (ISO 9698, 2019).

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One of the important changes of the ISO standard versions is how to estimate the measurement uncertainty. The old version, ISO 9698-1998 recommended formulas that took account only the statistically nature of radioactive decay and background. The new version recommends formulas of a real budget of uncertainty starting with counting efficiency uncertainty, uncertainty of the certified reference material used in measurement, counting rates uncertainties of sample and background, etc. This standard and its versions were applied in the Tritium Laboratory since 2000 when QA system was implemented.

In order to obtain or maintain a quality assurance (QA) system in our Tritium Laboratory is mandatory to participate to inter-laboratory exercises at least once every three years. Three years is the period between QA system evaluations of the Romanian Accreditation Body. Method validation (and verification) is one of the important requirements of the QA system along with uncertainty budget of the applied method. The easiest way to evaluate and compare the laboratory performance is to analyze reported results to intercomparison exercises. A proficiency inter-laboratory comparison exercise can give valuable information on the routine practice applied in the laboratory: percentage differences (D%) which is an indicator of laboratory's bias from reference value assigned to exercise, z score (z) which shows the laboratory value position to other participants, and the zeta score (ζ) which measures the reliability of the laboratory uncertainty budget. Results obtained for proficiency tests during 2000-2017 period are used to verify and validate measurements method of tritium specific activity in aqueous samples, focusing on the reported uncertainty of the method. As the linear regression approach started to be used in biological routine analyzes (Meijer et al., 2002), Verrenzen (Verrenzen et al., 2017) applied it for low level radioactivity measurements of tritium and ^{14}C. The long-term uncertainty method (LTUM) includes parameters of each inter-laboratory participation over a long period of time, in our case Tritium Laboratory of ICSI Rm. Valcea, and it is able to identify the constant and proportional bias effects, random error and total error of the measurements.

2. EXPERIMENTAL

2.1. Theory

The long-term uncertainty method (Mattar et al., 2015) represents the linear regression drawn using reference values of the proficiency test as independent variables (x), and laboratory reported results as dependent variable (y). The best-case scenario presumes that laboratory results should be equal to reference value of proficiency test, fig. 1, described by the equality line (y=x).

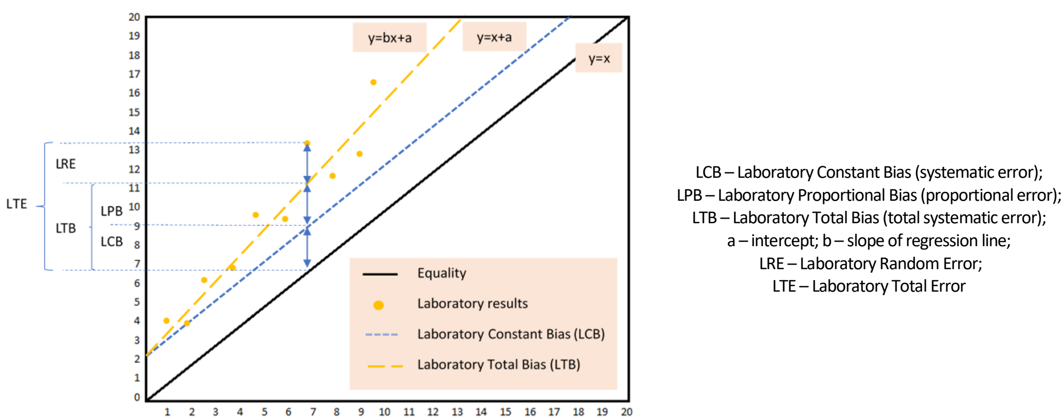

Figure 1. Parameters of Long Term Uncertainty Method LTUM

Usually, laboratory results will not be the same as reference values and the regression line will be as classical formula y = bx + a. The two equation parameters represent information about laboratory bias: the equation intercept "a" is the laboratory constant bias, and the slope "b" represents an equivalent of possible laboratory proportional bias, eq. 1, depending on the number of values (n) reported during the evaluated period.

$$LBP = \sqrt{\frac{(n-1)}{n} \times (b-1)^2 \times S_x^2} \qquad (1)$$

The square root of the sum of the square of the two biases, eq. 2, represents laboratory total bias (LBT), usually referred as systematic error.

$$LBT = \sqrt{LBC^2 + LBP^2} = \sqrt{a^2 + LBP^2} \qquad (2)$$

The scatter of the laboratory reported values around the regression line characterizes the laboratory random error produced by measurement uncertainty and reproducibility. The laboratory total error (LTE) can be estimated from regression parameters multiplied with a coverage factor k, eq. 3, and it represents the square root of the sum of squares of LBT and laboratory long term coefficient of variation LTCV, eq. 4.

$$LTE = k \times \sqrt{LBT^2 + LTCV^2} \qquad (3)$$

$$LTCV = \frac{S_{\frac{y}{x}}}{\bar{X}} \times \frac{100}{b} \qquad (4)$$

The variability of the regression line ($S_{y/x}$) or the residual standard deviation is defined as, eq. 5:

$$S_{\frac{y}{x}} = \sqrt{\frac{1}{(n-2)} x \left[\sum(y-\bar{y})^2 - \frac{[\sum(x-\bar{x})(y-\bar{y})]^2}{\sum(x-\bar{x})^2}\right]} \qquad (5)$$

2.2. Proficiency Tests and laboratory routine procedure

Tritium Laboratory of ICSI Rm. Valcea has the main task to measure tritium activity concentration in samples originated from two sources: Cryogenic Pilot for Tritium and Deuterium Separation (PESTD) and environmental monitoring program of PESTD. The tritium samples are usually prepared in aqueous form, whether it is a gaseous form, liquid form, or assimilated in living organisms as tissue free water tritium and organically bound tritium (UNSCEAR, 2016). A wide range of tritium concentration is measured in our laboratory: from Tritiated water used in the technological processes of Cryogenic Pilot PESTD to groundwater used in the Institute vicinity as drinking water. The proficiency tests chosen for participation tried to cover this wide range of tritium concentrations, but of primary interest were the low level tritium activity in water for two reasons: first, this level is hard to measures using direct measurement and second, this is the level that can be found in the environment (Stamoulis et al, 2011).

The Hydrology Department of the International Atomic Energy Agency (IAEA) organizes every 4 years an intercomparison exercise for measurement of low level tritium in water sample (TRIC2000, TRIC2004, TRIC2008, TRIC2012). Tritium activity concentration in these samples is very low, below 1 Bq l^{-1} requiring tritium enrichment, but the organizers send one to three samples with special request of direct measurement. The reference tritium activity concentrations are in Tritium Units (TU), and in order to compare with other proficiency tests, one can use 1 Bq l^{-1} corresponds to 8.390 ± 0.015 TU (Groning & Rozanski, 2003). Tritium Laboratory has participated also to other inter-laboratory exercises organized by the National Physical and LGC Standards Proficiency Testing (United Kingdom). All the reported results were used in LTUM analysis, even if some of the values were well below the limit of detection.

The samples were measured by liquid scintillation method with a Quantulus spectrometer 1220, for 1000 min/samples. The liquid scintillation cocktail used along the period 2000-2017 were different: OptiPhase Hisafe 3 (initial producer Wallac Oy, today PerkinElmer), UltimaGold LLT, and UltimaGold uLLT (initial producer Canberra Packard, today PerkinElmer). The ratio water sample: scintillate was the same no matter what cocktail was used 8:12 ml, in Canberra Packard-type polyethylene vials of 20 ml. Depending on the type of scintillate used, the efficiency ranged from 24.32% (OptiPhase Hisafe 3) to 25.05% (UltimaGold LLT) and 25.90% (UltimaGold uLLT). The background recorded (at the best figure of merit) for the tritium free water sample also varied, from 0.628 CPM (OptiPhase Hisafe3), to 0.846 CPM (Ultima Gold LLT) and 0.689 CPM (UltimaGold uLLT). The deuterium depleted water was used as tritium free water, obtained in our Institute, having a concentration of 15 ppm D/D+H (Varlam et al. 2019). The best performances were obtained using UltimaGold uLLT, the determined limit of detection being around 4 UT (confidence level, k=2).

3. RESULTS AND DISCUSSION

All values reported to proficiency tests starting from 2000 until 2017 were used in the LTUM analysis. The ζ score of the 31 values was between -2 to 2, fig. 2, fulfilling the acceptability criterion (Baglan et al, 2018).

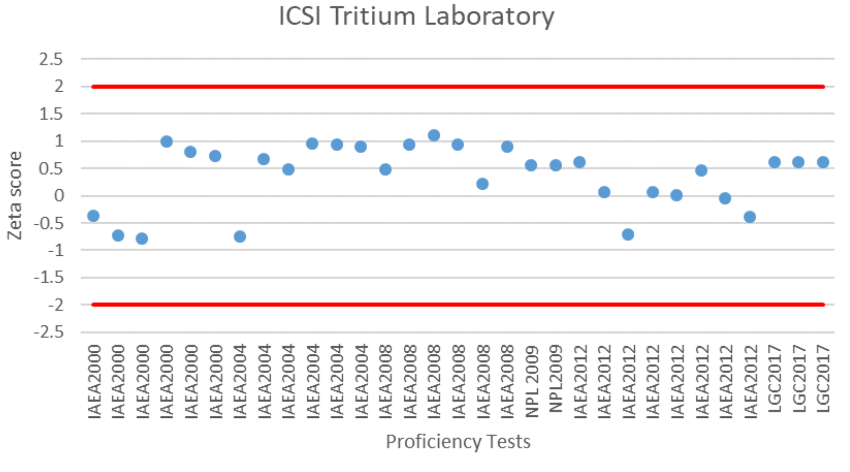

Figure 2. ζ score of the reported values in different intercomparison exercises, 2000-2017 period

The range of tritium reference values was between 0 and 8 kBq/l. Often samples with tritium activity concentration around 0 (e.g. 0.052 Bq/l, TRIC20012) were measured as negative values. The meaning of negative values is that the measured sample has lower tritium activity than the tritium free water used as blank water, and the recorded counting rate is lower than the measured background. These types of samples are important in establishing impact of nuclear facilities in the environment, and it is important to distinguish them in the environmental monitoring program. All the values reported especially to IAEA Tritium exercise were used in the LTUM analysis, fig. 3, the regression line equation (y = 1.0518x – 3.2218) having a negative intercept due to negative reported values.

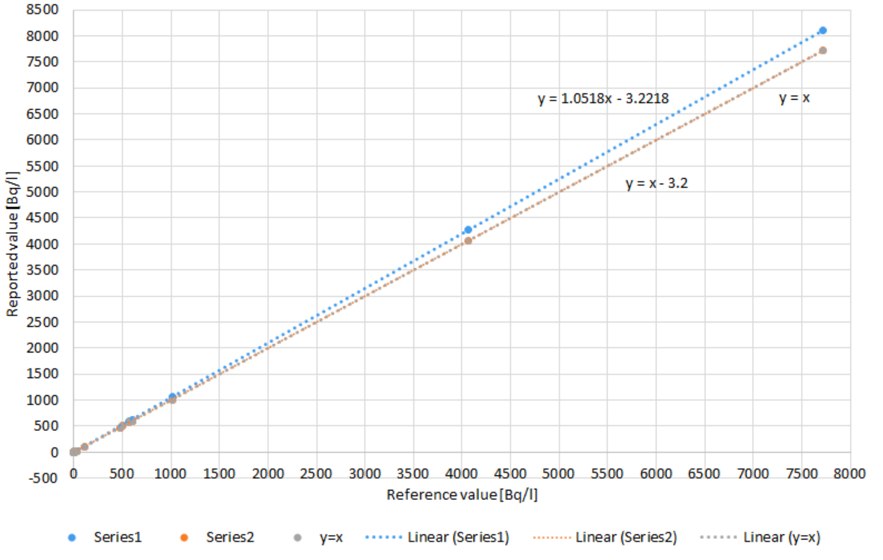

Figure 3. LTUM method applied to the proficiency test results of Tritium Laboratory (2000-2017)

The variability of the regression line, $S_{y/x}$, has a value of 8.2428, conducting to a long term coefficient of variation, LTCV, of 0.0143. The laboratory constant bias LBC is -3.2218 (due to reported negative values), and laboratory proportional bias LBP has a value of 0.0005 for all 31 reported results. The laboratory total bias LBT is calculated to a value of 0.0458 indicating an overall average measurement uncertainty LTE of 0.0481. This is in agreement with the uncertainty budget calculated according SR ISO 9698 (ASRO, 2015) of 5% (k=1), taking into account all its components (counting statistics, background correction, counting efficiency, sample and cocktail masses). The calculated regression line is very close to the equality line indicating small values of total bias due to reported values of samples with tritium activity below limit of detection. The graph shows a good linearity of the method in the full range of tritium activity concentration, 0-8 kBq/l. The LTUM analysis proves that there are no differences between calculated and actual uncertainty of tritium measurement.

4. CONCLUSIONS

The Long Term Uncertainty Method (LTUM) consists in a simple regression analysis on the reported results of the proficiency tests. The LTUM provides good estimates of long term stability, linearity, and range. It can quantify possible biases, both constant and proportional. The LTUM can evaluate the validity of the calculated uncertainty budget, without replacing uncertainty budget. It cannot give information about individual components in the total uncertainty.

Appling LTUM to the reported results of Tritium Laboratory of ICSI to different proficiency tests along a period of 17 years one can observes a good stability of the laboratory routine procedure, LCTV being around 1.4%, small total bias of 4.6% despite measurement performed on sample below the limit of detection, and consistency between calculated and actual measurement uncertainty.

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Conflict of Interest Statement: There is no conflict of interest on this article.

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