Uncertainty Evaluation of Free Water Tritium Measurement in Biological Tissues

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Abstract

This study evaluates the measurement uncertainty for tritium in free water of biological tissue using a computational model. The GUM method is employed to assess the uncertainty components of this detection method, which primarily include: uncertainty in sample moisture content, uncertainty introduced by the net count rate of sample measurement, uncertainty in method detection efficiency calibration, and uncertainty in sample weight measurement. Calculations of each component reveal that the relative standard uncertainties associated with sample moisture content and sample weight measurement are relatively small and thus negligible. The relative uncertainty of method efficiency is predominantly influenced by the activity of the standard source added during efficiency calibration and the intrinsic uncertainty of the standard source itself. The net count rate of the sample exerts the greatest influence on the detection method uncertainty. When the sample specific activity is near background levels, the uncertainty of the detection method is predominantly contributed by the uncertainty arising from the sample net count rate.

Full Text

Uncertainty Analysis of Tissue Free Water Tritium Determination in Biological Tissue

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Abstract

This paper evaluates the measurement uncertainty of tissue free water tritium (TFWT) in biological samples through a calculation model. Using the GUM method, the uncertainty components of this detection method are identified as: uncertainty in sample moisture content, uncertainty introduced by the sample's

net count rate, uncertainty in method detection efficiency calibration, and uncertainty in sample weight measurement. Calculations of each component reveal that the relative standard uncertainties of moisture content and sample weight measurement are relatively small and can be neglected. The relative uncertainty of method efficiency is primarily influenced by the activity of the standard source added during efficiency calibration and the inherent uncertainty of the standard source itself. The most significant contributor to detection method uncertainty is the sample's net count rate. When the sample's specific activity is near background levels, the method's uncertainty is predominantly contributed by the uncertainty arising from the sample's net count rate.

Keywords: tissue free water tritium, uncertainty, uncertainty component

1. Introduction

Tritium, as the only radioactive isotope of hydrogen, exists in extremely low quantities globally and does not pose a worldwide radiological risk [**?**]. As a low-energy pure β-emitter, tritium decays with a maximum electron energy of 18.6 keV, corresponding to a maximum range of 6 m in water or biological tissue. Since human epidermis and dermis thicknesses are 20–100 m and 1–3 mm, respectively, tritium only causes radiation damage when it enters the body [**?**]. The World Health Organization (WHO) has set the annual effective dose limit for tritium at 0.1 mSv, equivalent to consuming water with a tritium activity concentration of 10,000 $Bq \cdot L^{-1}$ daily for one year [**?**].

Tritiated water is readily absorbed by biological organisms to become tissue free water tritium (TFWT)—tritium in free water not bound to other tissue molecules. Plants absorb TFWT through two primary pathways: foliar absorption from air and root uptake from soil. Animals and humans mainly intake tritium through ingestion or inhalation. Tritium exchanges rapidly in the human body; after absorption, 90% of tritiated water is excreted within tritium's 10-day biological half-life, while the remaining 10% combines to form organically bound tritium [**?**]. The biological half-life of organically bound tritium is approximately 30 days, with a final small fraction persisting in adipose tissue or collagen and being excreted after about 450 days [**?**].

Tritium is a common radionuclide for monitoring radioactivity levels. The conventional method for measuring tissue free water tritium in biological samples involves freeze-drying fresh biological samples, collecting the condensate, purifying it through distillation, and measuring with a liquid scintillation spectrometer [**?**]. Yang Hailan and Yan Xuan used liquid scintillation counters to measure tritium specific activity in water [**?**], while Cao Yiyao et al. filtered the condensate after freeze-drying before measuring activity with a liquid scintillation spectrometer [**?**]. Liquid scintillation spectrometry is a relative measurement method that determines sample activity concentration by measuring background and efficiency under identical conditions, which inherently yields higher uncertainty compared to non-radioactive measurements. Wang Ruijun et al. analyzed un-

certainty in water tritium monitoring [**?**], but uncertainty evaluation for tritium measurement in biological tissues remains unaddressed. This study measures the radioactivity of tissue free water in biological samples using a standard method [**?**] and evaluates the detection method's uncertainty through the GUM method [**?**].

2. Methodology

2.1 Equipment

The following equipment was used: liquid scintillation counter (Quantulus 1220), freeze dryer (Labconco FreeZone6 Plus), pipette (Eppendorf Research plus, Class I), conductivity meter (ORION STAR A325), electronic balances (Mettler-Toledo XS105DU, Class I; Mettler-Toledo XS204, Class I; Mettler-Toledo XS4002S, Class II), drying oven, and automatic distillation apparatus.

2.2 Reagents and Consumables

Reagents used included: standard tritium liquid source (118 Bq/g, uncertainty = 3.5% (k=2)) and potassium permanganate ($KMnO_4$).

2.3 Sample Preparation

Different biological samples require different pretreatment methods. Plant samples (leaves, fruits, roots, and shoots) contain 30%–98% water by fresh weight. Edible portions were wiped to remove surface moisture, cut into small pieces to increase surface area and accelerate free water sublimation. Animal tissues contain 60%–80% free water; edible portions were similarly cut to enhance sublimation. Leafy plant samples and milk samples must be pre-frozen before freeze-drying. Other samples not immediately processed should be sealed and frozen [**?**].

This study used commercially available cabbage samples. Surface moisture and debris were removed with a dry cloth. Samples were weighed using the gravimetric method until constant weight was achieved, indicating complete freeze-drying, and the condensate was collected [**?**]. The condensate was placed in a distillation flask with a small amount of $KMnO_4$ and distilled using an automatic distiller. The first 30 mL fraction was discarded, and distillation continued. Throughout the process, $KMnO_4$ was ensured not to fully decompose, maintaining a purple color in the water sample. If the sample turned brown, additional $KMnO_4$ was added to restore the purple color. The conductivity of the distilled water was measured; if conductivity exceeded 10 m/cm, distillation with $KMnO_4$ was repeated until conductivity fell below 10 m/cm [**?**].

2.4 Sample Measurement

Approximately 8 g of distilled water was mixed with 12 mL of scintillation cocktail, shaken, dark-adapted for 12 h, and measured for 1440 min. The quench indicator parameter was measured and compared with those from background and efficiency calibration measurements. If the difference was significant, the sample was re-purified until the quench index closely matched that of background and efficiency calibrations [**?**]. Activity concentration was calculated from the net count rate.

2.5 Result Calculation

Beta rays emitted by tritium in the water sample are absorbed by the scintillation cocktail solvent and transferred to scintillator molecules. The visible photons emitted during scintillator de-excitation are detected by the liquid scintillation spectrometer's photomultiplier tubes, yielding tritium counts. After background and detection efficiency corrections, the sample's tritium activity is determined [**?**]. The measurement result is calculated as follows:

where A is the specific activity of tissue free water tritium in the biological sample, Bq/(kg · fresh); μ is the moisture content of tissue free water tritium in the biological sample, %; n_j is the net count rate of the sample, cpm; 60 is the conversion factor from minutes to seconds; E is the instrument detection efficiency; m_y is the weight of the measured sample, g; and 1000 is the conversion factor from g to kg.

3. Uncertainty Component Analysis and Evaluation

Using the GUM method to evaluate the detection method's uncertainty [**?**], the relative uncertainty u_r sources are identified from the mathematical model (1) as: uncertainty in moisture content $u_r(\mu)$, uncertainty introduced by net count rate $u_r(n)$, uncertainty in instrument detection efficiency $u_r(E)$, and uncertainty in sample weight measurement $u_r(m_y)$. The relative standard uncertainty is given by:

3.1 Uncertainty in Moisture Content $u_r(\mu)$

The moisture content is calculated as:

where W_{fresh} is the fresh sample weight, g; and W_{dry} is the dry sample weight, g.

From mathematical model (3), the relative uncertainty in moisture content $u_r(\mu)$ originates from the relative uncertainty in fresh weight measurement $u_r(W_{\text{fresh}})$ and dry weight measurement $u_r(W_{\text{dry}})$. These uncertainties derive from balance uncertainty and stability during weighing. Both fresh and dry samples were weighed using the subtraction method: the sample bag was tared on

the electronic balance before adding the sample. Each weighing was an independent test. According to uncertainty evaluation guidelines, calibration certificate data belongs to Type B evaluation information sources [**?**].

The balance calibration certificate indicates that for fresh sample weighing in the range 500 g < m ≤ 2000 g, the tare weighing error is $±$0.1 g. Assuming a rectangular distribution with coverage factor $\sqrt{3}$, the balance's standard uncertainty for fresh sample weighing is $u(W_{\text{fresh}}) = 0.058$ g, with relative standard uncertainty $u_r(W_{\text{fresh}}) = 0.01\%$.

For dry sample weighing in the range 0 g < m ≤ 500 g, the tare weighing error is $±$0.05 g. With a rectangular distribution and coverage factor $\sqrt{3}$, the balance's standard uncertainty for dry sample weighing is $u(W_{\text{dry}}) = 0.029$ g, with relative standard uncertainty $u_r(W_{\text{dry}}) = 0.06\%$.

After 10 weighings of both fresh and dry samples, the repeatability error was at the 10^{-6} level for fresh samples and 10^{-5} level for dry samples, which can be neglected. Since $u_r(W_{\text{fresh}})$ and $u_r(W_{\text{dry}})$ are uncorrelated:

Thus, the uncertainty in moisture content measurement primarily originates from dry sample weighing uncertainty.

3.2 Relative Standard Uncertainty of Sample Net Count Rate $u_r(n)$

The sample net count rate n_j is obtained by subtracting the background count rate n_b from the sample count rate n_s, i.e., $n_j = n_s - n_b$. The count rate n is the ratio of statistical counts N to measurement time t: $n = N/t$, where N_s is the sample count; N_b is the background count; t_s is the sample measurement time, min; and t_b is the background measurement time, min.

From calculation model (4), the net count rate uncertainty $u(n_j)$ primarily derives from uncertainties in sample count, background count, and measurement time. Current instrument time control precision reaches 10^{-4} s, with single sample measurement time of 86,400 s, yielding a relative uncertainty from measurement time of less than 10^{-8}, which is negligible. Therefore, only uncertainties in N_s and N_b need be considered.

Thus:

Radioactive decay follows Poisson distribution, i.e., $u(N) = \sqrt{N}$. Using commercially available cabbage samples with tritium content at background level, measurement with the liquid scintillation spectrometer yields a relative standard uncertainty of the sample net count rate $u_r(n_j) = 30.07\%$.

As shown by the $u_r(n_j)$ calculation formula, when sample and background measurement times are equal, higher sample count rates yield smaller $u_r(n_j)$ values. For cabbage samples at background level, the uncertainty contributed by net count rate reaches 30%.

3.3 Relative Standard Uncertainty of Detection Efficiency $u_r(E)$

The detection efficiency is measured by accurately weighing a standard tritium source, adding background water to approximately 8 g and 12 mL scintillation cocktail, measuring with a low-background scintillation counter, and calculating instrument detection efficiency:

where n_E is the standard source net count rate, cpm; C is the specific activity of the added standard source on the calibration date, Bq/g; e is 2.718; $T_{1/2}$ is the tritium half-life; t is the time interval from source calibration to measurement date, years; m is the mass of added standard source, g; and 60 is the unit correction constant.

From calculation model (7) [**?**], the relative standard uncertainty of detection efficiency $u_r(E)$ originates from: standard source net count rate uncertainty $u_r(n_E)$, half-life uncertainty $u_r(T_{1/2})$, standard source uncertainty $u_r(C)$, and balance weighing uncertainty $u_r(m)$. The relative standard uncertainty of detection efficiency is:

3.3.1 Relative Standard Uncertainty of Standard Source Net Count Rate $u_r(n_E)$ The standard source net count rate n_E is obtained by subtracting background count rate n_b from the standard source count rate n_y, i.e., $n_E = n_y - n_b$. The count rate n is the ratio of statistical counts N to time t: $n = N/t$, where N_y is the standard source count; N_b is the background count; t_y is the standard source measurement time, min; and t_b is the background measurement time, min.

From calculation model (9), the net count rate uncertainty $u(n_E)$ primarily derives from standard source count, background count, and measurement time uncertainties. Current instrument time control precision reaches 10^{-4} s, with background measurement time of 86,400 s and standard source measurement time of 1,800 s, yielding relative uncertainty from measurement time of less than 10^{-7}, which is negligible. Therefore, only uncertainties in N_y and N_b need be considered.

Thus:

Radioactive decay follows Poisson distribution, i.e., $u(N) = \sqrt{N}$. After standard source measurement, the relative standard uncertainty of the standard source net count rate is calculated as $u_r(n_E) = 3.37\%$.

This demonstrates that higher count rates in efficiency calibration samples yield smaller $u_r(n_E)$ values; thus, greater tritium activity added to efficiency calibration samples reduces $u_r(n_E)$.

3.3.2 Relative Standard Uncertainty of Standard Source Half-Life $u_r(T_{1/2})$ Consulting the tritium decay scheme [**?**], the half-life uncertainty is $u(T_{1/2}) = 0.001$ year. Assuming a rectangular distribution, the relative standard uncertainty of the half-life is:

Based on the calibration date from the standard source certificate and the efficiency calibration date, $t = 3.65$ years.

3.3.3 Relative Standard Uncertainty of Standard Source $u_r(C)$ The standard source certificate indicates an expanded relative uncertainty $U_{\text{rel}}(k = 2) = 3.5\%$. Thus, the relative standard uncertainty of the standard source is $u_r(C) = 1.75\%$.

3.3.4 Relative Standard Uncertainty of Standard Source Weighing $u_r(m)$ The standard source weight was measured using the subtraction method: the vial was tared on the electronic balance before adding the source. The balance calibration certificate indicates that for weighing range 0 g $\leq$ m $\leq$ 41 g, the maximum permissible error is \$±\$0.5 mg. Assuming a rectangular distribution with coverage factor $\sqrt{3}$, the balance indication error standard uncertainty is $u(m) = 0.00029$ g. Single weighing was used for the standard source, and repeatability error was negligible as previously established. Therefore, the relative standard uncertainty of standard source weighing is $u_r(m) = 0.43\%$.

3.3.5 Relative Standard Uncertainty of Detection Efficiency $u_r(E)$ The relative standard uncertainty of detection efficiency is $u_r(E) = 3.82\%$.

3.4 Relative Standard Uncertainty of Sample Weight Measurement $u_r(m_y)$

The relative uncertainty in sample weight measurement derives from balance uncertainty and stability. The subtraction method was used: the vial was tared on the electronic balance before adding the sample. Each weighing was an independent test. According to uncertainty evaluation guidelines, calibration certificate data belongs to Type B evaluation information sources.

The balance calibration certificate indicates that for fresh sample weighing in range 0 g < m $\leq$ 50 g, the tare weighing error is \$±\$0.5 mg. Assuming a rectangular distribution with coverage factor $\sqrt{3}$, the balance's standard uncertainty for fresh sample weighing is $u(m_y) = 0.00029$ g, with relative standard uncertainty $u_r(m_y) = 0.005\%$.

4. Synthetic Uncertainty

The uncertainty components and results for tissue free water tritium measurement in cabbage samples are summarized below.

Table 1 Uncertainty components and results for tissue free water tritium measurement in cabbage samples

Uncertainty Source	Relative Standard Uncertainty
Moisture content measurement $u_r(\mu)$	0.06%
Sample net count rate $u_r(n_j)$	30.07%
Detection efficiency measurement $u_r(E)$	3.82%
Sample weight measurement $u_r(m_y)$	0.005%

Based on the table, the relative combined standard uncertainty for tissue free water tritium measurement in cabbage samples is $u_{c,r} = 30.31\%$. With coverage factor $k = 2$, the confidence interval probability is 95%, giving a relative expanded uncertainty $U_r = 60.62\%$ ($k = 2$).

5. Conclusion

The GUM method evaluation identifies the main uncertainty components of this detection method as: sample moisture content uncertainty, sample measurement net count rate uncertainty, method detection efficiency uncertainty, and sample weight measurement uncertainty. Calculations show that when using a balance for sample weighing, the relative standard uncertainties of moisture content and sample weight are relatively small and can be neglected in combined uncertainty calculations. The relative standard uncertainty of method detection efficiency depends on the amount of standard source added and its inherent uncertainty; higher added standard source activity yields smaller relative standard uncertainty, with the detection efficiency relative standard uncertainty being 3.82%. For samples with specific activity at background level, the standard uncertainty contributed by sample net count rate reaches 30.07%. The combined detection method uncertainty is 30.31%, demonstrating that the detection method uncertainty is primarily dominated by sample net count rate uncertainty.

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Note: Figure translations are in progress. See original paper for figures.