

EIGHTH IAEA INTERLABORATORY COMPARISON ON THE DETERMINATION OF LOW-LEVEL TRITIUM ACTIVITIES IN WATER (TRIC2008)

REPORT

prepared by

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EXTENDED SUMMARY

The eighth IAEA interlaboratory comparison on the determination of tritium in water at environmental level (named TRIC2008) was started in Dec 2008. Six samples had been prepared beforehand at IAEA by gravimetric dilution of a high level tritium standard (SRM4927F) with tritium free water. Reference values and combined standard uncertainties were calculated from the dilutions. Samples were prepared in stainless steel barrels and filled into suitable plastic bottles for shipment. Registration for the exercise was handled at a special internet page, requiring information on the used analytical process from the participating laboratories.

Data reporting was requested by end of March 2009 via the same internet page, with an extension for ³He based measurements to June 2009. Altogether 61 laboratories reported back 63 independent data sets to the IAEA. Directly after end of the reporting deadline, by 1 April 2009 each laboratory could download an individual proficiency test assessment report comparing their individual results with the reference values. This report is now the final summary of all results and findings, including influences of observed parameters on the performance of laboratories.

In the exercise, the majority of laboratories were using electrolytic tritium enrichment of samples followed by liquid scintillation counting. A few laboratories used liquid scintillation counting without previous enrichment. Few laboratories used gas proportional counting (4 labs) or the T/³He ingrowth method (3 labs).

The results are displayed in the report in various ways, using S-plots and column plots with cumulative uncertainties per laboratory, to try to assess the general laboratory performance in the TRIC2008 exercise. Results were rated according to pre-set criteria. It is clear, however, that even a laboratory with methods under perfect control could be subject to outlying measurements just based on statistical reasons. In cases of laboratories with two or more values rated as “not acceptable” or more than two values rated at “warning level”, these laboratories should be particularly interested in finding out the underlying reasons (18 laboratories). Even with two values at the warning level (4 laboratories) or with a visible bias versus reference values, laboratories could benefit from a careful evaluation and assessment of their results.

Observations concerning data reporting and uncertainty statements (e.g. significant digits) are discussed. Additional information obtained from laboratories is briefly discussed to alert laboratories on factors which may influence performance or calculated uncertainties.

As lesson learned from this exercise, to ensure a timely completion, future exercises could be started separately for mass spectrometric T/³He laboratories and those using direct counting techniques. The next tritium interlaboratory comparison most probably will be undertaken with assigning results to laboratories (not anonymous anymore), since 25 out of 27 laboratories replied positively to such a change for the future.

1. INTRODUCTION

For over 40 years tritium interlaboratory comparisons at environmental level have been conducted by the International Atomic Energy Agency (IAEA). Reports of seven large tritium interlaboratory comparisons were published previously by the IAEA [1-7]. The last two exercises as well as this one were conducted as proficiency tests based on water samples with tritium values determined by gravimetric mixing. In this report the traditional term interlaboratory comparison will be used instead of proficiency test. Basic details of all conducted exercises so far are summarized below in table 1.

In each case, a set of water samples was distributed, covering the concentration range prevailing in environmental waters at that time. In 1965, 1970 and 1995, the tritium values were known only approximately. In 1975 and 1985, samples were prepared by gravimetric dilution of tritiated standard water NBS4926 (now referred to as SRM4926) with water of near-zero tritium concentration.

In the exercises of 2000 and 2004 as well as in the present one (code-named TRIC2008), samples were prepared by gravimetric dilution of the tritiated standard water SRM4927F with virtually tritium-free water. That reduced the calculated uncertainty for prepared samples and allowed for the data evaluation to concentrate fully on the laboratory performance without added interpretation ambiguities due to sample preparation effects.

Table 1: Details of all major IAEA tritium interlaboratory comparisons conducted so far.

Year	Number of final participants, (no. of laboratories receiving samples)	Reference date	Water samples distributed, tritium ratio and standard uncertainty at 1 σ - level at chosen reference date
1965	12 (29)		Sample A: < 100 TU Sample B: 200 - 800 TU Sample C: 1000 – 6000 TU
1970	35 (38)		A: ~ 10 TU B: ~ 50 TU C: ~ 250 TU
1975	41 (79)		A: < 0.2 TU B: 8.37 \pm 0.04 TU C: 33.1 \pm 0.1 TU D: 678.5 \pm 2.2 TU
1985	57 (85)		A: < 0.2 TU B: 5.94 \pm 0.03 TU C: 25.66 \pm 0.13 TU D: 100.2 \pm 0.5 TU
1994	57 (91)		A: ~ 0 TU B: ~ 1 TU C: ~ 5 TU D: ~ 19 TU
2000	86 (102)	2000-07-01	T1: 10.112 TU +0.073 / -0.037 TU T2: 2.152 TU +0.044 / -0.008 TU T3: 0 TU +0.036 / -0 TU T4: 5.252 TU +0.055 / -0.019 TU T5: 26.118 TU +0.131 / -0.095 TU T6: 505.83 TU +1.88 / -1.84 TU
2004	70 (74)	2004-07-01	T7 0 TU +0.050 / -0 TU T8 10.920 TU +0.064 / -0.040 TU T9 1.738 TU +0.050 / -0.006 TU T10 5.433 TU +0.054 / -0.020 TU T11 25.408 TU +0.105 / -0.092 TU T12 1011.58 TU +3.68 / -3.68 TU
2008	63 (74)	2008-12-01	T14 1.54 TU \pm 0.05 TU T15 4.07 TU \pm 0.05 TU T16 7.74 TU \pm 0.06 TU T17 14.46 TU \pm 0.08 TU T18 0.67 TU \pm 0.05 TU T19 568.7 TU \pm 2.3 TU

Laboratories were advised on the tritium activity range in advance, and were requested to provide detailed information on used techniques and procedures. Since the exercise of 1975, results are reported without direct identification of the laboratories, with anonymity assured through the use of randomly assigned lab IDs. Participation in IAEA inter-comparison exercises is voluntary and no participation fee is charged for.

Table 1 reveals a high, but gradually decreasing number of laboratories which have submitted tritium data on water at environmental levels. For the recent exercise, one reason might have been the initial deadline of March 2009, which provided a measurement time of about three months, sufficient for conventional tritium enrichment and counting methods. However, several ^3He ingrowth laboratories complained about the short ^3He ingrowth time for their measurements. Despite an extension of the reporting deadline to end of June 2009 (in total over six months) for those laboratories, five ^3He laboratories did not report back data by this extended deadline. This will have to be considered for future tritium tests, and probably to split the exercise into two parts for the needs of both major laboratory communities. However in spite of this, 63 reported data sets are a quite remarkable result. It shows the interest in low-level tritium analysis despite the decline of tritium concentrations in rainfall to very low levels, and the elapse of nearly 4 half-lives since maximum levels were recorded in 1963 following atmospheric H-bomb tests. The present low tritium environment has persisted now for about 20 years, and levels in the ocean and groundwater will continue to decline. Tritium activities in the southern hemisphere are only marginally above pre-H-bomb test levels. These low-level concentrations impose much greater technical difficulty in measurement than two decades ago.

Six samples of different tritium activity were initially prepared at the Agency's laboratory. The samples were prepared by accurate gravimetric dilution of the NIST tritiated water standard SRM4927F with water from the artesian well Grafendorf G3 (near Graz, Austria), which was used in the previous exercise as virtually tritium-free water. The same SRM4927F sub-dilution was taken as mother standard for this exercise as for TRIC2004 to prepare the individual samples.

Initially 74 laboratories declared their willingness to participate in this 8th interlaboratory comparison TRIC2008. They have received the set of six water samples in December 2008. Results on tritium activities of 63 independent data sets have been received from 61 laboratories. Address details for those laboratories can be found in Appendix E. The deadline for data reporting was set to 31 March 2009. From 1 April 2009 onwards, each laboratory could self-evaluate its performance by internet on the TRIC2008 homepage and download a short proficiency test report comparing its results versus the reference values.

For unknown reasons, altogether 18 laboratories have entered their results at the requested website, but failed to finally press the "submit" button for final submission. Therefore those laboratories were not able to access or download their individual proficiency test report.

2. SAMPLE PREPARATION

Different to earlier interlaboratory comparisons, the submitted results indicate that the new tritium half life value [8] is to date adopted by most laboratories to calibrate their measurements. We based all calculations of reference tritium values and their uncertainties on this half-life of 4500 ± 8 days¹ and the NIST tritiated water standard SRM4927F. In the calibration of the tritium standard, we have incorporated four uncertainty sources: (a) the calibration uncertainty attached to the certified NIST standard tritiated water SRM4927F (calibration date 3 Sep 1998) used for sample preparations at the stated standard uncertainty of 0.36 % (mostly the dominant contributor); (b) the small uncertainty in correcting the values to our reference date (1 December 2008) using the half-life 4500 ± 8 days; (c) the small uncertainty of our used gravimetric dilution procedures; (d) a contribution of a maximal tritium activity offset for each sample by assuming a residual tritium activity in the “tritium-free” water, which was used in preparing all six samples. The upper limit for (d) was derived from a statistical analysis of the submitted high-precision results for that “tritium-free” sample [7].

Throughout this report, the results of the sample tritium concentrations are expressed in terms of their tritium/hydrogen isotope ratio in TU (Tritium Unit) or their massic tritium activity [Bq/kg]. Strictly speaking, TU is not a “unit” but an atom ratio and may be referred to more rigorously as tritium ratio [9]. The tritium ratio of 1 TU corresponds to a tritium/(total hydrogen) ratio of $T/H = 10^{-18}$. The massic tritium activity is related to the tritium ratio via the following relationship:

1 Bq/kg corresponds to 8.390 ± 0.015 TU [10, 11], using the new value for the tritium half-life [8] and the CODATA 1998 value for the Avogadro constant [12].

Adoption of half-life 4500 days means that results from laboratories using other half-lives for their calibrations will be biased relative to the “true” tritium values and ranges of the samples as calculated for this exercise. For example, those laboratories calibrating their measurements by the former NIST water standard SRM4926C (calibration date 9 Sep 1982) and 4540 days (12.43 years) half-life, should bear in mind that their results will be positively biased by 1.55 % relative to the prepared values we provide here, based on SRM4927F (calibration date 3 September 1998). The necessary adjustments are discussed elsewhere [6, 9].

2.1 Massic Activity of SRM4927F at Reference Date

NIST’s calibration certificate gives the massic activity of SRM4927F as $634.7 \text{ kBq}\cdot\text{g}^{-1}$ on 3 September 1998, with a combined standard uncertainty of 0.36%; this uncertainty is the square root of the sum of squares of all error components in the calibration. We have applied the tritium half-life value 4500 ± 8 days evaluated by NIST to calculate the massic activity at our intercomparison reference date (1 December 2008). The standard

¹ The used tritium half life based on the NIST determination differs slightly from that listed in the DDEP evaluation of the same data with a different evaluation program of 4497 ± 9 days. However, the difference is not significant.

uncertainty of the half-life introduces an additional error component, which increases with time elapsed since 3 September 1998. Expressed as a percentage uncertainty, to be added in squaring with the combined standard uncertainty (0.36 %), this error is $2.378 \times 10^{-5} \times t$, where t is the elapsed time in days; this is only 0.09 % at our reference date 1 December 2008 (3742 days). The massic activity of SRM 4927F at that date is $356.7 \pm 2.3 \text{ kBq}\cdot\text{g}^{-1}$.

The website <http://srmccatalog.nist.gov/srmccatalog/certificates/srm-4927f.htm> provides full details of the SRM4927F calibration.

2.2 Sample Dilution Procedure

SRM4927F was diluted in 3 stages during a previous interlaboratory comparison exercise to obtain a daughter water of appropriate tritium activity to serve for common laboratory purposes [6](see Table 5 therein for details). The second dilution “D2-2000” was used in the TRIC2004 interlaboratory comparison and now again in TRIC2008. The diluting water for “D2-2000” had been a de-ionised sample from the artesian well G4 in Grafendorf, Austria, which was used as “tritium-free” water in TRIC2000 and earlier interlaboratory comparisons. This water was used at the IAEA Isotope Hydrology Laboratory for many years as tritium-free water in routine work. In TRIC2004 diluting water from the artesian well G3 in Grafendorf, Austria – in immediate vicinity of G4 - was used as “tritium-free” water. Its assigned tritium ratio is 0 TU with a 1 sigma uncertainty of 0.05 TU. Details see in the report of TRIC2004.

Also in the recent exercise the second dilution “D2-2000” was used to spike tritium free water G3 to produce the six samples T14 to T19. This time no tritium free water sample was itself included as sample. Details of the dilution procedures are given in Appendix A. All dilutions were performed using calibrated balances, checking the zero reading and a test weight before and after each weighing process. The process consisted of the weighing of (a) the empty containers, (b) the filled containers and, in case of the tritium standard transfer, (c) the empty transfer container (syringe). The combined uncertainty of the weighing procedure was calculated according to the law of uncertainty propagation, taking into account balance precision, maximum drift and display uncertainty. No buoyancy correction was applied.

2.3 Reference Values for the Prepared Samples T14 to T19

The six distributed samples T14 to T19 were prepared by spiking tritium free water with carefully weighed amounts of gravimetric dilutions of a primary tritium standard (NIST SRM 4927F). The reference values are presented in Table 2.

In principle the evaluated uncertainty is asymmetric, as the uncertainty contribution of possible tritium content of the tritium-free sample is only adding uncertainty to the upper side. The resulting uncertainty of the lower side for sample T14 would be in the order of only 0.01 TU. In practice the difference did not change the acceptance rating of any laboratory, and therefore the higher uncertainty value (minimum of 0.05 TU as the possible bias of residual tritium contained in this sample) was adopted to provide a

symmetric standard uncertainty. At low tritium ratio values, this uncertainty component is the major contributor to the combined uncertainty.

Table 2: Tritium ratios of the six prepared samples for the reference date 1 December 2008 with associated standard uncertainty (1sigma level), as calculated from gravimetric dilutions of a NIST tritium standard with tritium free water.

Sample name	Tritium ratio [TU]	Total combined standard uncertainty [TU]
T14	1.54	0.05
T15	4.07	0.05
T16	7.74	0.06
T17	14.46	0.08
T18	0.67	0.05
T19	568.7	2.3

2.4 Sample Homogeneity and Shipping

Each sample was prepared by weighing and transfer of tritium free water and tritium standard dilution into a stainless steel container. Then, the sample water was circulated by a pump in turbulent flow in a closed system for about one hour. This ensured complete isotopic homogeneity of the prepared samples as shown in previous exercises.

The water was then transferred into suitable half litre plastic bottles for shipment. This type of bottles was tested earlier for suitability for tritium sample storage and is used for all routine tritium samples taken worldwide for IAEA projects.

2.5 Laboratory Registration and Data Collection Process

For the first time an IAEA tritium interlaboratory comparison used internet based tools for registration, data submission and individual report creation. After announcement of TRIC2008 by emails to former participating laboratories and via an internet newsgroup, the relevant information on this exercise and the registration procedure could be found on the homepage <http://curem.iaea.org/tric2008>. The registration process included provision of mandatory information on the laboratory by a questionnaire, which had to be submitted to the IAEA. After successful registration, the parcels with the samples were sent out in December 2008 to all participants. Included in the shipment was an accompanying letter with the address of the reporting homepage <http://curem.iaea.org/tric2008/reporting/> and the individual user name and password for user access.

Measurement data could be entered and modified at any time at the webpage before the final deadline. When the final data submission was done (pressing the 'submit' button), no changes were allowed anymore. At this time a Reporting Form was created automatically (see example in Appendix F), which should be signed and sent to the IAEA.

2.6 Data Evaluation Procedure

The data evaluation was performed after the webpage based data collection using procedures as applied in previous proficiency tests of the IAEA Chemistry Unit[13]. The evaluation results are well comparable with those provided by use of the Interlaboratory Comparison Evaluation (ICE) program as used in earlier tritium interlaboratory comparisons. The new approach was chosen to be harmonized with the evaluation of interlaboratory comparison exercises performed by other groups at the IAEA. The evaluation criteria are covering the estimates of trueness and of precision of measurements.

For trueness evaluation the participants' results are assigned 'Acceptable' if:

$$A1 \leq A2,$$

where $A1 = |Value_{IAEA} - Value_{LAB}|$

$$\text{and } A2 = 2.58 \times \sqrt{Unc_{IAEA}^2 + Unc_{LAB}^2} .$$

For evaluation of the precision, the estimator P is calculated for each result according to the following formula:

$$P = \sqrt{\left(\frac{Unc_{IAEA}}{Value_{IAEA}}\right)^2 + \left(\frac{Unc_{LAB}}{Value_{LAB}}\right)^2} \times 100 \text{ [\%]} < LAP$$

P directly depends on the measurement uncertainty claimed by the participant. The acceptance limit for precision (LAP) for each sample is set to a value as given in Table 3. A change of these values would influence mainly the number of 'Warning' scores. Participants' results are scored as 'Acceptable' for precision when ($P < LAP$) or $P = (LAP)$.

Table 3: Acceptance limits for the evaluation of precision LAP (acceptable limit for precision) and trueness MAB (maximal acceptable bias), both in percent of reported values (see text).

Sample	LAP [%]	MAB [%]
T14	130^a	130^a
T15	50	50
T16	25	25
T17	18	18
T18	300^a	300^a
T19	5	5

^a tritium values close to the detection limit of most laboratories

The use of relative limits in the evaluation procedure (Table 3) caused few unexpectedly "acceptable" results. This happened when for low tritium ratios (with very high acceptable LAP and MAB values), when laboratories submitted in few cases strongly biased values with large measurement uncertainties. This should be avoided in the next exercise by switching to absolute values for LAP and MAB.

In the final evaluation, both scores for trueness and precision are combined. A result must obtain 'Acceptable' score in both criteria to be assigned final score 'Acceptable'.

Obviously, if a score ‘Not acceptable’ was obtained for both, trueness and precision, the final score will also be ‘Not acceptable’. In cases where either precision or trueness is ‘Not acceptable’, further check is applied. The value of the relative bias (RB) is compared with the maximum acceptable bias (MAB), which is defined by IAEA in advance, similarly as LAP. In this exercise, for simplicity reasons, MAB was set to the same percentage level as LAP (see Table 3) for each sample. If $(RB < MAB)$ or $(RB = MAB)$, the final score will be ‘Warning’. If $RB > MAB$, the result will be ‘Not acceptable’. ‘Warning’ will reflect mainly two situations. The first situation will be a biased result with small measurement uncertainty, however still within MAB. The second situation will appear when a result close to the assigned property value will be reported, but the associated uncertainty is large.

The evaluation was performed after end of the deadline of 31 March 2009. By 1 April 2009 the individual evaluation report was accessible for each laboratory as pdf-document and could be downloaded. An example of such report for laboratory ID 10 is provided in Appendix F.

3. PRESENTATION OF RESULTS

3.1 Individual Laboratory Data Display

The submitted results are listed in Appendix B (Table 6), with columns listing the laboratory identification number, the reported tritium ratio and reported measurement uncertainty at 1 σ -level in TU for the six samples. Results are ordered according to laboratory code number. Used measurement methods include Liquid Scintillation Counting, Gas Proportional Counting and ^3He Mass Spectrometry. Empty cells indicate data not submitted. Some results could not be assessed due to submission of non-numeric values (“below detection limit”).

Additionally, results for each sample are depicted graphically using S-plots (Figs.1-6), with laboratories sorted in increasing order of tritium ratio. These figures show the relation to the reference value and its uncertainty range from Table 2. Error bars are added at 2-sigma level from the submitted standard uncertainties. Accepted data are marked with filled circles, outliers (‘not acceptable’) are visually identified by use of open circles. Intermediate data at the “warning –level” are marked by open circles with cross inside. The laboratory code numbers (Lab ID) appear along the x-axes. Due to the new evaluation procedure (2.58 σ of combined sample-reference uncertainties) some results are accepted despite 2 σ uncertainty bars are not overlapping with those of the reference. This is different to past IAEA tritium interlaboratory comparisons.

All the S-plots are asymmetric around the reference values and their uncertainty limits, with more results on the high side. Because of this asymmetry of the S-plots, average results for the samples calculated from the whole population of laboratories are of limited usefulness, and are therefore not reported here.

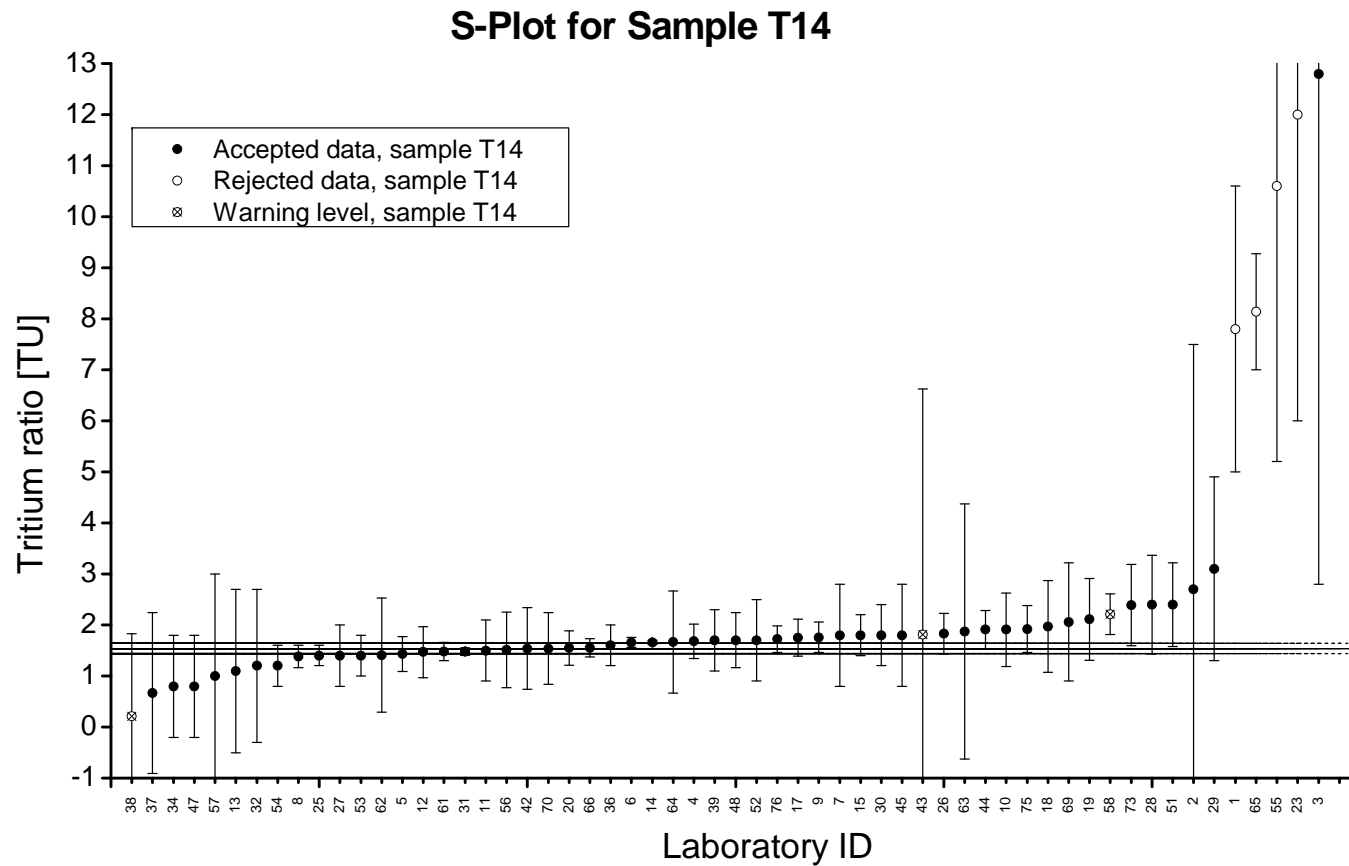


Fig.1: S-plot for sample T14. Rejected values are marked with open symbols. Values at warning level are marked with open symbols and a cross inside. For explanation on the acceptance of the value for lab 3 at right side see sections 2.6 and 3.6.

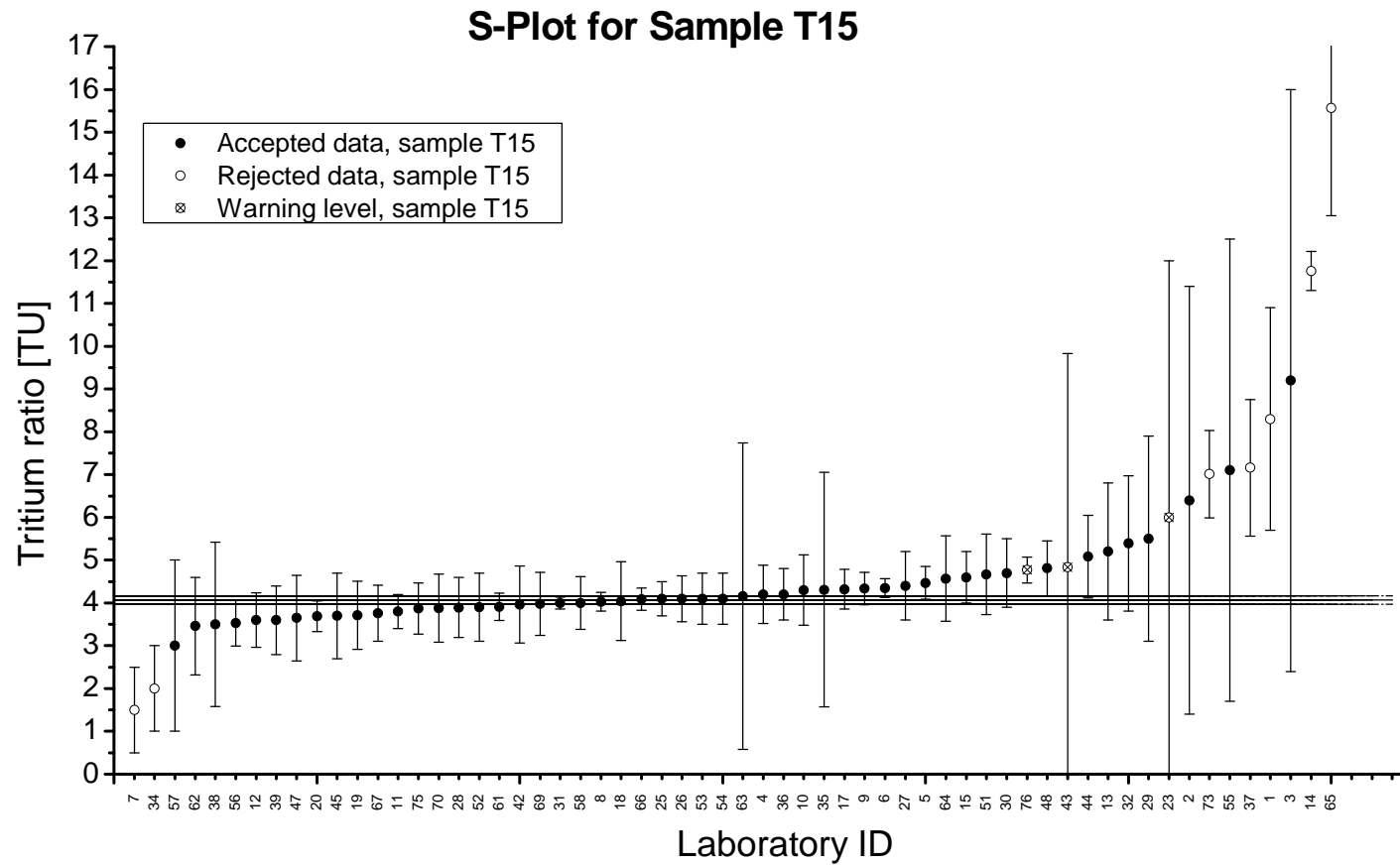


Fig.2: S-plot for sample T15. Rejected values are marked with open symbols. Values at warning level are marked with open symbols and a cross inside.

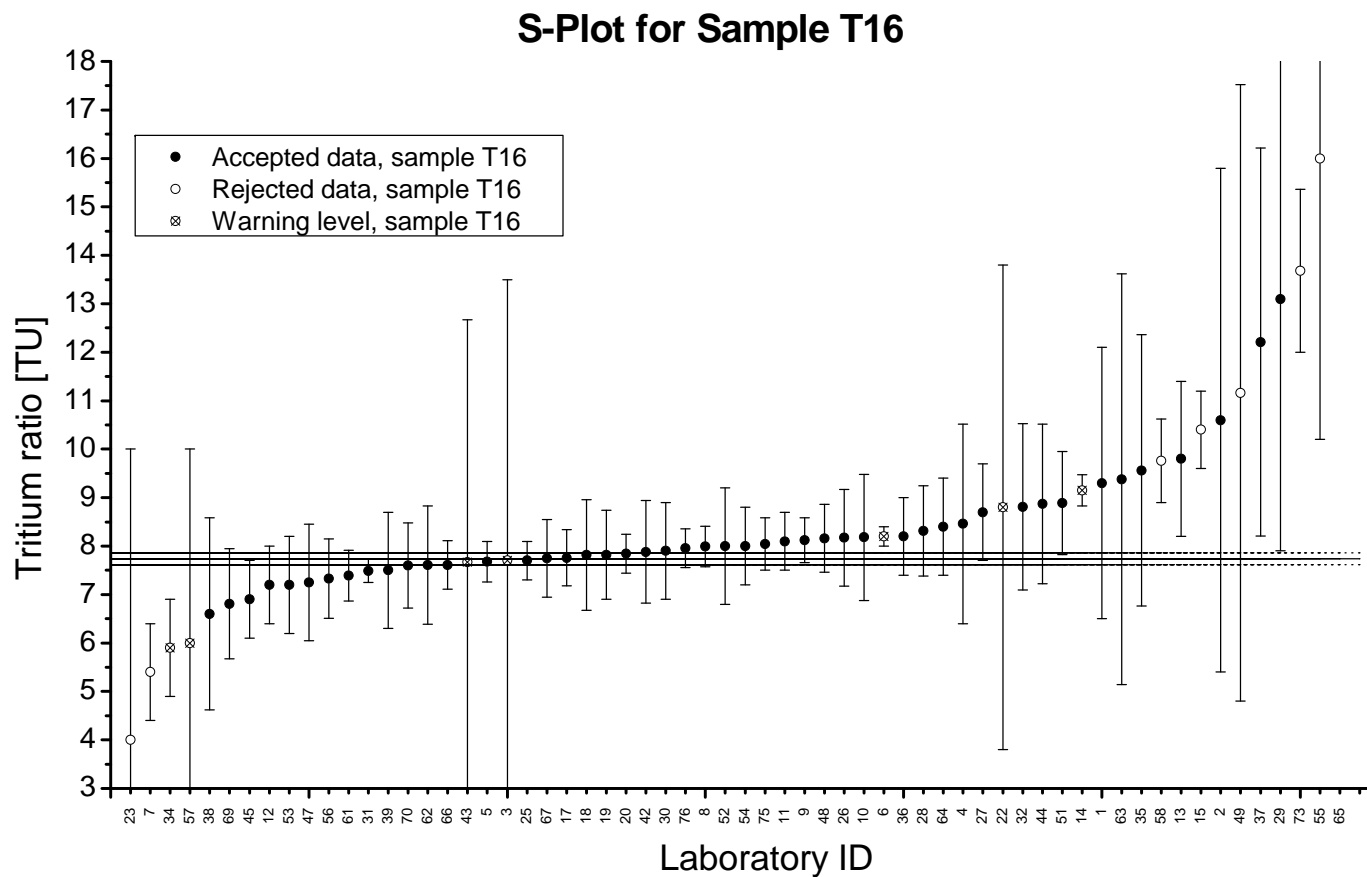


Fig.3: S-plot for sample T16. Rejected values are marked with open symbols. Values at warning level are marked with open symbols and a cross inside Values at the right side are outside the chosen scale..

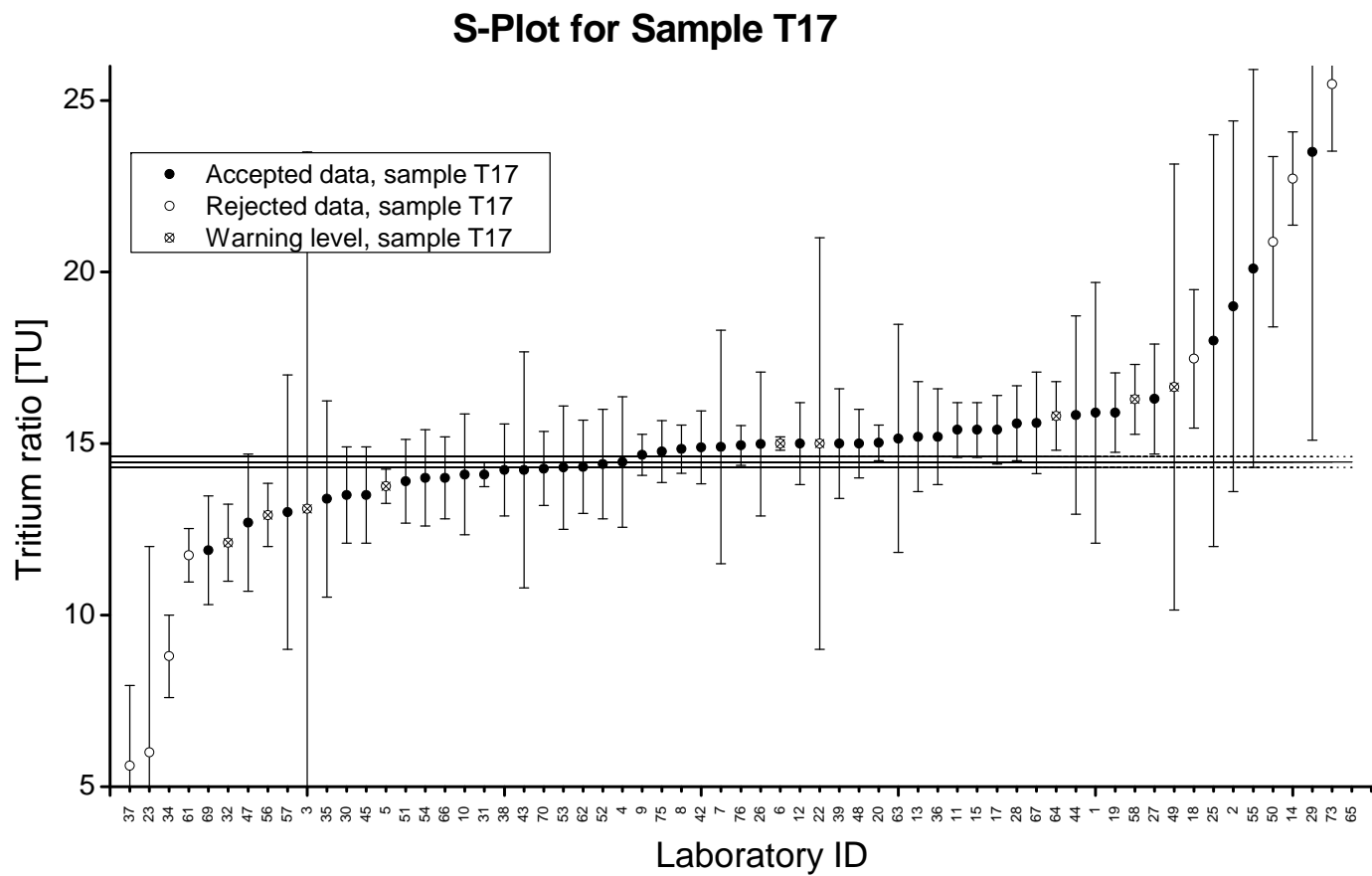


Fig.4: S-plot for sample T17. Rejected values are marked with open symbols. Values at warning level are marked with open symbols and a cross inside. Values at the right side are outside the chosen scale. For explanation on the accepted value for lab 29 at right side see sections 2.6 and 3.6.

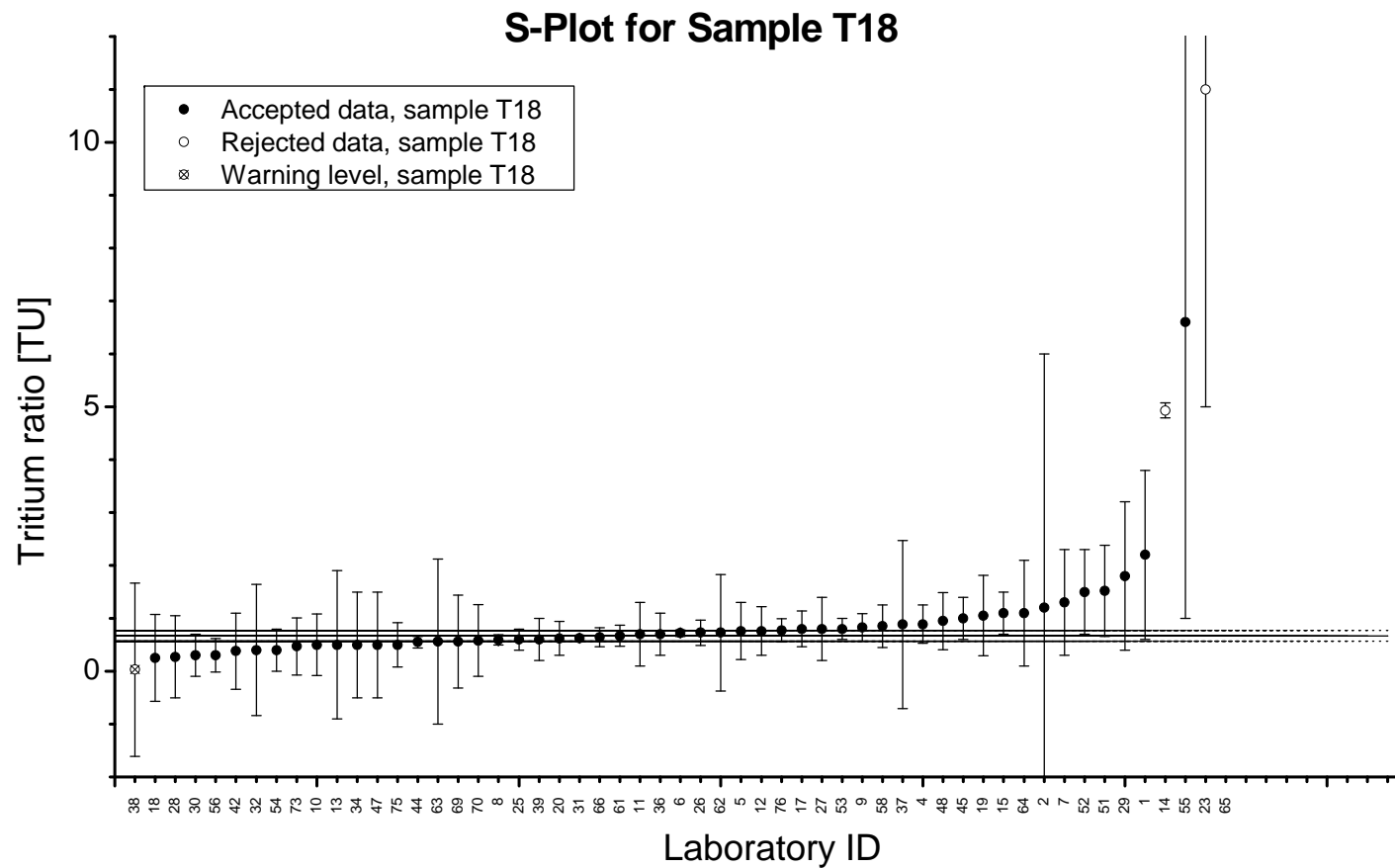


Fig.5: S-plot for sample T18. Rejected values are marked with open symbols. Values at warning level are marked with open symbols and a cross inside. Values at the right side are outside the chosen scale. For explanation on the accepted value for lab 55 at right side see sections 2.6 and 3.6.

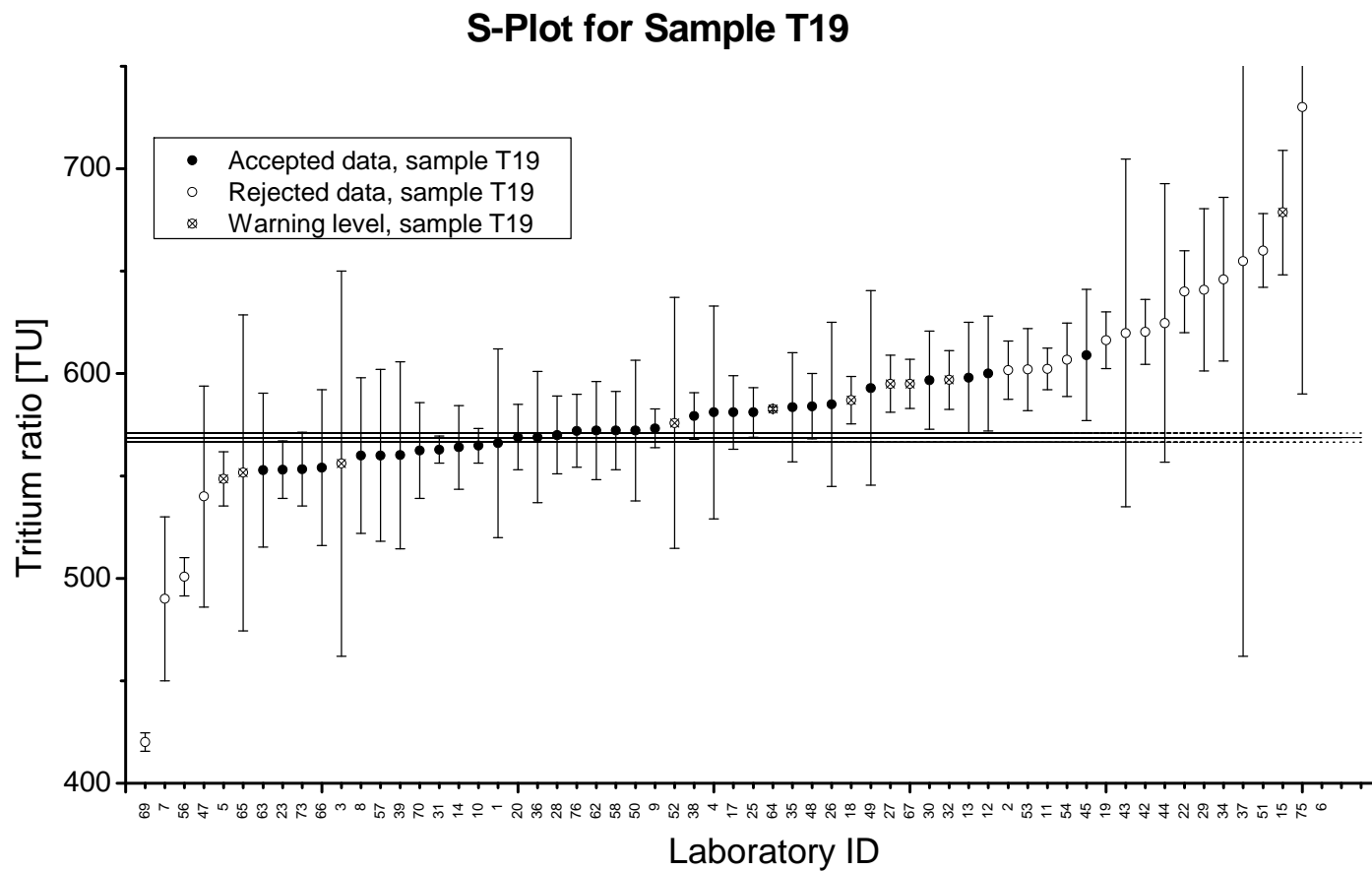


Fig.6: S-plot for sample T19. Rejected values are marked with open symbols. Values at warning level are marked with open symbols and a cross inside. Values at the right side are outside the chosen scale.

3.2 Results for the High Level Sample T19

This sample can be measured accurately by direct gas or liquid scintillation counting, and was intended to be measured in this way by the participating laboratories. It should allow an independent check of the tritium calibration of a laboratory. Although the spread of the submitted results could be slightly higher due to the various used calibrating standard waters and half-lives, it should be much easier to achieve conformity with the reference value than for samples requiring a tritium enrichment process. However, as in previous interlaboratory comparisons, a disappointingly high number of laboratories submitted results which were gross outliers. From 61 provided results, 19 (31 %) had to be identified as outliers. 4 results were on the low side (range 420 – 540 TU) and 15 were too high (601 – 1894 TU).

High results for sample T19 can be due to storage of internal laboratory standard waters in insecure bottles over time (shift to lower tritium concentrations due to exchange with atmospheric vapour of lower concentration). This in turn would shift any measured sample towards higher reported tritium values. Low results can be due to a variety of handling or calculation errors, or perhaps reliance on standard waters obtained at second or third hand without performing adequate cross-calibration checks. Reference is made to the discussion of this topic in the TRIC2000 report [6].

3.3 Comparison of Reported Uncertainties

In order to enable laboratories to compare their reported uncertainty with that of other participating laboratories, two distributions of the reported uncertainties were compiled, one for samples T14 to T18 (low level - Fig.7) and one for sample T19 (high level - Fig.8).

Several parameters, which are highly variable among laboratories, have to be considered in assessing these two diagrams:

- (a) longer counting times (accumulation times for ^3He), lower and more stable background count rates and better counting sensitivity significantly improve the uncertainty;
- (b) several laboratories counted directly the samples without prior tritium enrichment (causing an uncertainty being a magnitude higher);
- (c) it is by no means certain that all the laboratories have correctly assessed their measurement uncertainties by combining all contributing components according to the Guide to the Expression of Uncertainty in Measurements (GUM) [14]; see also section 3.4.2.

In Fig. 7, for each laboratory the cumulative reported uncertainties for the five samples at environmental tritium levels are stated. In cases where less than five samples were measured (biasing the ranking of laboratories), the analyzed number of samples is indicated in brackets at the laboratory ID number. The large increase of reported uncertainties towards the right side of Fig.7 indicates the laboratories counting directly without using any tritium enrichment. For sample T19, all laboratories should have measured the sample in similar manner directly without tritium enrichment (Fig.8). There is no obvious reason for the largely discrepant results except the use of liquid scintillation analysers in non low-level counting mode resulting in high noise or improper separation of a high background signal.

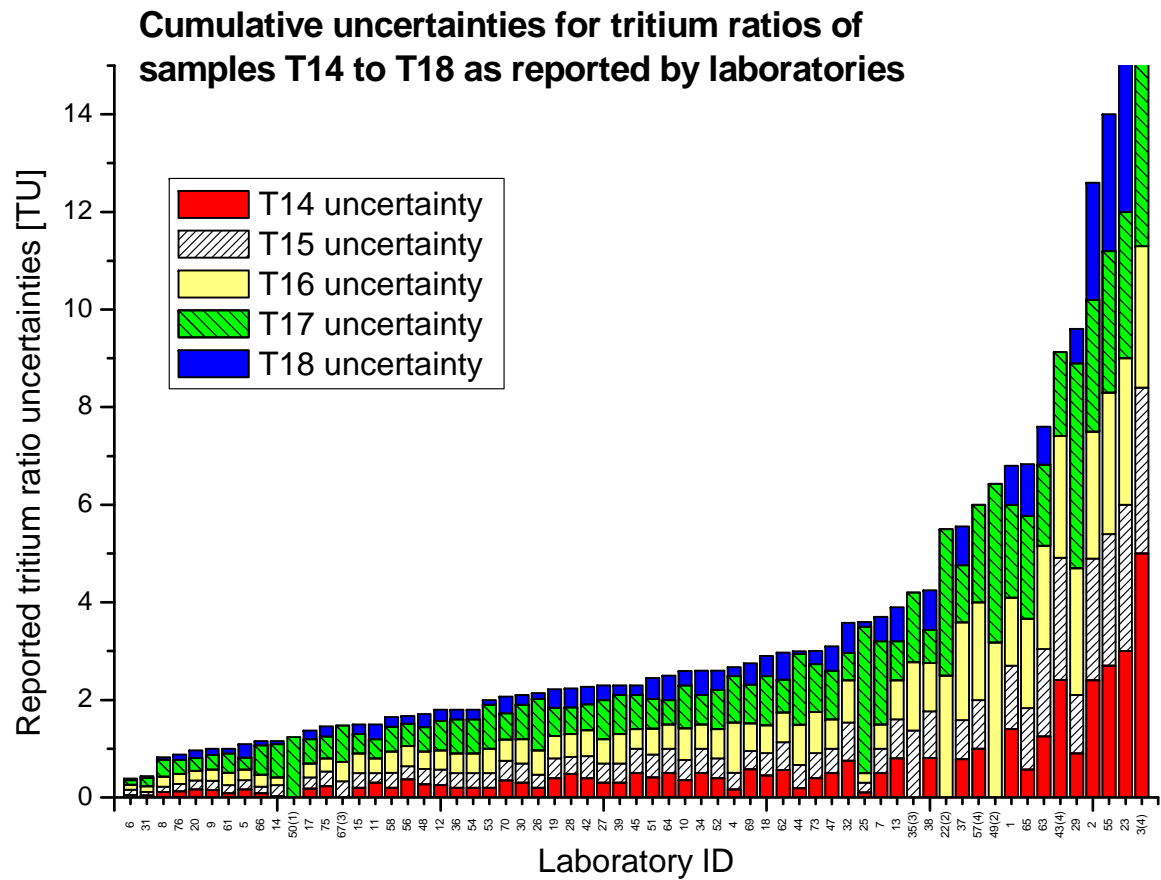


Fig.7: Cumulative uncertainties for samples T14 to T18 as reported by laboratories in increasing order. For laboratories with less than 5 analyzed samples (biasing the ranking), the respective number of samples is added in brackets to the Lab ID.

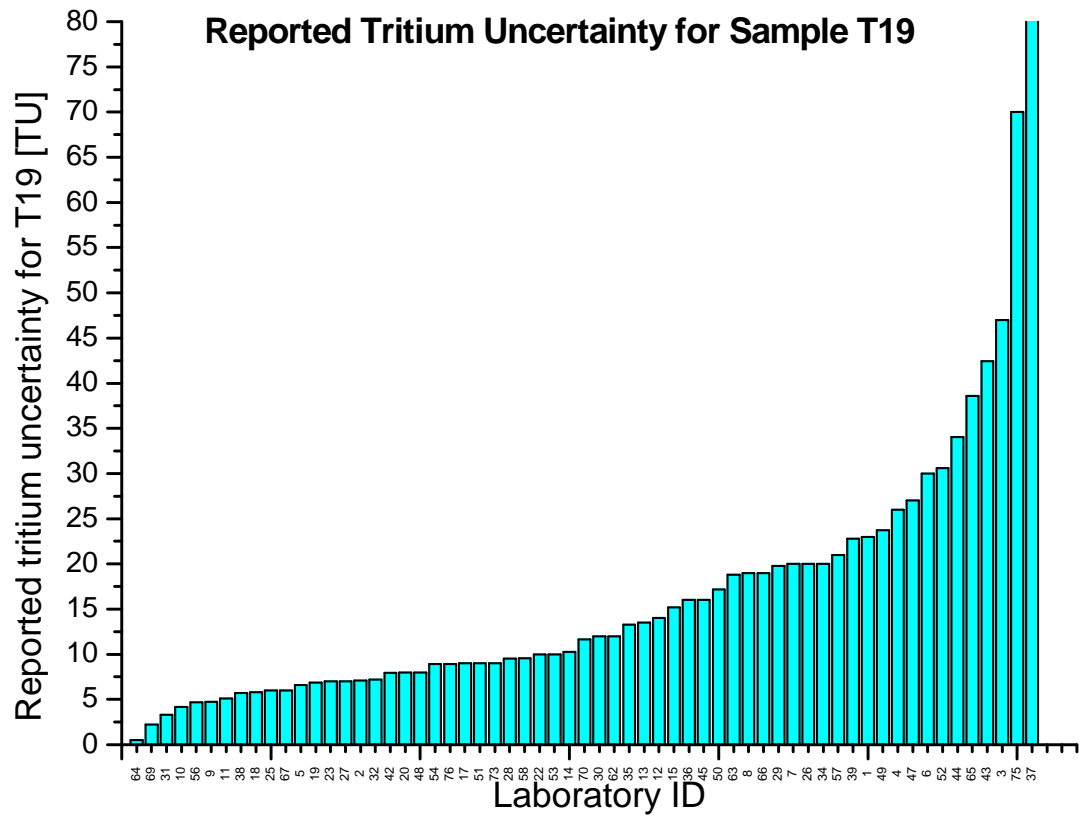


Fig.8: Reported uncertainty for sample T19 as stated by laboratories.

3.4 Laboratory Performance Indicators – Accuracy and Precision

As in the last reports an attempt was made to provide an estimate of laboratory performance by judging individual results versus the well-determined reference values of the samples as prepared gravimetrically at the IAEA.

3.4.1 Accuracy:

The most obvious performance ranking can be performed by calculating the deviation of the tritium ratio reported by the laboratory (in TU) from the reference value (Table 2). Incorporating values from six different samples is particularly helpful in this respect to provide a statistically significant estimate of the laboratory performance, as any deviations can be of random nature or caused by a systematic bias. The sum of deviations for samples T14 to T18 for each laboratory is shown in Fig. 9 (x-axis sorted according to the absolute sum of deviations). This provides a good estimate for the accuracy of environmental tritium values reported for an individual laboratory within the span of covered tritium ratios in TRIC2008.

Several features can be derived from Fig. 9. The sum of deviations from the reference value ranges from 0.6 TU (lab 70) to 67 TU (lab 66). The majority of laboratories show distinct deviations and bias for all samples only in positive or only in negative direction. A balanced distribution of deviations around the reference values (zero in the plots), – as to be expected for random errors following a normal distribution – occurs only for a minority of about 20 laboratories. This could indicate problems of the remaining laboratories with the calibration of tritium measurements. A residual bias in one direction could be caused by a wrong value assigned to the internal laboratory tritium standard (see also section 3.2).

Obviously, the ranking of laboratories in Fig. 9 is only correct for laboratories having measured all five samples T14 to T18. Those eight laboratories with less than five results are consequently marked with the respective number of analysed samples indicated in brackets at the Lab ID (x-axis).

Due to the different activity level of sample T19 and the commonly used direct measurement approach without enrichment and with much higher uncertainties, the deviations from the reference tritium ratio for sample T19 are presented separately in Fig.10. In this figure, the laboratories are sorted from most negative deviation to most positive deviation of sample T19.

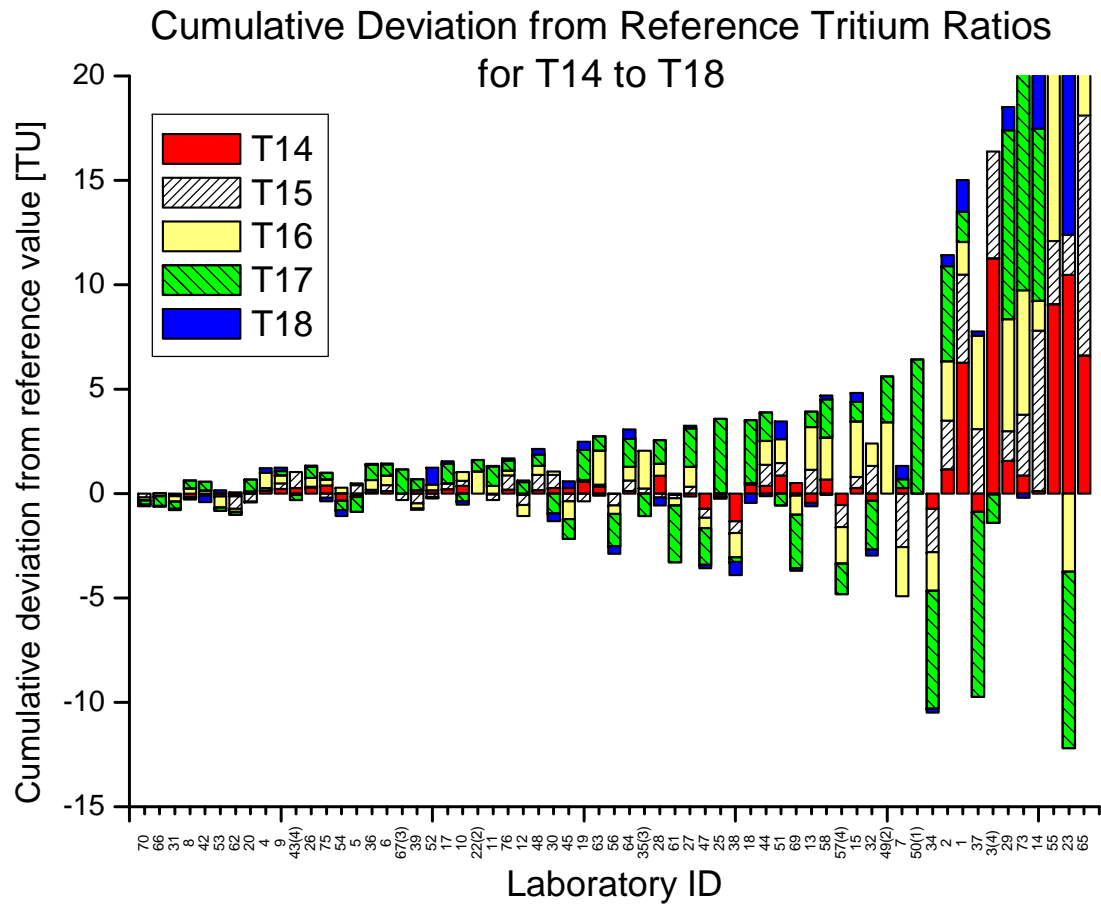


Fig.9: Sum of deviations from the reference tritium ratios for samples T14 to T18 in increasing absolute order in TU.

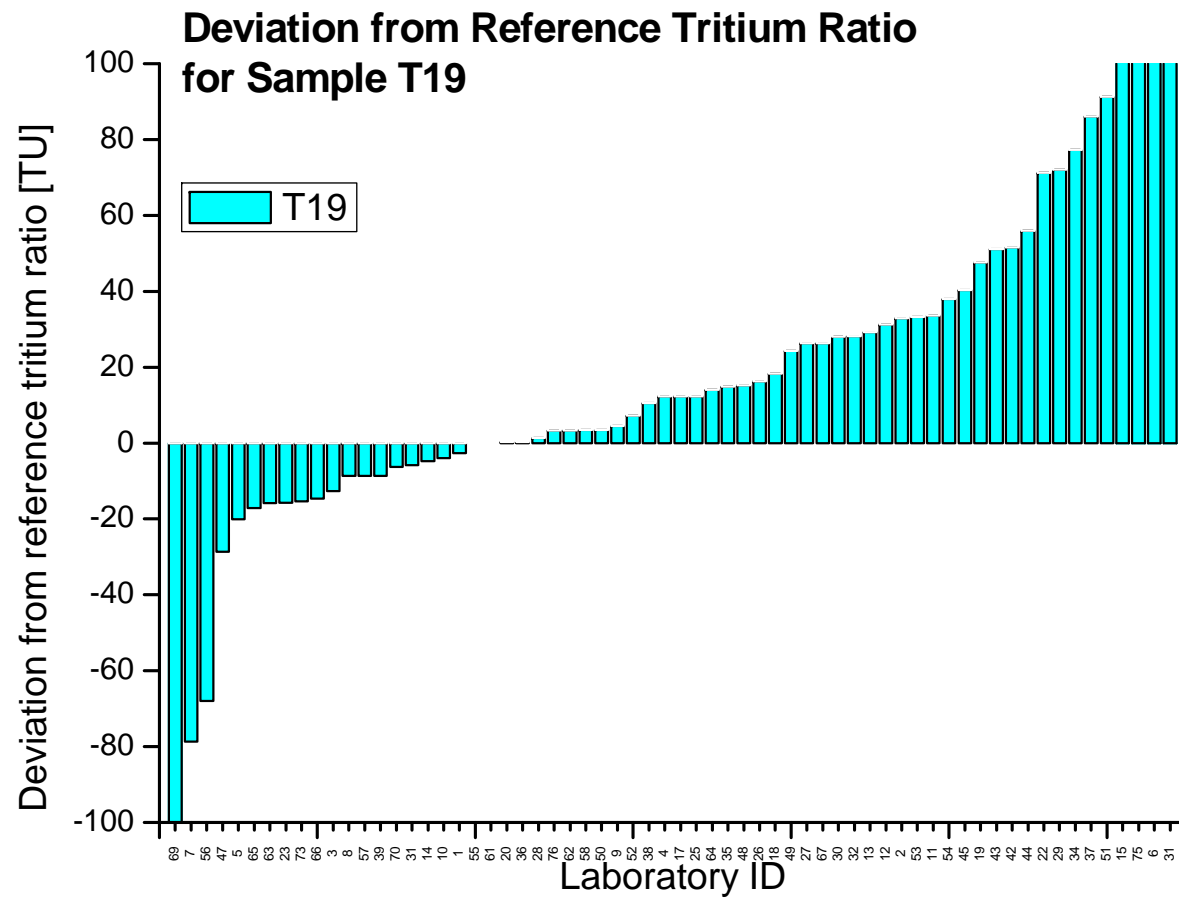


Fig.10: Deviation from the reference tritium ratio for sample T19 in increasing order.

3.4.2 Assessment of the Claimed Measurement Uncertainty:

Additional information on laboratory performance in terms of claimed measurement uncertainty is provided by the comparison of the deviation from the respective reference value for a given measurement with the laboratory's uncertainty statement. The used approach focuses on the reported uncertainty associated with each measurement and on the assessment of its reliability. The absolute deviation for each sample is calculated, and then divided by the reported uncertainty (Z-score). Therefore, the deviation for each sample is expressed on a sigma scale, directly comparing the reported 1σ -uncertainty for each sample of a laboratory with the actual deviation from the reference value. Each laboratory's "sigma-deviations" for the six samples T14 to T19 are presented in Fig. 11, sorted by increasing sum of absolute "sigma-deviation" values. Here all six results can be combined due to the use of the sigma scale.

Assuming the absence of any systematic bias for each individual laboratory, all results should be normal distributed. Under this assumption the respective reference value should lay with 95 % probability within 2σ uncertainty ranges around the reported values. As this holds true for all six samples, following in each case a normal distribution, the average standard deviation at a 1σ -level (67 % probability) for each of the six measurements should be close to one; or expressed differently, the sum of all absolute standard deviations for six samples should be close to six sigma in Fig. 11. While it is clear that the assumed absence of any systematic bias is not a realistic approach, it helps to delineate effects causing real deviations.

As a subjective quality criterion, for six samples reported, statistically the sum of deviations should not exceed 8σ and it should not fall below 4σ . As it can be seen from Fig. 11, 33 laboratories (52 %) exceed the value of 8σ , which clearly is an indicator for an underestimation of uncertainty in those laboratories (including the possibility of systematic biases). On the other side, 12 laboratories (19 %) provided data deviating in sum less than 4σ from the reference values of samples T14 to T19, which signals their quite conservative approach in stating significantly too high uncertainties. Only 18 laboratories (29 %) are found in the acceptable medium range of 4 - 8σ . These numbers have not changed significantly from those as evaluated previously for TRIC2004 [7].

It has to be stressed, however, that the results of Fig. 11 do not tell everything about the actual suitability of reported data for a certain purpose. This is illustrated in Fig. 12, where a similar plot as in Fig. 11 is presented for samples T14 to T18. In addition to the sum of absolute "sigma-deviations" for the considered five samples (Fig.12, plot A), the cumulated reported absolute tritium uncertainty for the same five samples (in TU) is plotted in the lower part (Fig.12, plot B). Obviously, no correlation exists between the magnitude of uncertainty as claimed by the laboratories (in TU) and its realization during the exercise as assessed by the sum of absolute "sigma-deviations" for the five samples. As already stated in the TRIC2004 report, this finding indicates the strong need to further improve in several cases the uncertainty evaluation and need for meaningful uncertainty statements for tritium measurements. The uncertainty evaluation for tritium at environmental low-level activities using electrolytic enrichment and liquid scintillation counting is discussed in [10], providing numerical examples to facilitate the application of the described principles.

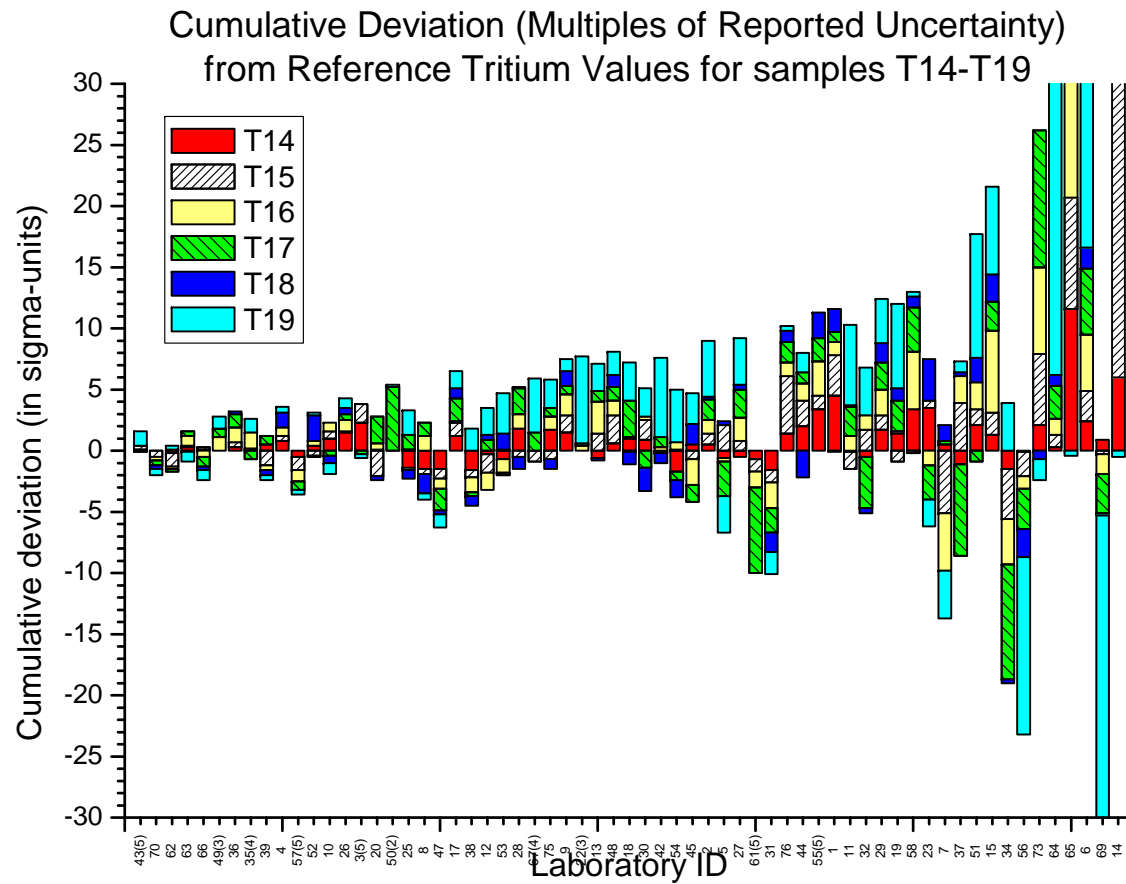


Fig.11: Sum of deviations from the true values for samples T14 to T19 in increasing absolute order, here reported as sigma-deviation by dividing the calculated deviation for each sample by the stated uncertainty. For details see text.

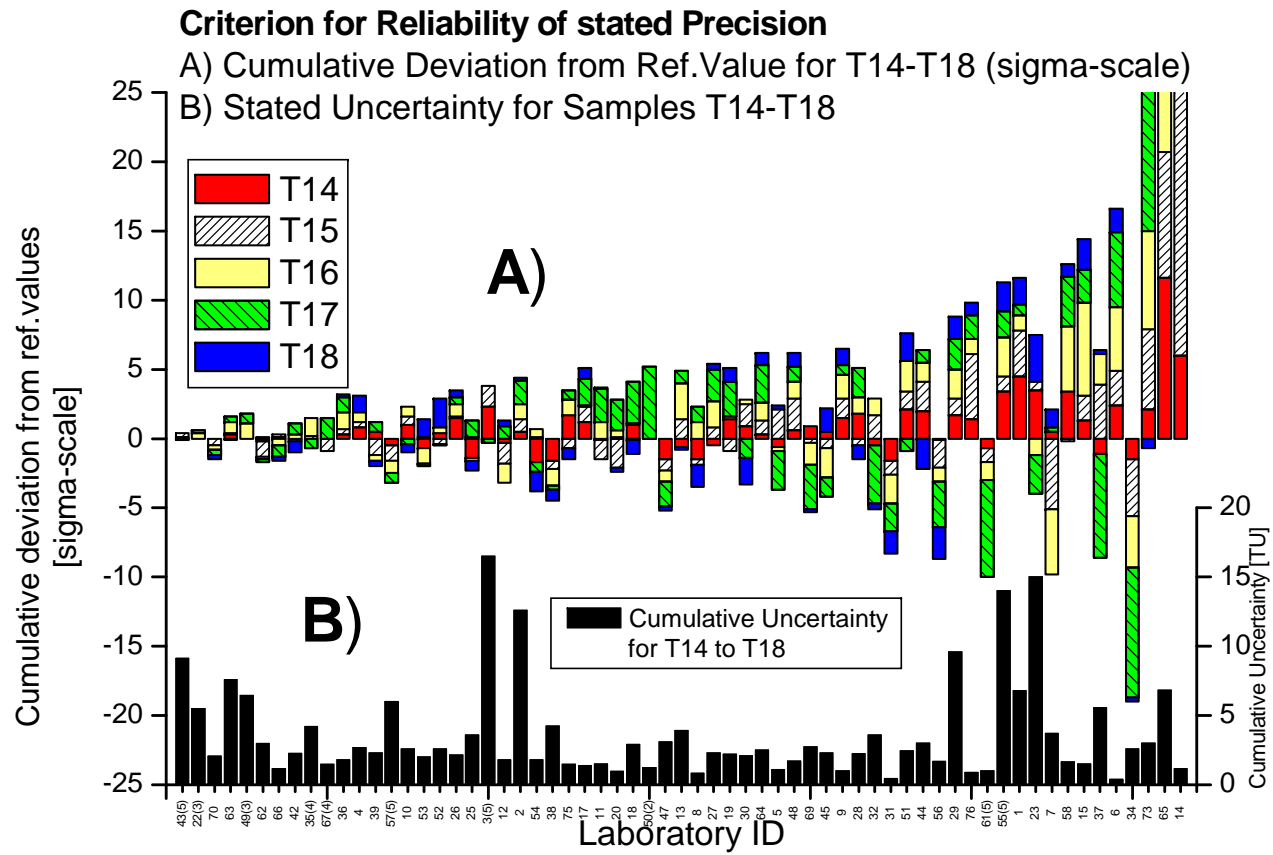


Fig.12: A) Sum of deviations from the reference value for samples T14 to T18 in increasing absolute order, reported as sigma-deviation by dividing the calculated deviation for each sample through the stated uncertainty. B) Reported cumulative uncertainty for samples T14 to T18.

3.5 Reporting of Results

Some basic guidelines for the reporting of data are presented here.

Results should always be expressed with an appropriate number of decimal places, with the same number of digits applied to result and uncertainty. The appropriate number of digits can be judged by the magnitudes of the reported value and measurement uncertainty. As an example, consider a laboratory operating normally within a range lower than a tritium ratio of 20 TU, and able to achieve 3 % standard measurement uncertainty for all but near-zero results. A result of 10.00 TU would bear an uncertainty of 0.30 TU; one of 5.00 TU would have an uncertainty of 0.15 TU. In this case, it is important to report results and uncertainties to 2 decimal places. If sample tritium values in the order of 100 TU are measured, reporting to 2 decimal places is no longer appropriate at associated uncertainty values in the range of 3 TU, and maximal 1 digit should be reported (compare to Table 6). Similar considerations should be applied in determining the appropriate number of decimal places for results reported as massic activities (e.g. Bq.kg⁻¹).

In Table 6 of Appendix B, still in 24 cases laboratories have reported a different number of digits for value and its associated uncertainty.

The sample date to which a result refers, should always be reported.

All laboratories should be able to clarify the basis of their calibrations, and even include this as a footnote to results in published papers or reports to clients. The necessary fundamental information comprises the identity and certified calibration (with date) of the tritiated water standard which is the cornerstone of the calibration procedures, and the half-life applied to estimate its decay over the years. It is encouraging that the majority of laboratories reported the used tritium half-life to be the recent value of 4500 ± 8 days. Several laboratories reported to use “Packard” or “Wallac” tritium standards; in few cases these were probably sealed controls to monitor counter stability during routine liquid scintillation counting, which should not be used for any calibration purpose.

Two laboratories reported about post-deadline corrections of their data based on comparison with the reference values. In one case, presented in Table 7 in Appendix C, laboratory 31 had previously changed their tritium standard used for internal calibration. They recognized a very small, but significant bias of their measurements (1.3 %) versus the reference values of TRIC2008. This bias disappeared when using the old tritium standard. The most probable explanation is a very slight offset introduced during the standard preparation. This problem can be solved only by careful independent dilution of another standard and comparison with the two other ones. This may exemplify the use to detect even little effects, important for high precision tritium measurements.

In the second case, laboratory 75 had reported a value of 730 ± 70 TU. An error was detected in the energy range in the LSC (put to 0-156 keV). After correction of this error, the revised result would have been 552 ± 79 TU.

A few more observations could be made using additional parameters as reported by laboratories in the questionnaires (selected parameters listed in Table 8 in Appendix D). These parameters are listed without consistency checks and should be used with care.

Eight laboratories referred to IAEA tritium standards used for their calibration. IAEA does not provide any tritium standard for calibration purposes, so this practice should be abolished and an official tritium standard used for preparation of an appropriate dilution.. Similarly, few laboratories referred to standards, which may have been just quenched or unquenched standards for check of the LSC performance, but should not be used for calibration purposes of the whole tritium analysis process.

About six laboratories still use outdated values for the tritium half life.

Several laboratories used mixing ratios of water to scintillation cocktail much higher than 1. This could indicate problems with the water capacity of the used liquid scintillation cocktail (54 % for Ultima Gold LLT) and could cause formation of a separate water phase in the vial affecting the counting characteristics.

Statements for several parameters cover a very wide range; e.g. for the background count rate expressed in counts per minute (cpm) values were stated from 0.02 to 20, even for the same type of instrument.

3.6 Lessons Learned from the TRIC2008 Exercise

Several observations were made during this exercise, which should be considered for future tritium interlaboratory comparisons.

The initial set reporting deadline of three and half months should ensure timely conclusion of the exercise. The laboratories using liquid scintillation counting or gas proportional counting did comply with the deadline. Due to the special requirements for laboratories using the ^3He ingrowth technique, a longer timeframe would be desirable. It should be considered whether both types of exercises could be split up (or being started three months earlier for ^3He laboratories).

Some problems were caused by the pdf-version of the questionnaire supplied to the participants. It was tested beforehand at the IAEA, and was intended to provide an easy means for filling in the pdf-form and submit it to IAEA by built-in email functionality. However, a number of participants could not use it due to IT security settings in their local networks. In those cases Excel-sheets with the same information were sent out additionally to the concerned laboratories, causing some delays.

With the submission of questionnaires mandatory for participation, the number of initial participants (74) was similar than for the previous TRIC2004 exercise, while more than 102 laboratories signed in for TRIC2000 (in the latter case the additional laboratory information was only requested, but submitted only in 50 % of cases). So, keeping it mandatory, it provides essential information used to check the appropriateness of submitted results.

During the data reporting stage, a significant portion of laboratories failed to officially submit their final results by pressing the submit button on the reporting webpage. Those laboratories therefore were not able to download their individual evaluation reports. In future this feature may be replaced by an automated action to consider all entered data as finally submitted by the end of the deadline.

A fine-tuning of evaluation criteria may be necessary. For example in Fig.1 for all practical considerations in the field of isotope hydrology, the result of laboratory 3 at the most right hand should be considered as outlier, which is not the case in the recent modus. This is due to the evaluation criteria for acceptable deviations using a relative percentage limit instead of a fixed absolute value. This will be changed in the evaluation procedure for the next exercise.

It could be explored in future to separate the evaluation completely between laboratories using tritium enrichment and those which perform direct measurements, as the intended use of such measurements seems to be rather different. It may provide a better insight into real performance, when separating the two clusters.

During circulation of the draft report to all participating laboratories, the question was posed whether laboratories would also participate if this exercise would not be anonymous, but the laboratory names would be associated to the results. From 27 answers received, 25 answered positively, only two laboratories would not participate if names would be associated to results.

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APPENDIX A: DETAILS OF THE SAMPLE PREPARATION

Since from the perspective of low-level tritium laboratories, SRM4927F is an extremely active tritiated water, the first two dilution stages had not been performed at the Isotope Hydrology Laboratory, but at the distant IAEA Laboratories in Seibersdorf. A de-ionised “tritium-free background water” was used to dilute the standard in two stages. This water from the artesian well Grafendorf G4 (near Graz) dates back to 1992 and was used for previous tritium interlaboratory comparisons. Repeated analyses of the de-ionised water indicated that its tritium ratio is less than 0.1 TU. Its massic activity is less than 5×10^{-9} times that of the resulting daughter water after 2 dilution stages, and any influence on the calculated values can therefore be neglected.

Table 4: Dilution procedure for the original tritiated water standard SRM4927F (reproduced from [6]).

Dilution stage	1	2
Weight of tritiated water (in brackets uncertainty) [g]	4.9063 (0.0003)	20.9142 (0.0003)
Weight of added T3 dilution water (uncertainty) [g]	994.38 (0.07)	999.89 (0.07)
Dilution factor (relative uncertainty)	203.674 (0.009%)	48.8091 (0.007%)
Combined dilution factor (relative uncertainty)	203.674 (0.009%)	9941.12 (0.012%)

In the recent exercise a sufficient supply of water was sampled from another artesian well in Grafendorf with name G3, which is at the same location as the formerly used well G4, but tapping a slightly shallower aquifer. That water was tested during TRIC2004 for its upper margin of tritium content. It was used in that exercise as one sample (T7) and was also used as diluting water for preparation of the remaining five samples. The tritium ratio of this water was assessed to be equal to zero, with a possible residual tritium concentration of this water of maximal 0.05 TU at the 1σ -level, using the submitted results. That diluting water T7 was not distilled or de-ionised, in order to ensure that the samples would be put through the routine pre-measurement distillation step by the participating laboratories. In the final dilution stage, the measured weights of diluting water were corrected for the dissolved solid content; this correction is 262 mg/kg water, i.e. -0.0262% .

On the reference date 2008-12-01 the standard tritium daughter water (“D2-2000”) had a tritium activity of 301004 TU. The weighing parameters for its dilution to create the six

samples are summarised in the accompanying Table 5. Numbers in brackets are standard uncertainties at 1 sigma level. The factor 8.390 was applied to convert Bq/kg to TU.

Table 5: Dilution procedure for the six samples T14 to T19 used in this interlaboratory comparison, using as tritiated standard the ‘Dilution Stage 2’ of Table 4 and as dilution water the Grafendorf well G3. Values in brackets are uncertainties at the 1- σ level.

	T14	T15	T16	T17	T18	T19
Weight of SRM4927F daughter “D2-2000” [g]	0.421 (0.002)	1.123 (0.002)	2.141 (0.002)	3.989 (0.002)	0.158 (0.002)	17.044 (0.002)
Weight of T7 water [g]	82157.17 (0.17)	83088.97 (0.17)	83212.51 (0.17)	83006.75 (0.17)	71233.86 (0.17)	9004.48 (0.06)
Dilution factor	195148.7	73989.40	38867.19	20809.91	450848.2	529.3079

APPENDIX B: INDIVIDUAL LABORATORY RESULTS

Table 6: All sample results as reported by the individual participating laboratories (please refer to section 3.5 on significant digits – e.g. for lab IDs 37, 44, 65 – and on consistent reporting of value and uncertainty, e.g. for T15 lab 47, 58, 70 etc.). The uncertainties $u(\text{sample})$ were requested to be stated at the $1-\sigma$ level. Blank fields indicate not-submitted data. All outlier values (‘not acceptable’) in the tables are gray-shaded, all values at ‘warning’-level are diagonally striped. For details on the outlier determination procedure see text. The TRIC2008 reference values are stated in bold in the header lines.

Lab Ref.	T14 1.54	u(T14) 0.05	T15 4.07	u(T15) 0.05	T16 7.74	u(T16) 0.06	T17 14.46	u(T17) 0.08	T18 0.67	u(T18) 0.05	T19 568.7	u(T19) 2.3
	All tritium values and standard uncertainties are stated as tritium ratio in TU											
1	7.8	1.4	8.3	1.3	9.3	1.4	15.9	1.9	2.2	0.8	566	23
2	2.7	2.4	6.4	2.5	10.6	2.6	19	2.7	1.2	2.4	601.6	7.1
3	12.8	5.0	9.2	3.4	7.7	2.9	13.1	5.2	<1.8		556	47
4	1.68	0.17	4.20	0.34	8.46	1.03	14.46	0.95	0.89	0.18	581	26
5	1.43	0.17	4.47	0.19	7.68	0.21	13.76	0.25	0.76	0.27	548.6	6.6
6	1.66	0.05	4.35	0.11	8.2	0.1	15	0.1	0.72	0.03	1894	30
7	1.8	0.5	1.5	0.5	5.4	0.5	14.9	1.7	1.3	0.5	490	20
8	1.38	0.11	4.03	0.11	7.99	0.21	14.84	0.35	0.594	0.047	560	19
9	1.76	0.15	4.34	0.19	8.12	0.23	14.67	0.30	0.83	0.13	573.27	4.75
10	1.91	0.36	4.30	0.41	8.18	0.65	14.10	0.88	0.50	0.29	564.8	4.2
11	1.5	0.3	3.8	0.2	8.1	0.3	15.4	0.4	0.7	0.3	602.3	5.1
12	1.47	0.25	3.60	0.32	7.2	0.4	15.0	0.6	0.76	0.23	600	14
13	1.1	0.8	5.2	0.8	9.8	0.8	15.2	0.8	0.5	0.7	598	13.5
14	1.66	0.02	11.76	0.23	9.15	0.16	22.72	0.68	4.93	0.07	563.97	10.24
15	1.8	0.2	4.6	0.3	10.4	0.4	15.4	0.4	1.1	0.2	678.6	15.2
17	1.75	0.18	4.32	0.23	7.76	0.29	15.4	0.5	0.80	0.17	581	9
18	1.97	0.45	4.04	0.46	7.82	0.57	17.47	1.01	0.25	0.41	586.95	5.81
19	2.11	0.40	3.71	0.40	7.82	0.46	15.90	0.58	1.05	0.38	616.32	6.89
20	1.55	0.17	3.69	0.18	7.84	0.20	15.02	0.26	0.62	0.16	569	8
22					8.8	2.5	15	3			640	10
23	12	3	6	3	4	3	6	3	11	3	553	7
25	1.4	0.1	4.1	0.2	7.7	0.2	18	3	0.6	0.1	581	6
26	1.83	0.20	4.10	0.27	8.17	0.50	14.99	1.05	0.73	0.12	585	20
27	1.4	0.3	4.4	0.4	8.7	0.5	16.3	0.8	0.8	0.3	595	7
28	2.398	0.484	3.893	0.349	8.31	0.466	15.59	0.544	0.27	0.389	570	9.5
29	3.1	0.9	5.5	1.2	13.1	2.6	23.5	4.2	1.8	0.7	640.8	19.8
30	1.8	0.3	4.7	0.4	7.9	0.5	13.5	0.7	0.3	0.2	596.8	12.0
31	1.482	0.037	4.00	0.07	7.49	0.12	14.10	0.18	0.624	0.029	562.9	3.3
32	1.20	0.75	5.39	0.79	8.81	0.86	12.11	0.56	0.40	0.62	596.85	7.21
34	0.8	0.5	2.0	0.5	5.9	0.5	8.8	0.6	0.5	0.5	646	20
35	<5.34		4.31	1.37	9.56	1.40	13.39	1.43	<5.34		583.6	13.3
36	1.6	0.2	4.2	0.3	8.2	0.4	15.2	0.7	0.7	0.2	569	16
37	0.666	0.788	7.160	0.798	12.21	2.001	5.607	1.173	0.883	0.796	654.83	96.38
38	0.21	0.81	3.50	0.96	6.60	0.99	14.23	0.67	0.03	0.82	579.24	5.70
39	1.7	0.3	3.6	0.4	7.5	0.6	15.0	0.8	0.6	0.2	560.1	22.8
42	1.54	0.40	3.96	0.45	7.88	0.53	14.89	0.53	0.38	0.36	620.37	7.92

Lab	T14	u(T14)	T15	u(T15)	T16	u(T16)	T17	u(T17)	T18	u(T18)	T19	u(T19)
43	1.81	2.41	4.83	2.50	7.67	2.50	14.23	1.72			619.8	42.46
44	1.909	0.187	5.087	0.482	8.872	0.823	15.824	1.445	0.551	0.055	624.671	34.025
45	1.8	0.5	3.7	0.5	6.9	0.4	13.5	0.7	1.0	0.2	609	16
47	0.8	0.5	3.65	0.5	7.25	0.6	12.7	1	0.5	0.5	540	27
48	1.70	0.27	4.81	0.32	8.16	0.35	15.0	0.5	0.95	0.27	584	8
49	<12.37		<12.47		11.16	3.18	16.65	3.25	<12.34		592.97	23.72
50							20.88	1.24			572.15	17.16
51	2.4	0.41	4.67	0.47	8.89	0.53	13.9	0.61	1.52	0.43	660	9
52	1.7	0.4	3.9	0.4	8.0	0.6	14.4	0.8	1.5	0.4	575.9	30.6
53	1.4	0.2	4.1	0.3	7.2	0.5	14.3	0.9	0.8	0.1	602	10
54	1.2	0.2	4.1	0.3	8.0	0.4	14.0	0.7	0.4	0.2	606.7	8.9
55	10.6	2.7	7.1	2.7	16.0	2.9	20.1	2.9	6.6	2.8		
56	1.51	0.37	3.53	0.27	7.33	0.41	12.92	0.46	0.3	0.16	500.73	4.68
57	1	1	3	1	6	2	13	2	<1		560	21
58	2.21	0.2	4	0.31	9.76	0.43	16.29	0.51	0.85	0.2	572.14	9.58
61	1.48	0.09	3.91	0.16	7.39	0.26	11.74	0.39	0.67	0.10		
62	1.41	0.56	3.46	0.57	7.61	0.61	14.32	0.68	0.73	0.55	572.1	12.0
63	1.87	1.25	4.16	1.79	9.38	2.12	15.15	1.66	0.56	0.78	552.82	18.8
64	1.67	0.50	4.57	0.50	8.4	0.5	15.8	0.5	1.1	0.5	582.72	0.50
65	8.14	0.57	15.57	1.26	26.3	1.83	30.18	2.11	15.11	1.06	551.56	38.6
66	1.55	0.09	4.09	0.13	7.61	0.25	14.0	0.6	0.64	0.09	554	19
67	<3		3.76	0.33	7.75	0.4	15.6	0.74	<3		595	6
69	2.06	0.58	3.98	0.37	6.81	0.57	11.89	0.79	0.56	0.44	420.14	2.23
70	1.54	0.35	3.88	0.4	7.6	0.44	14.27	0.54	0.58	0.34	562.4	11.65
73	2.39	0.40	7.01	0.51	13.68	0.84	25.48	0.98	0.47	0.27	553.35	9.03
75	1.92	0.23	3.87	0.30	8.04	0.27	14.77	0.45	0.50	0.21	730	70
76	1.72	0.13	4.77	0.15	7.96	0.20	14.95	0.29	0.77	0.11	572	8.9

APPENDIX C: REVISED DATA SET FOR LAB 31 (not considered in evaluation and figures)

Table 7: Comparison of two data sets by lab no. 31: One as originally submitted, using a new tritium standard (SRM4927F); and a new data set using an old formerly used tritium standard (SRM4926C, data only submitted in September 2009).

Sample	Data in TU using SRM4927F	Revised data in TU using SRM4926C	Standard deviation in TU
T14	1.482	1.503	0.037
T15	4.00	4.05	0.07
T16	7.49	7.59	0.12
T17	14.10	14.29	0.18
T18	0.624	0.633	0.029
T19	562.9	570.5	3.3

APPENDIX D: ADDITIONAL PARAMETERS AS REPORTED BY LABORATORIES

Table 8: Selection of parameters as reported by laboratories in a (requested) questionnaire, which potentially could have an influence on reported data or their quality.

LabID	Method	Enrichment	Standard provider	Std type	Half-life [d] or [y]	enrichment factor	Instrument model	LSC cocktail	water volume	scintill. volume	Counting time [min]	background count rate [cpm]	detection limit
1	LSC	no	CMI	ER 25X	12.33 y		Quantulus-1220	Ultima Gold LLT	10	10	1500	1.1	7
2	LSC	no	PerkinElmer	H-3 for Aqueous	4500 d		Quantulus-1220	Ultima Gold LLT	8	12	2000	0.91 - 1.00	6 (k=3)
3	LSC	yes	CMI	Tritium etalon s	4510 d	10	Tricarb 2900 TR	Ultima Gold LLT	10	10	510	11.2	1.5
4	LSC	yes	NIST	SRM 4926E	4500 ± 8 d	19.3	Quantulus-1220	Ultima Gold LLT or I	8	12	500-1000	1.00 ± 0.07	0.5
5	LSC	yes	PTB	PTB4453	12.3y	20	Quantulus	Quicksafe 400	8	12	1000	0.02	0.85
6	3He-T				12.32y						6 months		0.01
7	LSC	yes	PerkinElmer	3H Ultima Gold	4500d	8.1	TriCarb 3170TR/SL	Ultima Glod LLT	20	12	1000	1.45 ± 0.02	5 TU / 0.65 TU
8	3He-T		NIST	SRM 4361C	12.32y						1-3 months		0.005
9	LSC	yes	NIST	SRM 4927F	4500d	30	Quantulus 1220I	Ultima Gold LLT	10	12	600	0.8	0.05Bq/l
10	LSC	yes	NIST	SRM 4927F	4500d	18	Packard 2770 TR	Quicksafe	10	12.5	460	1	0.5TU
11	LSC	yes	NIST	NIST/ Inhouse	12.43y	20/5	Quantulus 1220	Ultima Gold LLT	10	11	1000	1	0.7
12	LSC	yes	NIST	SRM 4361C	4500d	15/30	TRICARB 3170SL	Ultima Gold LLT	9	11	600	0.9-1.1	0.5TU/0.3TU
13	LSC	yes	NIST	SRM-4926	4500d	14.71	TRICARB 3170TR/SL	Ultima Gold	8	12	500	0.9	1TU
14	LSC	yes	IAEA	IAEA-D&TRIC2	12.328y	n.a.	Quantulus 1220	Optiphase Hisafe-3	8	12	1000	0.8	5TU
15	LSC	yes	other	Lab. Standard	12.32y	20	Quantulus 1220	Ultima Gold LLT	10	7.5g	420	0.61	0.6 TU
17	LSC	yes	NBS	SRM 4962C	4500d	variable	Packard various models	Ultra Gold	9	8	1000	1-2.4	variable
18	GAS	yes	IAEA	TRIC 2004	12.43y	12.5	Gas proportional counter	Ethane			2800	2.4	0.2
19	LSC	yes	Amersham	TRR-9	12.32y	15	Quantulus 1220	Ultima Gold LLT	10	10	500	1.5	1.7
20	LSC	yes	NIST	SRM 4361C	12.33y	0.87	Wallac 1414	Ultima Gold LLT	10	10	1500	1.8	0.5
22	LSC	no	Wallac		12.35y	n.a.	Quantulus 1220	Ultima Gold LLT	8	12	600	0.75	15
23	LSC	no	NIST	SRM 4926E	4500d	n.a.	Quantulus 1220	Perkin Elmer UGLL	10	10	300-900	0.55	10
25	LSC	yes	Amersham	TRY64 Batch1	4500d	35	Quantulus 1220	Ultima Gold LLT	10	11	20	20	0.5
26	LSC	yes	IAEA		12.32y	30	TriCarb 3170TR/SL	Ultima Gold LLT	8	12	2800	1.01	7.0 TU / 0.2 TU
27	LSC	yes	NIST	SRM 4926E	4500d	23	TRI-CARB1600 TR	Ultima Gold LLT	12	12	700	2.6	0.3
28	LSC	yes	NIST	SRM 4926E	4500d	0.87	Packard LSC 2750	Ultima Gold	10	10	450	2.2	0.3-0.4
29	LSC	yes	NIST	4361C	4500d	60%	Quantulus 1220	Ultima GoldLLT	9	10	270	1.7	1
30	LSC	yes	Wallac		12.32y	9.5	Quantulus 1220	Ultima Gold	20	10	320	1.42	1
31	LSC	yes	NIST	4927F	12.32y	60							
32	LSC	yes	NIST	SRM 4927F	4500d	15.8	TRICARB 2050 CA	Ultima Gold LLT	10	10	60	1.97	
34	LSC	yes	NIST	4927F	4500d	10	TRICARB 3170TR/SL	Ultima Gold	10	10	500	1	0.3
35	LSC	yes	AEA	TRY44	12.312y	n.a.	Packard Quantulus	Ultima Gold LLT	10	10	1000	0.8	11
36	LSC	yes	NIST	SRM 4361C	4500d	15/24	Quantulus1220	Ultima Gold LLT	20	11	1000	0.6-0.7	0.4
37	LSC	yes	IAEA	IAEA	4500d	10	TRICARB 3170TR/SL	Ultima Gold	10	10	400	1.26	0.5
38	GAS	yes	IAEA	IAEA Spike	12.32y		Gas proportional counter	Methane			1300	1.22	2.5
39	LSC	yes	NIST	4361C	4500d	20	TRICARB 2770TR/SL	Ultima Gold LLT	10	11	480	1.37	4.5
42	LSC	yes	IAEA	IAEA spike	12.32y	20	Quantulus 1220	Ultima Gold LLT	8	12	500	1.35	
43	LSC	yes	NIST	SRM 4927F	4500d	n.a.	Quantulus 12220	Ultima Gold LLT	8	12	500	1.54	0.09
44	LSC	yes	NIST	SRM 4926D	12.43y	70	TRICARB 2770TR/SL	Ultima Gold	10	12	300	1.4	0.7
45	LSC	yes	CERCA LEA	E2 LHA	12.32	25	TRICARB 2900 TR	Ultima Gold LLT	8	12	600	3.6	0.8
47	LSC	yes	NIST	SRM 3947F	4500d	26	Quantulus 1220	HSIFE3	10	12.5	400	0.9	0.2
48	LSC	yes	NIST	NIST standard	12.32y	18	Quantulus 1220	Optiphase TriSafe	8	12	500	2.37	0.8
49	LSC	yes	QSA Global		12.312y	n.a.	TRICARB ultra low level	Ultima Gold LLT	10	10	1000	0.81	3.5
50	LSC	yes	Wallac	H-3 for organic	12.32y	n.a.	Packard 2900 TR low level	Ultima Gold LLT	9	10	500	2	0.25
51	LSC	yes	PTB	PTB-6.11.4683	4500d	13-15	TriCarb 3170, 2770,2550	Ultima Gold LLT	10	10	400	2	1.3
52	LSC	yes	Spec-Chec	SRM 4926E	4500d	15	Quantulus 1220	Optiphase Hisafe III	8	12	20	1.12	2.5
53	LSC	yes	NIST	SRM 4962E	12.32y	60	TRICARB 3170 TR/SL	Ultima Gold	5	15	1000	0.2	0.1
54	LSC	yes	NIST	4361C	4500	2005-06-11	LKB Quantulus/ALOKA LE	Ultima Gold LLT	9/70	13.5/70	900-1200	0.7/4.2	0.3/0.1
55	LSC	yes	NIST	4361C	12.38y	n.a.	Quantulus 1220	Ultima Gold LLT	10	12	750	0.55	9
56	LSC	yes	CMI	ER 25	4530.37d	9.13	TRICARB 3170 TR/SL	Ultima Gold	9	11	2800	1.6-2	1TU
57	LSC	yes	CEA	internal "RT"	12.32y	11	TRI-CARB 2250 CA	Instagel Plus / Pico	6//10	14//10	50	12.72	1TU/10TU
58	LSC	yes	NIST	SRM 4427F	4500d	19	TRICARB 3100 TR	Ultima Gold	10	12	303	1.8	2
61	3He-T		NIST	SRM 4361C, M	4500d	n.a.					1-3 months		
62	GAS	yes	IAEA	IAEA	12.32y		Gas proportional counter	Methane			3000	0.22	0.05
63	LSC	yes	PerkinElmer	Tritiated Water	12.32y	15	TRI CARB 2250CA TR	Ultima Gold LLT	10	12	480	1.6	1
64	LSC	yes		Tritium etalon s	4500d	20.7	Quantulus 1220	Hisafe 3	10	12	400	0.96	0.07
65	LSC	yes											
66	GAS	yes	NIST	SRM 4926E	12.32 years	60%	Gas proportional counter	hydrogen plus propane			1000	0.4	0.09 TU
67	LSC	yes	AEA Technol	TRY44	.33+/-0.02years		Quantulus 1220 (without c	Ultima Gold LLT	10	10	1200	0.69	3
70	LSC	yes	IAEA	IAEA	12.32y		ALOKA 3	QuickSafe Zinsser	70	70	1500	1.8	0.51
75	LSC	yes	NIST	SRM 4926E	4500	20	Tri Carb 3170/SL	Ultima Gold	10	10	1000	1.12	0.6
76	LSC	yes	NIST	SRM4927F	4500 d	28	Quantulus 1220	Quicksafe	10	12.5	460	1	

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APPENDIX F: RESULT REPORTING AND EVALUATION FORMS

In the following 6 pages, the forms used for data reporting and for individual laboratory evaluation are listed, taking as example data for laboratory ID 10 (IAEA).

The data “Reporting Form” consists of 2 pages. A similar form was created after final submission of data by the web application for each laboratory.

The “Individual Evaluation Report” consists of 4 pages. Again as example the report for laboratory ID 10 is attached. The respective report for each individual laboratory was accessible from the TRIC2008 webpage after the end of the deadline, from 1 April 2009 onwards. In this report, the data evaluation process is explained and the final rating for the laboratory measurements stated (‘acceptable’-A / ‘warning’-W / ‘non acceptable’-N).

Reporting Form F-01

IAEA Tritium Intercomparison Exercise TRIC2008

Address Information, Laboratory No. 10a

Sample requested by: Laboratory No. 10a

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Signature:

Date:

I confirm that I checked the data printed on this form.
I agree, that this data will be used for the proficiency test evaluation.

Reporting Form F-02

IAEA Tritium Intercomparison Exercise TRIC2008

Data Sheet, Laboratory No. 10a

*Reference date: 01 December 2008

Table of Results

Sample	Tritium Activity (*) [TRU]	Unc (**) (one sigma)
T14	1.91	0.36
T15	4.30	0.41
T16	8.18	0.65
T17	14.10	0.88
T18	0.50	0.29
T19	564.8	4.2

** Standard uncertainty [$\pm 1s$] is expressed as ...

Individual Evaluation Report
for
Laboratory No. 10a

Your personal customer number: 0

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*Atoms for Peace: The First Half Century
1957-2007*

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DISCLAIMER:

This report has been generated automatically and is for your personal information only. The official results of the proficiency test will be published in the final report. If you believe, that any information provided on this form might be incorrect please contact us as soon as possible.

The TRIC-2008 Proficiency test

Evaluation Criterias

Based on more than 40 years experience with open world-wide laboratory intercomparison studies, it was decided to use a modified u-score evaluation, where the trueness and precision of participants' results are evaluated separately.

For trueness evaluation the participants' results are assigned 'Acceptable' if:

$$A1 \leq A2$$

where

$$A1 = |Value_{IAEA} - Value_{Lab}|$$
$$A2 = 2.58 \times \sqrt{Unc_{IAEA}^2 + Unc_{Lab}^2}$$

For evaluation of precision estimator P is calculated for each participant, according to the following formula:

$$P = \sqrt{\left(\frac{Unc_{IAEA}}{Value_{IAEA}}\right)^2 + \left(\frac{Unc_{Lab}}{Value_{Lab}}\right)^2} \times 100 \quad [\%]$$

P directly depends on the measurement uncertainty claimed by the participant. The acceptance limit for precision (LAP) for each analyte respectively is defined in Tables 1 - 3 including any adjustment due to the concentration or activity level of the analytes concerned and the complexity of the analytical problem. Participants' results are scored as 'Acceptable' for precision when (P < LAP) or (P = LAP).

In the final evaluation, both scores for trueness and precision are combined. A result must obtain 'Acceptable' score in both criteria to be assigned final score 'Acceptable'. Obviously, if a score 'Not Acceptable' was obtained for both, trueness and precision, the final score will also be 'Not Acceptable'. In cases where either precision or trueness is 'Not Acceptable', further check is applied. The value of the relative bias (RB) is compared with the maximum acceptable bias (MAB), which is defined by the IAEA in advance, similarly as LAP. If (RB < MAB) or (RB = MAB), the final score will be 'Warning'. If RB > MAB, the result will be 'Not Acceptable'. 'Warning' will reflect mainly two situations. The first situation will be a biased result with small measurement uncertainty, however still within MAB. The second situation will appear when result close to the assigned property value will be reported, but the associated uncertainty is large.

References:

- 1.) Guide to the Expression of Uncertainty in Measurement, International Organization for Standardization, Geneva, 1995.
- 2.) Quantifying Uncertainty in Nuclear Analytical Measurements, TECDOC-1401, International Atomic Energy Agency, Vienna, 2004.
- 3.) C. J. Brookes, I. G. Betteley, and S. M. Loxton, Fundamentals of Mathematics and Statistics, Wiley, UK, 1979.
- 4.) ISO 5725 (E), 'Accuracy (trueness and precision) of Measurement Methods and Results', International Organization for Standardization, Geneva, 1994.

The TRIC-2008 Proficiency test

Acceptance Limits

Please find below in the tables the acceptance limits for LAP (%) and MAB (%) in relation to the matrix and the analyte that have been used for the evaluation.

Parameter Table

Sample	LAP(%)	MAB(%)
T14	130	130
T15	50	50
T16	25	25
T17	18	18
T18	300	300
T19	5	5

Example

The TRIC-2008 Proficiency test

Laboratory No. 10a, Results submitted on 2009-03-25

2009-04-29

Individual Evaluation

Reference Date: 01 December 2008

Sample	IAEA Value [TRU]	IAEA Unc [1sigma]	Lab Value [TRU]	Lab Unc [1sigma]	Lab Unc %	Rel. Bias %	z-Score	u-Test	Ratio Lab/IAEA	A1	A2	Trueness	P(%)	Precision	Final Score
T14	1.54	0.05	1.91	0.36	18.85	24.03	0.18	1.02	1.24	0.37	0.94	A	19.13	A	A
T15	4.07	0.05	4.30	0.41	9.53	5.65	0.11	0.56	1.06	0.23	1.07	A	9.61	A	A
T16	7.74	0.06	8.18	0.65	7.95	5.68	0.23	0.67	1.06	0.44	1.68	A	7.98	A	A
T17	14.46	0.08	14.10	0.88	6.24	-2.49	-0.14	-0.41	0.98	0.36	2.28	A	6.27	A	A
T18	0.67	0.05	0.50	0.29	58.00	-25.37	-0.08	-0.58	0.75	0.17	0.76	A	58.48	A	A
T19	568.7	2.3	564.8	4.2	0.74	-0.69	-0.14	-0.81	0.99	3.90	12.35	A	0.85	A	A

Example