

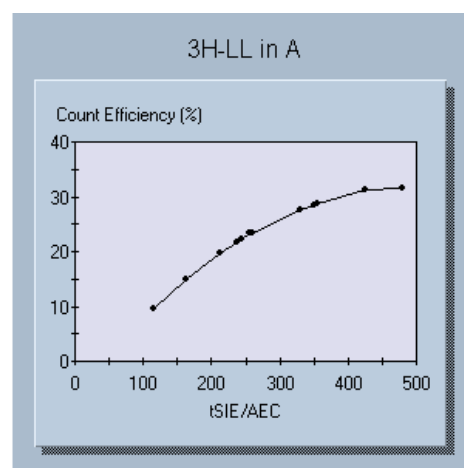
Investigation of Uncertainty Sources in the Determination of Beta Emitting Tritium in the UAL

A. Specification

A liquid scintillation counter (LSC) is used to determine the activity concentration in Bq/dm^3 of the beta emitting tritium in urine samples.

Measurement procedure

For the LSC measurement a quench curve is needed. To measure the quench curve the absorption of 99 urine samples and water had been measured with a spectral photometer. From these results 13 had been selected to represent the whole absorption spectrum from 0.025 for water up to 1.44 for a very dark coloured urine sample. From each sample 2mL had been taken into a low diffusion plastic vial and spiked with H-3 with 10000DPM activity. 14mL scintillation cocktail had been added to the vial.



The measure consists of the following stages:

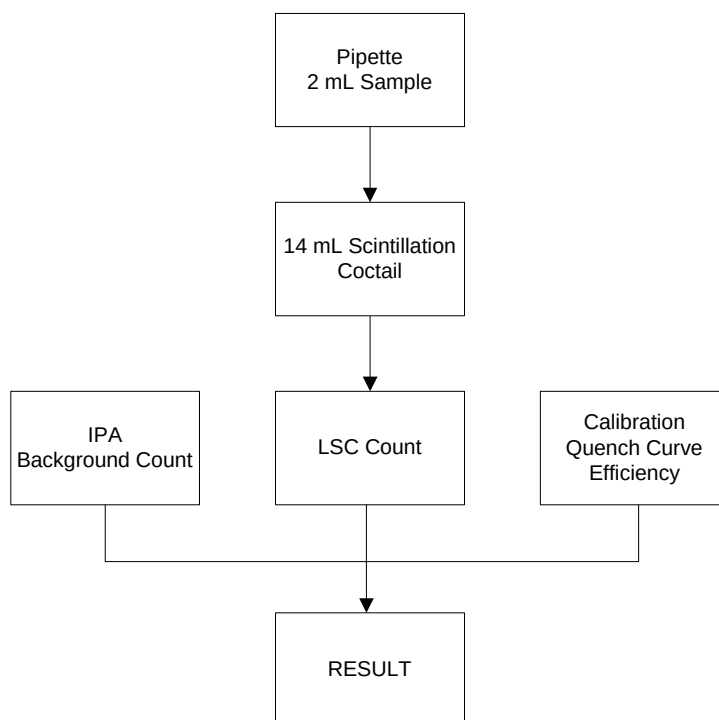


Figure 1: H-3 Measurement

Calculation

The measurand is the H-3 activity concentration in Bq/L, based on the energy region of 0-18.6 keV, is given by:

$$A = \frac{C}{60 \cdot \varepsilon \cdot V_a \cdot 0.01 \cdot R_{av} \cdot K} \text{ [Bq/L]}$$

Where:

- A = the current remaining activity, [Bq/L]
C = the Counts Rate in the region for tritium, [cpm]
 ε = the Interpolated Counting Efficiency
 V_a = the Aliquot Volume, [L]
 R_{av} = the Mean Recovery Factor, [%]
K = the Decay Correction Factor: $K = e^{-\frac{\ln 2}{T_{1/2}} \cdot t_e}$
 t_e = the Elapsed time from the sampling date to the measuring date, [years]
 $T_{1/2}$ = the Half Life of Tritium, [years]

The factor of 60 is used to convert cpm to cps to obtain activity in Bq.

Efficiency is the ratio of measured counts to the number of decay events, which occur during a measurement interval. The counting efficiencies are determined by using efficiency curves (quench curve)

Identifying and Analysing Uncertainty Sources

The estimation of uncertainties contains the following steps:

- Exploration of all factors influencing the measurement,
- Quantification of the uncertainties connected to each factors by measurement results or by expert judgment if applicable,
- Estimation of the overall uncertainty of the measurement.

Uncertainty Sources

- Counts in the counting region for H-3
- Quench Curve – Counting Efficiency
- Sample Volume
- Recovery factor
- Measuring time (<0.1%)

- Decay correction
- Temperature

The different effects and their influences are shown as a cause and effect diagram in Figure 2.

Quantifying the uncertainty components

For collection and analysis of the counts coming from tritium the QuantaSmart software is used.

Net Counts

Determined by the evaluation software

Background correction

$$C_{Net} = C_{gross} - C_{background}$$

where:

- C_{net} = the Net Counts Rate for the counting region of H-3, [cpm]
- C_{gross} = the Gross sum of the Sample Counts rate within the counting region of H-3, [cpm]
- $C_{background}$ = the Background Counts Rate for the counting region of H-3, [cpm]

The evaluation software reports **2 Sigma % (%2s)** parameter. This value represents the percent of uncertainty in a gross count value (with 95% confidence limits). It is calculated as:

$$\%2s = \frac{200}{\sqrt{C_{gross} \cdot t}}$$

Where:

t = Measuring time in minutes

Aliquot Volume

A 2 ml aliquot is taken with a pipette for the Tritium analysis.

The volume is subject to three major sources of uncertainty:

- The uncertainty in the certified adjustable pipette.
- Repeatability of the adjusted pipette
- The actual temperature differs from the temperature at which the volume of the pipette was calibrated

Calibration: The manufacturer quotes an inaccuracy for 2.5mL of 1.2%. A rectangular distribution is assumed.

$$\frac{1.2\%}{\sqrt{3}} = 0.70\%$$

Repeatability: The uncertainty due to the variations of filling was estimated from a series of ten fill and weight experiment and gave a standard uncertainty of **0.2%**, which is very similar to the value given by the manufacturer.

Temperature: According to the manufacturer the volumetric pipette had been calibrated at temperature range of 20 - 25 °C. As the temperature of the laboratory is within this range, the uncertainty from this effect can be omitted.

The contributions are combined to the standard uncertainty $u(V)$ as:

$$u(V) = \sqrt{0.7^2 + 0.2^2} = 0.73\%$$

Quench Curve - Efficiency

Quench due to colour of the sample

For the Quench calibration 13 urine samples were used and spiked with a known activity of Tritium. According to the certificate of the reference solution the overall uncertainty for the activity concentration is 2.5% at the 99.7% confidence level. It means that the standard uncertainty is $2.5\%/3 = \mathbf{0.83\%}$.

The activity in the Quench set is obtained as:

$$A_{spike} = K \cdot C_{A,reference} \cdot m$$

Where:

A_{spike}	=	the Current Activity in the Quench set, [dpm]
$C_{A,reference}$	=	the Activity-concentration of the reference solution, [dpm/g]
K	=	the Decay Correction Factor: $K = e^{-\frac{\ln 2}{T_{1/2}} \cdot t_e}$
t_e	=	the Elapsed time from the reference date to the measuring date, [years]
$T_{1/2}$	=	the Half Life of Tritium, [years]
m	=	the Mass taken from the reference solution in g

The uncertainty for the activity in the Quench set is:

$$u(A_{spike}) = A_{spike} \cdot \sqrt{\left(\frac{u(C_{A,reference})}{C_{A,reference}}\right)^2 + \left(\frac{u(m)}{m}\right)^2 + \left(\frac{u(K)}{K}\right)^2}$$

The manufacturer identifies three uncertainty sources for the tare weighing:

- The repeatability
- The readability (digital resolution) of the balance scale
- The contribution due to the uncertainty in the calibration function of the scale (linearity and sensitivity).

Model equation: $m = m_{rep} + m_{lin} + m_{read}$ [g]

The uncertainty associated with the mass of the solutions is estimated using data from the manufacturer's recommendations for the analytical balance model BP221S.

Repeatability: the standard deviation is quoted as ± 0.0001 g. Normal distribution.

Readability : the digital resolution of the balance is 0.0001 g. A rectangular distribution is assumed:

$$\frac{0.0001g}{\sqrt{3}} = 5.77E-05g$$

Linearity : the difference from the actual weigh on the scale pan and the reading of the scale is within the limits of ± 0.0002 g. A rectangular distribution is assumed.

$$\frac{0.0002g}{\sqrt{3}} = 1.15E-04g$$

These components have to be taken into account twice because of the weight by difference.

The three components are combined to give the standard uncertainty $u(m)$.

$$u(m) = \sqrt{0.0001^2 + 2 \cdot (5.77E-05^2) + 2 \cdot (1.15E-04^2)} = 2.08E-04g$$

$$\frac{u(K)}{K} = \frac{\ln(2) \cdot t_e}{(T_{1/2})^2} \cdot u(T_{1/2})$$

$$u(A_{spike}) = 8749dpm \cdot \sqrt{\left(\frac{2.44E+05}{2.93E+07}\right)^2 + \left(\frac{2.08E-04}{5.00E-02}\right)^2 + 2.15E-03^2} = 83.58dpm$$

Therefore the relative standard uncertainty for the activity in the quench set is **0.95%**

The count efficiency for the Quench set is calculated as:

$$\varepsilon_i = \frac{C_i}{A_{spike}} \cdot 100$$

Where:

ε_i = the Count Efficiency for the i^{th} vial, [%]
 A_{spike} = the Activity in the Quench set, [dpm]
 C_i = the Counts Rate in the region for tritium for the i^{th} vial, [cpm]

$$u(\varepsilon_i) = \varepsilon_i \cdot \sqrt{\left(\frac{u(C_i)}{C_i}\right)^2 + \left(\frac{u(A_{spike})}{A_{spike}}\right)^2}$$

QIP	Current Activity, [dpm] @ 2000-12-15		u(K)/K @ 2000-12-15	Counts Rate, [cpm]		Counting Efficiency %	
	Value	Unc.		Value	Unc.	Value	Unc.
116.34	8749	± 83.58	2.15E-03	846.95	± 5.31	9.64	± 0.110
162.75	8749	± 83.58	2.15E-03	1301.94	± 6.59	14.84	± 0.160
162.79	8749	± 83.58	2.15E-03	1312.27	± 6.61	14.96	± 0.162
212.79	8749	± 83.58	2.15E-03	1734.64	± 7.60	19.79	± 0.208
236.54	8749	± 83.58	2.15E-03	1903.04	± 7.96	21.71	± 0.226
244.71	8749	± 83.58	2.15E-03	1958.94	± 8.08	22.35	± 0.233
256.69	8749	± 83.58	2.15E-03	2040.82	± 8.25	23.32	± 0.242
259.24	8749	± 83.58	2.15E-03	2043.77	± 8.25	23.29	± 0.242
331.25	8749	± 83.58	2.15E-03	2407.37	± 8.96	27.47	± 0.282
351.33	8749	± 83.58	2.15E-03	2504.32	± 9.14	28.58	± 0.292
355.02	8749	± 83.58	2.15E-03	2508.04	± 9.14	28.63	± 0.293
424.48	8749	± 83.58	2.15E-03	2732.27	± 9.54	31.19	± 0.317
479.59	8749	± 83.58	2.15E-03	2752.89	± 9.58	31.42	± 0.319

For the Efficiency Curve fitting there is not too much information from the software. For that reason, the ORIGIN software was used for the non-linear curve fit of the empirical data. In Excel the least square fit analysis was performed to determine the standard deviation.

Excel Least Squares fit to $A_0 + A_1 * x + A_2 * x^2 + A_3 * x^3 \dots$

- Theory = $\text{CoefA0} + \text{CoefA1} * x + \text{CoefA2} * x^2$
- Delta = Y experiment - Theory
Sum = Sum of Delta Squared
Standard Error = $\text{SQRT}(\text{Sum} / (n * (n - 1)))$

Coefficients		Experimental Data		For Least Squares		
		X	Y	Theory	Delta	Delta Squared
		116.34	9.64	9.87	-0.2328	0.0542
		162.75	14.84	15.03	-0.1929	0.0372
		162.79	14.96	15.04	-0.0771	0.0059
		212.79	19.79	19.80	-0.0114	0.0001
		236.54	21.71	21.78	-0.0659	0.0043
A0	-6.18228	244.71	22.35	22.41	-0.0622	0.0039
A1	0.15717	256.69	23.32	23.31	0.0146	0.0002
A2	-1.65E-04	259.24	23.29	23.49	-0.1994	0.0398
		331.25	27.47	27.80	-0.3312	0.1097
		351.33	28.58	28.70	-0.1189	0.0141
		355.02	28.63	28.85	-0.2194	0.0481
		424.48	31.19	30.85	0.3447	0.1188
		479.59	31.42	31.30	0.1222	0.0149

Sum = Chi Squared	Standard Unc. (Sε), [%]
0.4513	0.1939

The relative standard uncertainty for the interpolated efficiency is calculated from the combination of the uncertainty associated with the least square fit analysis and the combined uncertainty of the counting efficiency.

$$\frac{u(\varepsilon)}{\varepsilon} = \sqrt{\sum \left(\frac{u(\varepsilon_i)}{\varepsilon_i} \right)^2 + \sum \left(\frac{S\varepsilon}{\varepsilon_i} \right)^2} = \sqrt{0.001428 + 0.001352} = 0.052721$$

Therefore the relative standard uncertainty for the interpolated counting efficiency is **5.27%**

Recovery Factor

For the determination of the recovery factor four control samples are used with different activities .The records in every H-3 work list can be found and it is the following:

H-3 Act. Conc. on the 1996-03-01			
		$\lambda =$	1.55E-04 1/day
Std. I	9.79E+05	$\pm 8.16E+03$	Bq/L
Std. II	1.98E+05	$\pm 1.64E+03$	Bq/L
Std. III	1.01E+04	$\pm 8.27E+01$	Bq/L
Std. IV	1.96E+03	$\pm 1.62E+01$	Bq/L

The control samples were prepared using blank urine samples and tritium reference solution. Accuracy of the scintillator addition was observed to be **0.03%** checking the repeatability of five measurements. This uncertainty can be neglected. The recovery factor is calculated as:

$$R_i = \frac{A_i}{A_{spike,i,t}} \cdot 100;$$

$$A_i = \frac{C_i}{\varepsilon_i \cdot 0.01 \cdot V_a \cdot 60};$$

$$A_{spike,i,t} = A_{spike,i} \cdot K = A_{spike,i} \cdot e^{-\lambda \cdot t_e} = A_{spike,i} \cdot e^{-\frac{\ln 2}{T_{1/2}} \cdot t_e}$$

Where:

- R_i = Recovery Factor in % of the i^{th} Spike Control Sample
- A_i = Measured Activity Concentration in Bq/L of the i^{th} Spike Control Sample
- $A_{spike,i,t}$ = Activity Concentration in Bq/L at t elapsed time of the i^{th} Spike Control Sample
- $A_{spike,i}$ = Activity Concentration in Bq/L at reference time of the i^{th} Spike Control Sample
- K = Decay Correction Factor
- C_i = Counts Rate in CPM of the i^{th} Spike Control Sample
- ε_i = Count Efficiency for the i^{th} Spike Control Sample
- V_a = Aliquot Volume in L taken from the i^{th} Spike Control Sample

λ	=	Decay Rate in 1/years for Tritium Isotope
t_e	=	Elapsed Time in years between the Reference and Measuring Date
$T_{1/2}$	=	Half Life in years for Tritium Isotope

The uncertainty for the Recovery Factors is:

$$u(R_i) = R_i \cdot \sqrt{(0.005 \cdot \%2s)^2 + \left(\frac{u(\varepsilon_i)}{\varepsilon_i}\right)^2 + \left(\frac{u(A_{spike,i})}{A_{spike,i}}\right)^2 + \left(\frac{u(V_a)}{V_a}\right)^2 + \left(\frac{u(K)}{K}\right)^2}$$

$$\frac{u(K)}{K} = \frac{\ln(2) \cdot t}{(T_h)^2} \cdot u(T_h)$$

From the four control samples the average recovery factor is calculated as:

$$R_{av} = \frac{\sum_{i=1}^4 R_i}{4}$$

The uncertainty of the average recovery factor is calculated as:

$$u(R_{av}) = \frac{1}{4} \cdot \sqrt{\sum_{i=1}^4 u(R_i)^2}$$

With this formula in GUM Workbench we can take into account the proportional relevance of each component, rather than treating each component equally.

Environmental effects

To reduce the effect of photoluminescence and static electricity the samples are placed in the counter, which is refrigerated for two days. At this time the temperature of the samples and the counter should be the same.

Combined Standard Uncertainty

The relative standard uncertainty for the decay corrected activity concentration is calculated as:

$$\frac{u(A)}{A} = \sqrt{(0.005 \cdot \%2s)^2 + \left(\frac{u(\varepsilon)}{\varepsilon}\right)^2 + \left(\frac{u(R_{av})}{R_{av}}\right)^2 + \left(\frac{u(V)}{V}\right)^2 + \left(\frac{u(K)}{K}\right)^2}$$

For the determination of the combined standard uncertainty the GUM Workbench will be used.

File	Evaluation Software Report	Combining Relative Standard Uncertainty	GUM Workbench
20040330_1233	0.79%	6.06%	6.0%
	Attached	Table below	Attached

Quantified Uncertainty by different methods

Practical Example Intercomparison 2004 Sample C

File 20040330_1233

Reference Date 2004-03-01

Measuring date: 2004-03-30

Method	Description	Uncertainty in Percent @ 1s
Evaluation Software	Counts in the region of 0-18.6 keV	0.79
	statistical (Poisson distribution)	*
		*
	Square of combined uncertainty of the above factors	0.62
Investigated	Interpolated Counting Efficiency (includes *)	5.27
	Spiked Activity	*
	Aliquot taken	*
	Decay correction	*
	Counts (Poisson distribution)	*
	Curve Fitting	*
	Square of combined uncertainty of the above factors	27.77
	Recovery (includes *)	2.81
	Control samples average	*
	Interpolate Counting Efficiency	*
	Counts (Poisson distribution)	*
	Volume of Control aliquot	*
	Square of combined uncertainty of the above factors	7.90
	Volume of Sample aliquot	0.73
	Decay Correction	<0.1
	Square of combined uncertainty of the above factors	0.53
Expert Judgment	Luminescence and static electricity	< 0.1

The overall combined uncertainty for the activity in this example is:

$$u(A) = \sqrt{0.62 + 27.77 + 7.9 + 0.53} = 6.06\% \text{ at 1 sigma reliability}$$

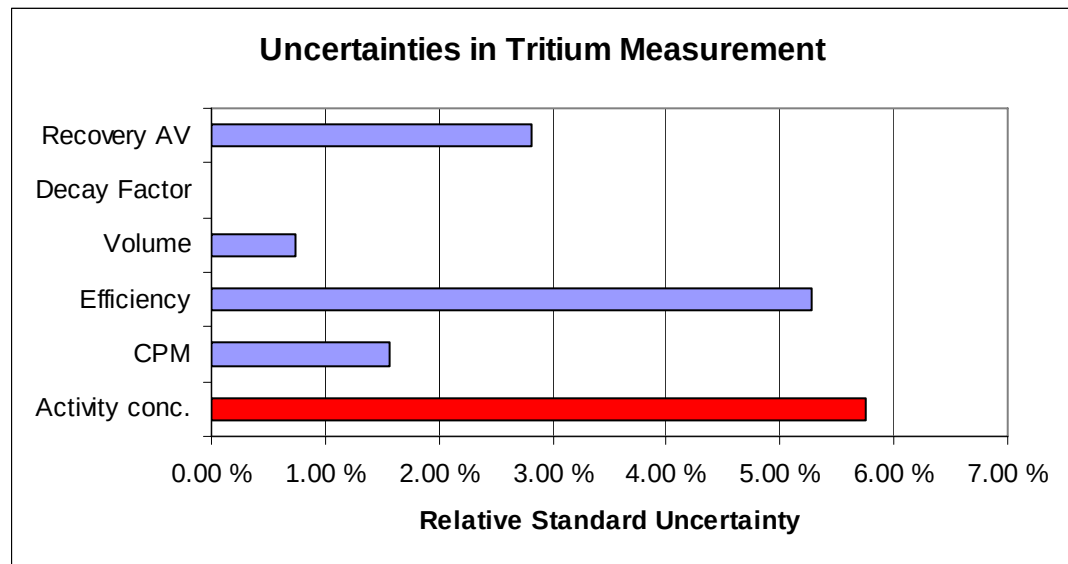
Spreadsheet calculation of tritium measurement uncertainty

Ref./Sampling Date	Measuring Date	Half Life			K	u(K)/K
1996-03-01	2004-03-30	1.24E+01	± 0.1	years	0.6371	3.99E-03
2004-03-01	2004-03-30	1.24E+01	± 0.1	years	0.9956	3.92E-05

Name: Sample C

		CPM	Efficiency	Volume	Decay Factor	Recovery I	Recovery II	Recovery III	Recovery IV	Recovery AV
	Value	1.69E+02 cpm	20.2%	2.00E-03 L	0.996	87.61%	86.75%	89.52%	84.59%	87.12%
	Relative Standard Uncertainty	1.57 %	5.27 %	0.73 %	3.92E-03 %	0.20 %	0.45 %	2.08 %	5.80 %	
	u(R_i)					5.40 %	5.40 %	5.50 %	6.13 %	2.81 %
CPM	169.00	170.33	169.00	169.00	169.00					169.00
Efficiency	20.20%	20.20%	21.26%	20.20%	20.20%					20.2%
Volume	2.00E-03	2.00E-03	2.00E-03	2.01E-03	2.00E-03					2.00E-03
Decay Factor	9.96E-01	9.96E-01	9.96E-01	9.96E-01	9.96E-01					9.96E-01
Recovery AV	87.12%	87.12%	87.12%	87.12%	87.12%					89.57%
Activity conc.	8.04E+03 Bq/L	8.10E+03	7.64E+03	7.98E+03	8.04E+03					7.82E+03
		6.31E+01	-4.02E+02	-5.83E+01	-3.15E-01					-2.20E+02
	2.14E+05	3.98E+03	1.62E+05	3.39E+03	9.93E-02					4.82E+04
u(A)	4.63E+02 Bq/L	5.76 %								

Result @ 2σ: 8.04E+03 Bq/L +/- 11.51%



This graph shows the different contributions to the measurement uncertainty of the activity concentration of H-3.

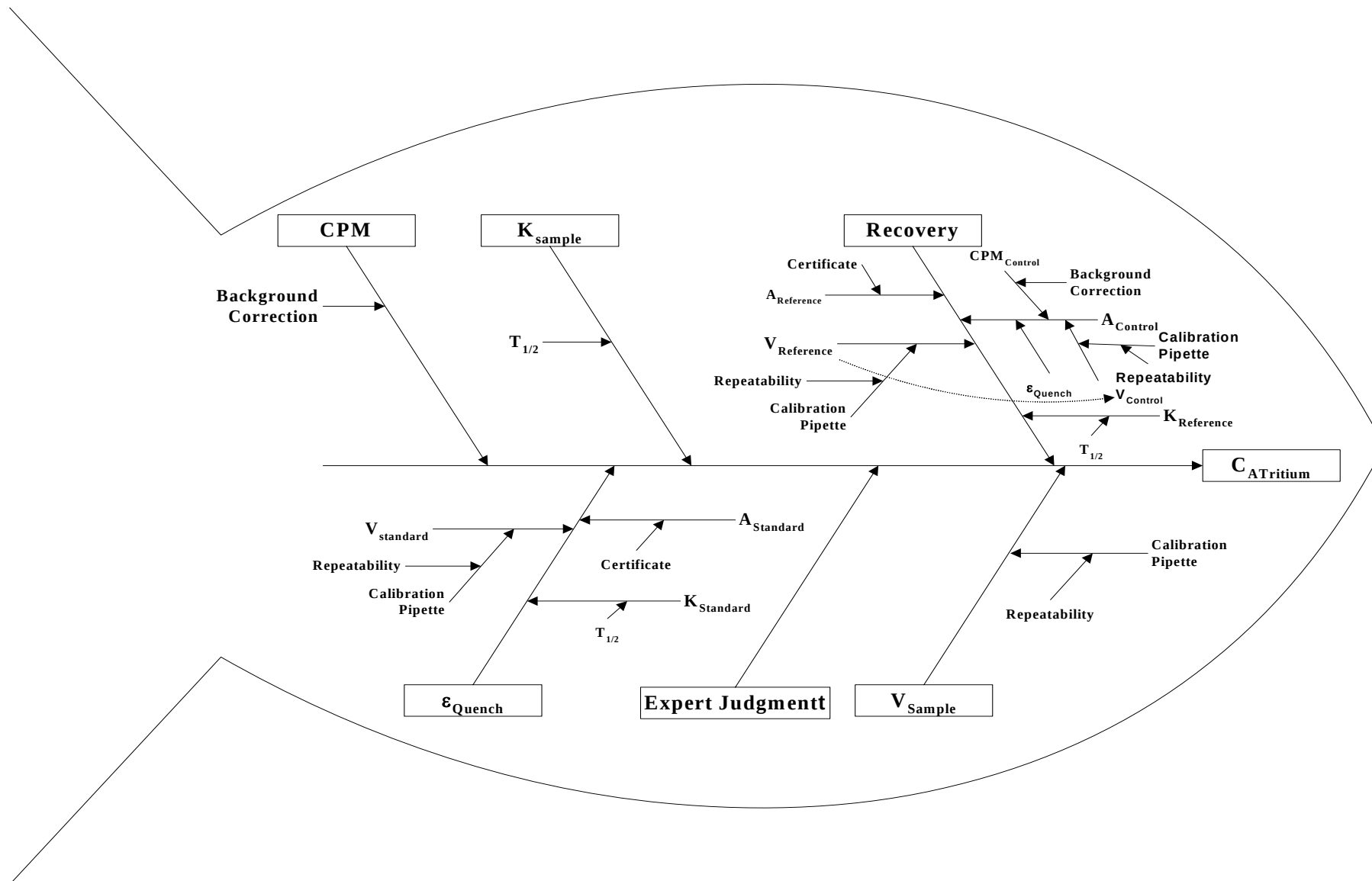


Figure 2. Cause and effect diagram: Uncertainties in Tritium measurement