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Statistical evaluation of the detection limit and reproducibility of tritium activity measurements in the USGS, Denver YMP Laboratory between 1995 and 1999 (Liquid Scintillation Spectrometry Method)

The detection limit and reproducibility of tritium analyses by low-energy beta-counting technique using liquid scintillation spectrometry in the Denver USGS YMP laboratory has been evaluated based on a simple statistical analysis of the results for a background standard ("dead water" with assumed zero tritium activity) and the replicate analyses of unknown samples. Al Yang and Gordon Rattray provided all the information for this evaluation and this supporting information is listed in DTN number GS030508312272.004 (Tables 1 and 2) and MOL.20000127.0086.

Detection limit for tritium

The detection limit of an analytical method is defined as the smallest concentration that can be reported as present in a sample with a specified level of confidence. Detection Limit (L_D) is the "true" net signal, which is *a priori* expected to lead to detection. According to Vandecasteele and Block, (1993) for "well known" background $L_D = 3.29\ S_B$ at the 95% confidence level, where S_B is the standard deviation for background analyses. A value for S_B was determined from the long-term reproducibility of background measurements based on the analysis of "dead water" with no tritium that were obtained between 01/27/95 and 03/01/99 in the USGS YMP tritium laboratory (Table 1). To convert the standard deviation of the measured counting rate for the background in counts per minute (cpm) into the tritium activity in tritium units (TU) the following conventional formula was used (Technical procedure NWM-USGS-HP-204):

$$^{3}\text{H activity (TU)} = C/[K*M*E*e^{-\lambda t}],$$

where C = average sample count rate above background (cpm), K = $7.148*10^{-4}$ dpm/g TU (conversion factor), M = mass of sample (g), E = ~ 0.25 (cpm/dpm) (counting efficiency experimentally determined from a NIST standard with known ^3H activity), $\lambda = 1.528*10^{-4}$ (day^{-1}) (tritium decay constant), and t = time elapsed between sample collection date and date counted. For typical conditions in the Denver YMP tritium lab (8 g sample mass and ~22-25% counting efficiency), 1 TU is equivalent to an observed counting rate of 0.0138 cpm.

Values for the standard deviation of background measurements varied during different data collection intervals from 1995 to 1999 (Table 1). The corresponding values for tritium activities ranged from 2.5 to 5.2 TU. Assuming that the background value is "well known", the detection limits for tritium determinations varied from 10.5 to 17.1 to 8.2 TU for the different time periods shown in Table 1. These estimates of the tritium detection limit are 2 to 4.3 times larger than the value of 4 TU reported previously by Yang et al. (1996) (TIC#231266).

Table 1. Standard deviations, background count rates, and tritium detection limits for analyses of TU determined by liquid scintillation spectrometry in the USGS, Denver YMP Tritium Laboratory between 1995 and 1999.

Period of data collection	Standard deviation of background count rates (cpm)	Standard deviation of background count rates (TU)	Tritium detection limits (TU)
01/27/95 to 02/01/97	0.044	3.2	10.5
02/26/97 to 07/14/97	0.072	5.2	17.1
07/14/97 to 03/01/99	0.035	2.5	8.2

Reproducibility of tritium analyses

Reproducibility of the tritium analyses was estimated using 29 duplicate and 6 triplicate analyses for 35 unknowns. Average tritium concentrations ranged from 0.5 to 145 TU and were measured between 10/20/93 and 10/1/97 (Table 2 in MOL.20000127.0086). The value for standard deviation (SD) was determined using the formula (Youden, 1964):

$$SD= \{\Sigma(x_i - x_{i\ mean})^2 / \Sigma(DF)\}^{1/2},$$

where i ranges from 1 to n and n is the number of samples analyzed in replicate. A number of degrees of freedom (DF) is calculated for each set of analyses (DF=1 for duplicates and 2 for triplicates). In this case, ΣDF=41 (1 DF for each of 29 duplilcates plus 2 DF for each of 6 triplicate sets). This analysis yields an SD value of 5.7 TU.

No dependence between the variability of the results and tritium concentration was found, therefore the value for 2 × 5.7 TU (11.4 TU) can be used as blanket 2σ external error for all tritium analyses. Based on the reproducibility of replicates, the estimate of the external error of tritium analysis is somewhat 30% larger than previously reported estimates for the precision of tritium analysis in the Denver laboratory of ±4 TU (1σ) based on the counting statistics alone (Yang et al., 1998) (TIC#243710), thus pointing to the presence of additional error sources (variability of the counting efficiency, changing chemical stability of the fluorescent cocktail, and others). This external error value should be quadratically added to the previously published internal error of tritium analysis and, according to the formula: $\sigma_{total} = (\sigma_{internal}^2 + \sigma_{external}^2)^{0.5}$, the final blanket 2σ error for tritium analysis in Denver YMP laboratory was about ±14 TU.

When the estimates of detection limits and reproducibility for tritium analyses described above are combined, only analyses having tritium activities greater than 22 to 31 TU can be considered to contain tritium that is detectable above analytical background at the 95% confidence level.

References

Technical procedure NWM-USGS-HP-204, Liquid Scintillation Spectrometry Method for Tritium Measurement of Water Samples, R0, p. 11, NNA.11920131.0117

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