Uncertainty Assessment in Liquid Scintillation Counting

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“The evaluation of uncertainty is neither a routine task nor a purely mathematical one; it depends on detailed knowledge of the nature of the measurand and of the measurement method and procedure used. The quality and utility of the uncertainty quoted for the result of a measurement therefore ultimately depends on the understanding, critical analysis, and integrity of those who contribute to the assignment of its value.”

EURACHEM/CITAC. Quantifying uncertainty in analytical measurement.
Tech. Rep. Guide CG4, EURACHEM/CITEC, 2000. Second edition.

Guide to Uncertainty in Measurement (GUM, JCGM 100:2008)

- Originally published in 1993 by ISO
- Responsibility for maintaining transferred to Joint Committee on Guides in Measurement (JCGM), chaired by the BIPM, in 1997
- JCGM 100:2008. Guide to the expression of uncertainty in measurement (GUM)
- Associated documents
  - JCGM 101:2008. Supplement 1 to the GUM: *Propagation of distributions using a Monte Carlo method*
  - JCGM 102. Supplement 2 to the GUM: *Models with any number of output quantities*
  - JCGM 103. Supplement 3 to the GUM: *Modelling* (in preparation)
  - JCGM 104. An introduction to the GUM and related documents

Premises

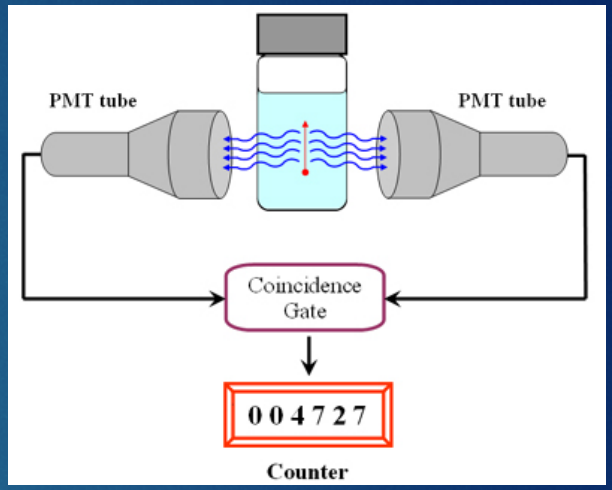
- Quality of a measurement can be characterized by considering systematic and random errors equally
  - Corrections for systematic effects also have random component
- It is impossible to determine how well the value of the measurand is known, only how well it is believed to be known
  - Requires infinite amount of information to be defined
  - Since this is impossible, some uncertainty is always present

Basic procedure

- Develop measurement model (relationship between input variables and measurand)
- Determine estimates for input values
- Evaluate standard uncertainty on input estimates
- Evaluate covariances
- Calculate result of measurement (estimate of measurand from measured inputs)
- Determine combined standard uncertainty from the uncertainties (and covariances) on input estimates
- Determine coverage factor, if needed
- Report value with its associated uncertainty, explaining how measurement result and uncertainty estimate were determined

LSC measurements of radioactivity

A counting process (photons, electrons, particles, etc.)



General measurement model

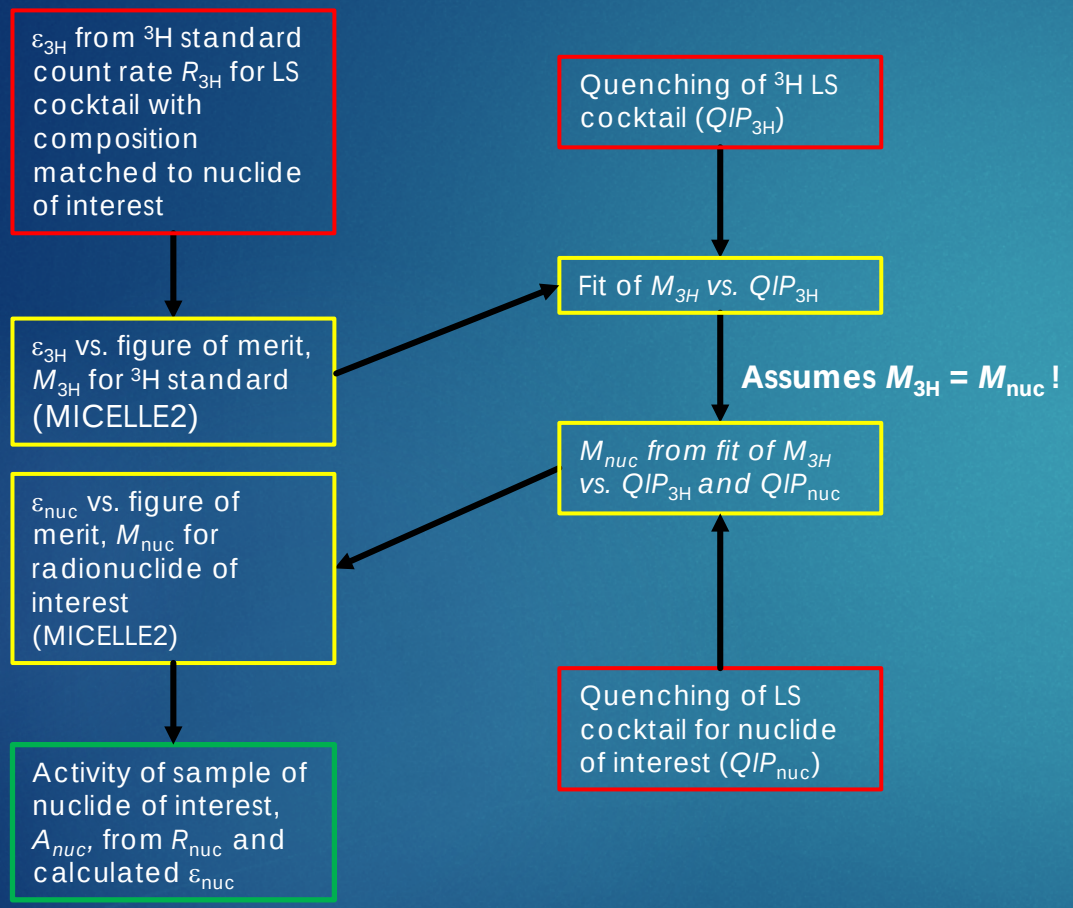
$$R(t) = C/T$$

$$= R_B + A_0\,(m/M)\,\varepsilon\,\Gamma\,f_i\,f_j\,\ldots + A_x\,\varepsilon_x\ldots..$$

Detection efficiency and correction factors

If we could count every event, our job would be easy. Most effort goes into figuring out what we are missing!

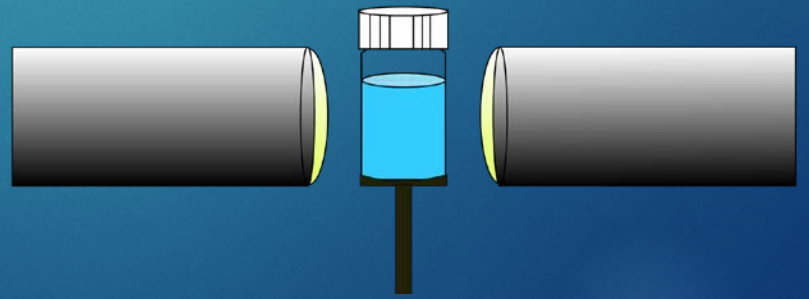
Developing a measurement model



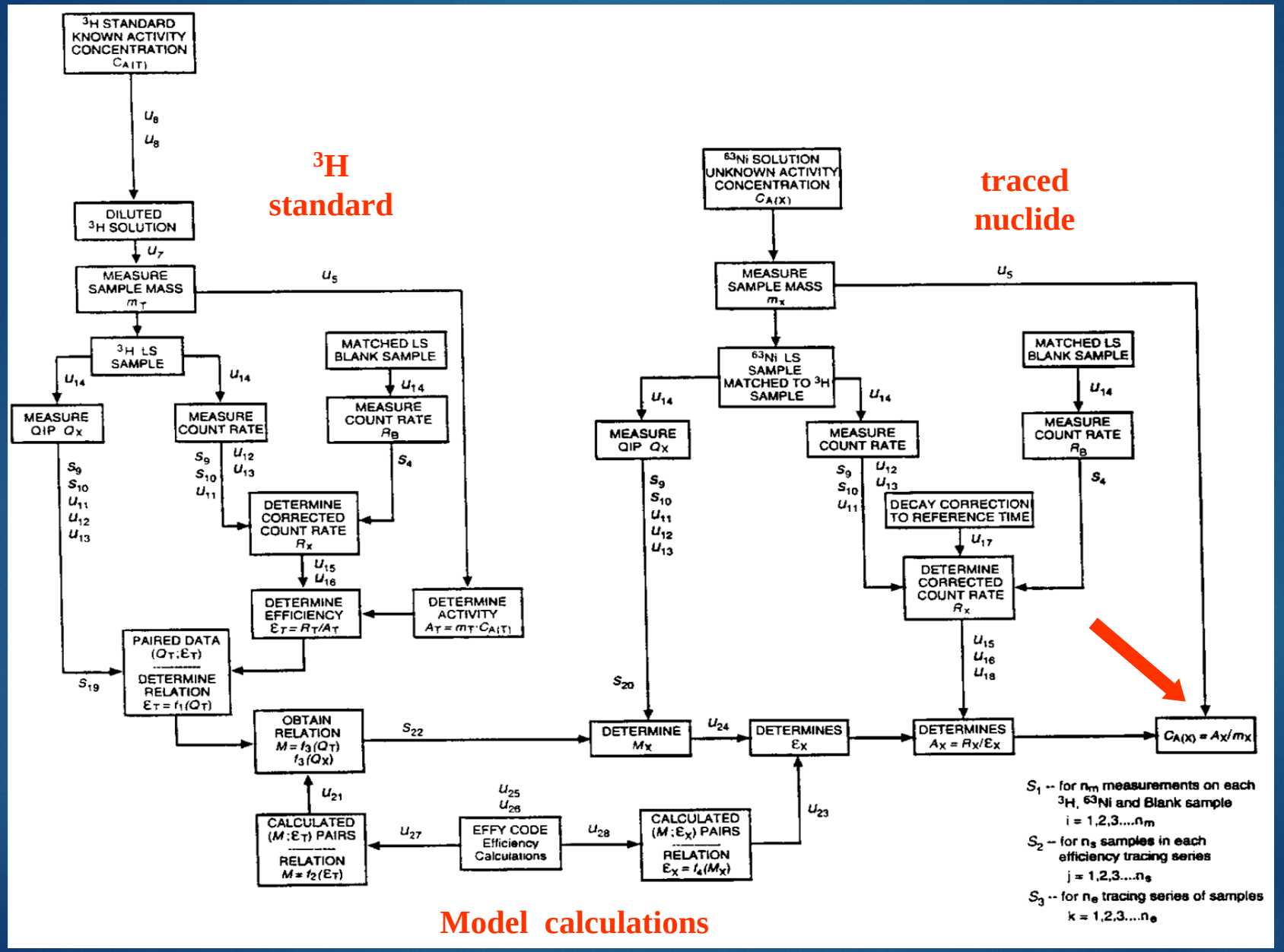
CIEMAT/NIST efficiency tracing method

- Uses ^{3}H standard and calculational model to determine detection efficiency of a radionuclide of interest
- Originally developed for pure β emitters
- Can be applied using commercial LS counters
- With a LOT of work, can be applied to EC nuclides

$$\varepsilon = \int_0^{Emax} \left(1 - \exp\left[-\frac{EQ(E)W(E)}{M}\right]\right)^2 P(Z,E)\,dE \times \left(\int_0^{Emax} P(Z,E)\,dE\right)^{-1}$$



CIEMAT/NIST method -- measurement & uncertainty model



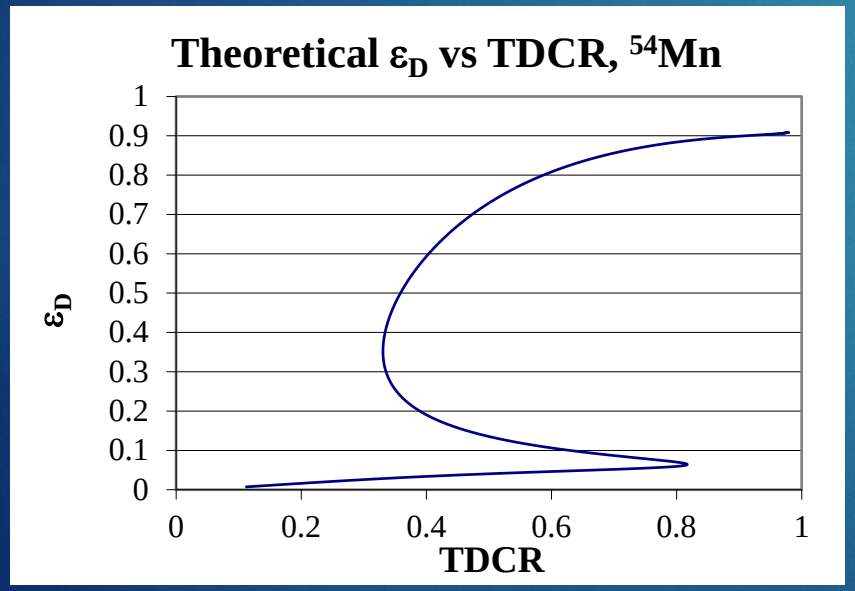
Some components are simply standard deviations of measurements (Type A evaluations)

Others need to be evaluated using other techniques

Triple-to-Double Coincidence Ratio (TDCR) Method

- Uses a specially-designed three photomultiplier tube (PMT) instrument
- Coincidences refer to the photons emitted from the scintillator – NOT the radionuclide!

$$\varepsilon_{D,} = \sum_{\substack{X=A,B,C \\ Y=A,B,C\neq X}} \int_0^{E_{max}} S(E)\left(1-e^{-\varepsilon_X \vartheta}\right)\left(1-e^{-\varepsilon_Y \vartheta}\right)dE - 2\int_0^{E_{max}} S(E)\left(1-e^{-\varepsilon_A \vartheta}\right)\left(1-e^{-\varepsilon_B \vartheta}\right)\left(1-e^{-\varepsilon_C \vartheta}\right)dE$$



Solve system of equations to find individual PMT efficiencies

$$\frac{R_T}{R_{AB}} - \frac{\int_0^{E_{max}} S(E)\left(1-e^{-\varepsilon_A \vartheta}\right)\left(1-e^{-\varepsilon_B \vartheta}\right)\left(1-e^{-\varepsilon_C \vartheta}\right)dE}{\int_0^{E_{max}} S(E)\left(1-e^{-\varepsilon_A \vartheta}\right)\left(1-e^{-\varepsilon_B \vartheta}\right)dE} = 0$$

$$\frac{R_T}{R_{BC}} - \frac{\int_0^{E_{max}} S(E)\left(1-e^{-\varepsilon_A \vartheta}\right)\left(1-e^{-\varepsilon_B \vartheta}\right)\left(1-e^{-\varepsilon_C \vartheta}\right)dE}{\int_0^{E_{max}} S(E)\left(1-e^{-\varepsilon_B \vartheta}\right)\left(1-e^{-\varepsilon_C \vartheta}\right)dE} = 0$$

$$\frac{R_T}{R_{AC}} - \frac{\int_0^{E_{max}} S(E)\left(1-e^{-\varepsilon_A \vartheta}\right)\left(1-e^{-\varepsilon_B \vartheta}\right)\left(1-e^{-\varepsilon_C \vartheta}\right)dE}{\int_0^{E_{max}} S(E)\left(1-e^{-\varepsilon_A \vartheta}\right)\left(1-e^{-\varepsilon_C \vartheta}\right)dE} = 0$$

$$\vartheta = A\int_0^{E_{max}} \frac{dE}{1+kB\,\frac{dE}{dx}}$$

Metrology with LSC

Key is to look for components of uncertainty

- Use different spectrometers
  - differing characteristics: log vs. linear amplification; detection thresholds; dead times; etc.
- Use a variety of LS cocktail compositions to obviate (or account) chemical composition effects
  - Different scintillation fluids
  - Vary carrier, water concentrations
- Use a wide quenching / efficiency range so that extrapolated result is efficiency independent
- Use different techniques for varying detection efficiency
- Use both CIEMAT/NIST and TDCR whenever possible

Estimating standard uncertainties

- Type A evaluations
  - Experimental variance $s^2(q)$ and experimental standard deviation $s(q)$ indicate dispersion about central (mean) value
  - Experimental variance of the mean $s^2(\bar{q})$ and experimental standard deviation of the mean $s(\bar{q})$ indicates how well $\bar{q}$ estimates μ_q.
- Type B evaluations
  - Non-statistical methods
  - Can still be based on data from experiment
  - Often involves experience or even “guesses”
- In both cases, we are trying to find quantities that are similar to variances (or standard deviations)
- This terminology is going away with upcoming revisions

Identifying major uncertainty components: our experience

Component	Description	Magnitude	Comments
Measurement Repeatability	Variability on *A* due to uncertainty on repeated measurements of a single source (without replacement)	0.1 % to 0.3 %	Embodies other components (background, stability, time, etc.)
Measurement Reproducibility	Variability on *A* due to uncertainty on measurements of multiple sources (with same composition)	0.1 % to 0.3 %	Embodies other components (background, time, etc.)
Source stability	Variability on *A* due to (uncorrected) time-dependent effects	?	Data should not be used if stability effects are major component.
Efficiency dependence	Variability on *A* due to efficiency dependence on QIP (should be independent)	<0.1 % to 0.5 %	Typically larger for TDCR, EC nuclides
Nuclear and atomic data	Variability on *A* due to uncertainty on input data used in model calculations	0.1 % to 0.5 %	Typically larger for TDCR, EC nuclides

These are merely typical/nominal values for demonstration! The magnitudes are highly variable and may not be present in every experiment.

Statistical tests (*F*, *t*, etc.) are useful to determine if effects are present.

Methods for evaluating uncertainties

- Analytical form

$$u_c^2(y) = \sum_{i=1}^{N} \left[\frac{\partial f}{\partial x_i}\right]^2 u^2(x_i)$$

$Y = f(X_1, X_2, \ldots, X_N)$ *measurand Y, input quantities* X_i

- Sensitivity analysis
  - $\frac{\partial f}{\partial x_i}$ are *sensitivity coefficients*

  - Estimate (or calculate) $u^2(x_i)$
  - Sensitivity coefficient can be evaluated by noting effect of $x_i \pm u(x_i)$ on y
- Monte Carlo
  - In some techniques, it is impossible or impractical to write the model in a closed, analytical form (complexity of input data, "black box" instrumentation, etc.)
  - Approach is to assemble large number of input data sets based on uncertainties of the input values
  - Assumes $u(x_i)$ is normally distributed about x_i

Example : half-life correction

^{64}Cu: 12.7004(20) h

$$f_{decay} = e^{-\ln(2)t/T_{1/2}}$$

Analytical method:

$$u_{decay}^2 = \left[\frac{\partial}{\partial T_{1/2}} e^{-\ln(2)t/T_{1/2}}\right]^2 u_{T_{1/2}}^2$$

$$= \left[e^{-\ln(2)t/T_{1/2}} \frac{d}{dT_{1/2}} \left(\frac{-\ln(2)\, t}{T_{1/2}}\right)\right]^2 u_{T_{1/2}}^2$$

$$u_{decay} = \left(e^{-\ln(2)t/T_{1/2}}\right) \left(\frac{\ln(2)t}{{T_{1/2}}^2}\right) u_{T_{1/2}}$$

For a 2-hour decay correction, u_{decay} = (0.8966)(0.008595 h^{-1})(0.0020 h) = 0.0015 %

Sensitivity factor method:

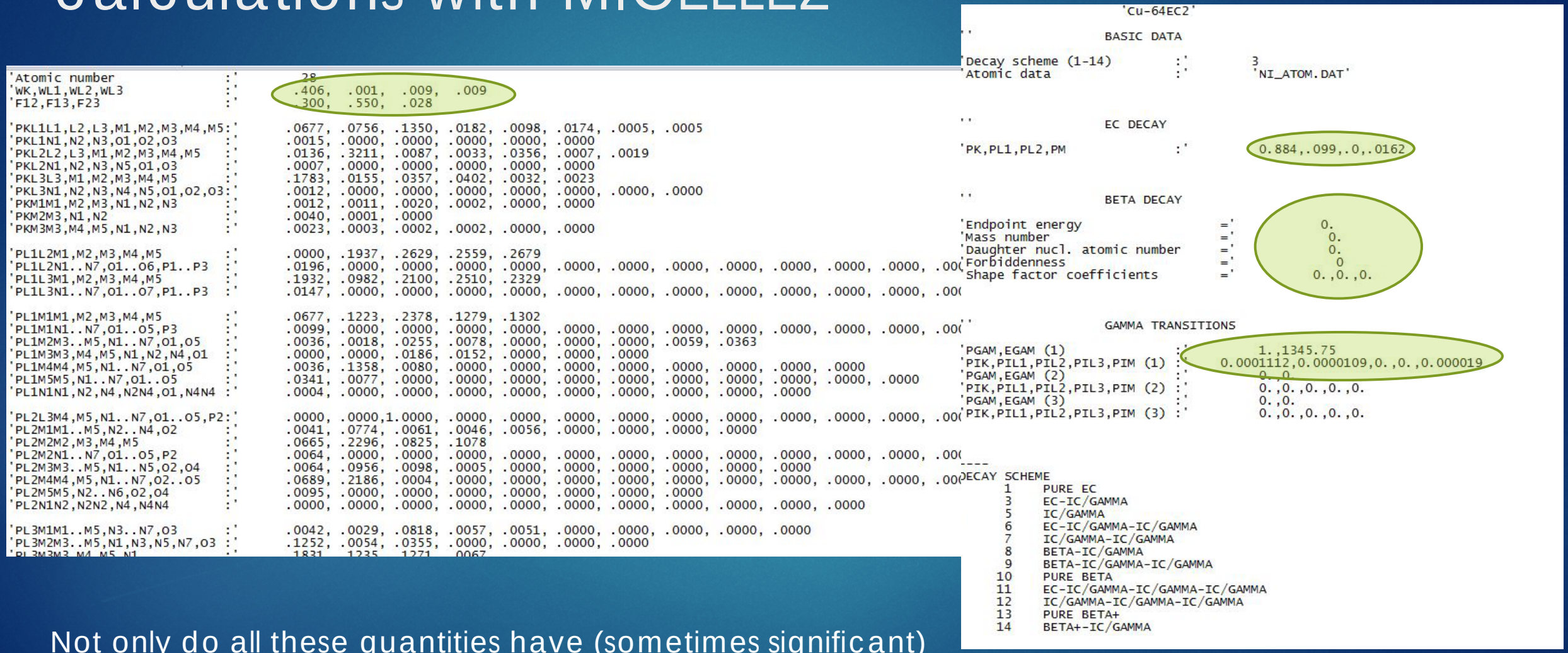
$$e^{-\ln(2)(2\,h)/(12.7004\,h)} = 0.896593 \quad e^{-\ln(2)(2\,h)/(12.7024\,h)} = 0.896608$$

Taking ratio gives Δ = 0.0017 %

Monte Carlo uncertainty analysis

- Uncertainty on measurand for some components cannot always be written as simple equation.
- Examples
  - Nuclear and atomic input data
  - Model used for efficiency calculation
  - Methods involving complicated fitting or equation solving processes
  - Input quantities where the PDF is asymmetric
- Monte Carlo approaches are good for these cases (but can almost always be used even for simple ones)

Example: input data for TDCR efficiency calculations with MICELLE2



```
'Cu-64EC2'
''                    BASIC DATA
'Decay scheme (1-14)        :'        3
'Atomic data                :'        'NI_ATOM.DAT'

''                    EC DECAY
'PK,PL1,PL2,PM              :'        0.884,.099,.0,.0162

''                    BETA DECAY
'Endpoint energy                =' 0.
'Mass number                    =' 0.
'Daughter nucl. atomic number   =' 0.
'Forbiddenness                  =' 0
'Shape factor coefficients      =' 0.,0.,0.

''                    GAMMA TRANSITIONS
'PGAM,EGAM (1)              :'        1.,1345.75
'PIK,PIL1,PIL2,PIL3,PIM (1) :'        0.0001112,0.0000109,0.,0.,0.000019
'PGAM,EGAM (2)              :'        0.,0
'PIK,PIL1,PIL2,PIL3,PIM (2) :'        0.,0.,0.,0.,0.
'PGAM,EGAM (3)              :'        0.,0.
'PIK,PIL1,PIL2,PIL3,PIM (3) :'        0.,0.,0.,0.,0.

DECAY SCHEME
     1    PURE EC
     3    EC-IC/GAMMA
     5    IC/GAMMA
     6    EC-IC/GAMMA-IC/GAMMA
     7    IC/GAMMA-IC/GAMMA
     8    BETA-IC/GAMMA
     9    BETA-IC/GAMMA-IC/GAMMA
    10    PURE BETA
    11    EC-IC/GAMMA-IC/GAMMA-IC/GAMMA
    12    IC/GAMMA-IC/GAMMA-IC/GAMMA
    13    PURE BETA+
    14    BETA+-IC/GAMMA
```

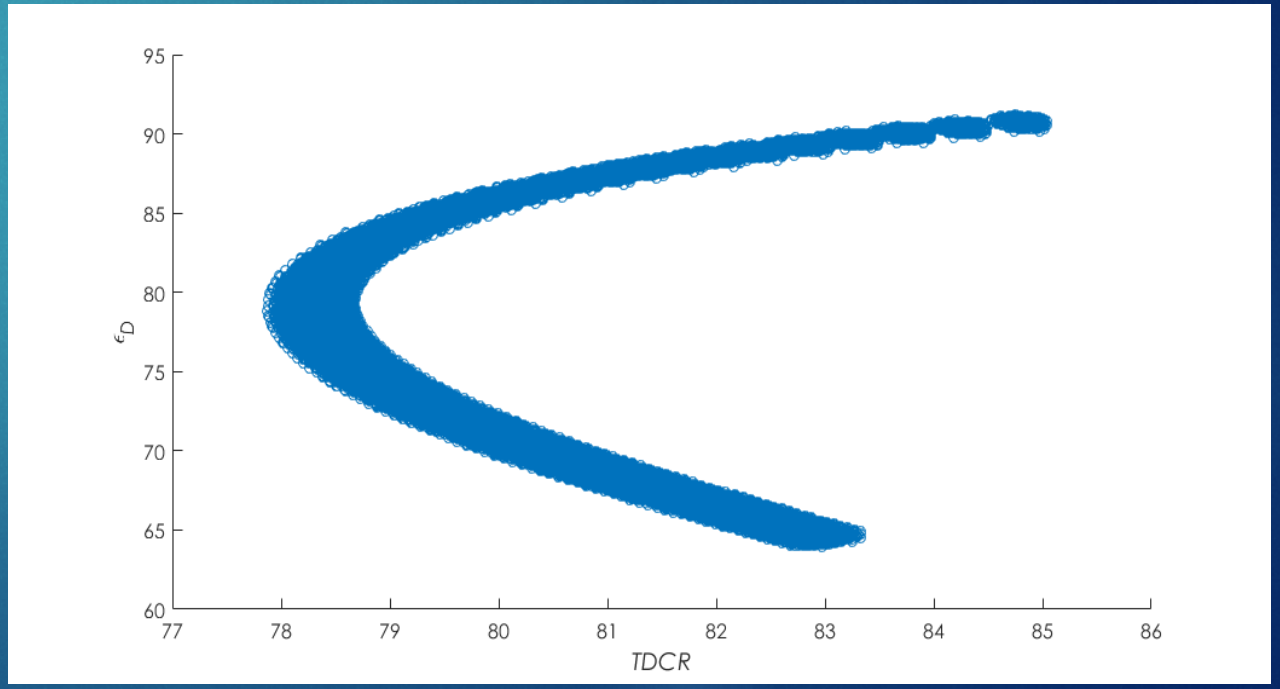
```
'Atomic number              :'        28
'WK,WL1,WL2,WL3             :'        .406,  .001,  .009,  .009
'F12,F13,F23                :'        .300,  .550,  .028

'PKL1L1,L2,L3,M1,M2,M3,M4,M5:'        .0677, .0756, .1350, .0182, .0098, .0174, .0005, .0005
'PKL1N1,N2,N3,O1,O2,O3      :'        .0015, .0000, .0000, .0000, .0000, .0000
'PKL2L2,L3,M1,M2,M3,M4,M5   :'        .0136, .3211, .0087, .0033, .0356, .0007, .0019
'PKL2N1,N2,N3,N5,O1,O3      :'        .0007, .0000, .0000, .0000, .0000, .0000
'PKL3L3,M1,M2,M3,M4,M5      :'        .1783, .0155, .0357, .0402, .0032, .0023
'PKL3N1,N2,N3,N4,N5,O1,O2,O3:'        .0012, .0000, .0000, .0000, .0000, .0000, .0000, .0000
'PKM1M1,M2,M3,N1,N2,N3      :'        .0012, .0011, .0020, .0002, .0000, .0000
'PKM2M3,N1,N2               :'        .0040, .0001, .0000
'PKM3M3,M4,M5,N1,N2,N3      :'        .0023, .0003, .0002, .0002, .0000, .0000

'PL1L2M1,M2,M3,M4,M5        :'        .0000, .1937, .2629, .2559, .2679
'PL1L2N1..N7,O1..O6,P1..P3  :'        .0196, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .00(
'PL1L3M1,M2,M3,M4,M5        :'        .1932, .0982, .2100, .2510, .2329
'PL1L3N1..N7,O1..O7,P1..P3  :'        .0147, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .00(

'PL1M1M1,M2,M3,M4,M5        :'        .0677, .1223, .2378, .1279, .1302
'PL1M1N1..N7,O1..O5,P3      :'        .0099, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .00(
'PL1M2M3..M5,N1..N7,O1,O5   :'        .0036, .0018, .0255, .0078, .0000, .0000, .0000, .0059, .0363
'PL1M3M3,M4,M5,N1,N2,N4,O1  :'        .0000, .0000, .0186, .0152, .0000, .0000, .0000
'PL1M4M4,M5,N1..N7,O1,O5    :'        .0036, .1358, .0080, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000
'PL1M5M5,N1..N7,O1..O5      :'        .0341, .0077, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000
'PL1N1N1,N2,N4,N2N4,O1,N4N4 :'        .0004, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000

'PL2L3M4,M5,N1..N7,O1..O5,P2:'        .0000, .0000,1.0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .00(
'PL2M1M1..M5,N2..N4,O2      :'        .0041, .0774, .0061, .0046, .0056, .0000, .0000, .0000, .0000
'PL2M2M2,M3,M4,M5           :'        .0665, .2296, .0825, .1078
'PL2M2N1..N7,O1..O5,P2      :'        .0064, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .00(
'PL2M3M3..M5,N1..N5,O2,O4   :'        .0064, .0956, .0098, .0005, .0000, .0000, .0000, .0000, .0000, .0000
'PL2M4M4,M5,N1..N7,O2..O5   :'        .0689, .2186, .0004, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .00(
'PL2M5M5,N2..N6,O2,O4       :'        .0095, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000
'PL2N1N2,N2N2,N4,N4N4       :'        .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000, .0000

'PL3M1M1..M5,N3..N7,O3      :'        .0042, .0029, .0818, .0057, .0051, .0000, .0000, .0000, .0000, .0000
'PL3M2M3..M5,N1,N3,N5,N7,O3 :'        .1252, .0054, .0355, .0000, .0000, .0000, .0000
'PL3M3M3,M4,M5,N1           :'        .1831  .1235  .1271  .0067
```

Not only do all these quantities have (sometimes significant) uncertainties, many are also correlated!

Approach

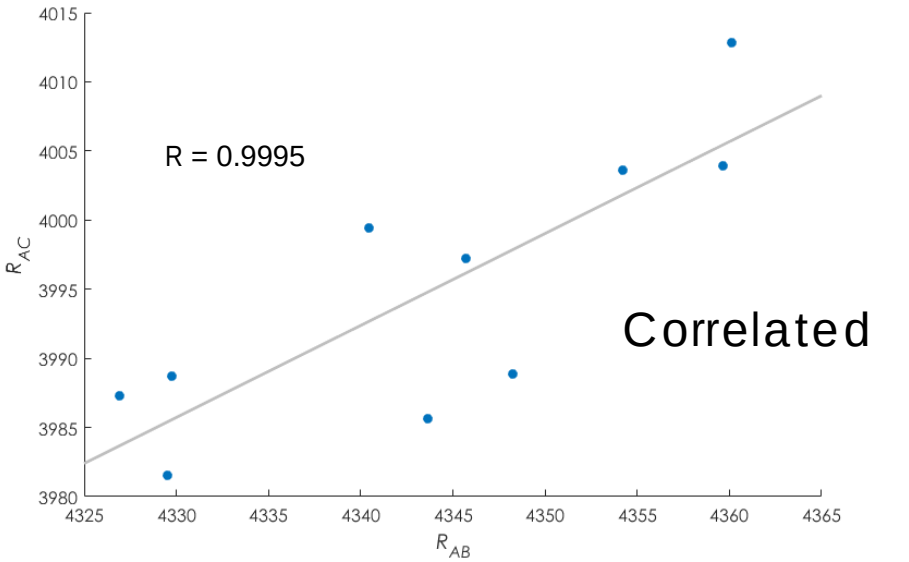
- Identify the mean value for all input quantities, uncertainties
- Identify/assign the PDF for the uncertainty (Normal, Gamma, etc.)
- Construct large number of input data sets by drawing random input values from distributions of each variable
- Beware of correlated variables, normalizations!
- Run calculation for all data sets
- Beware of potentially biased sampling!

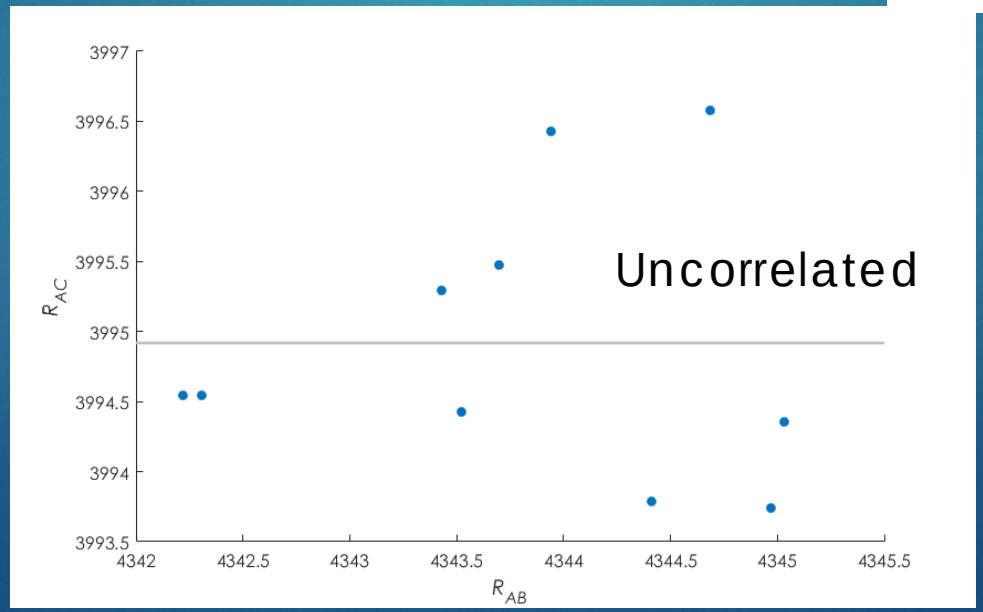
Example: Run of 8500 MICELLE2 calculations for ^{64}Cu, drawing random variables from mean and standard uncertainties for nuclear and atomic data (assume Normal distribution).



Correlation

- Example: TDCR variables strongly correlated
- For $R_T/R_D = K$, what is u_K?
- We don't know functional form (or distribution) for calculating activity from the counting data alone
- Can be calculated using Monte Carlo methods, but uncorrelated are needed
- Data can generally be de-correlated using a linear transform
  - Mahalanobis
  - Cholesky
- See Poster 143





Conclusions

- Uncertainty analysis is a vital component to any measurement and needs to be done correctly and carefully
- Key to a meaningful uncertainty analysis is a complete understanding of the measurement and the relationship between variables.
- Every uncertainty analysis is different (i.e., no cookbook)
- Need to look for uncertainty components
- Many methods exist to evaluate magnitude of uncertainty components, including Monte Carlo
- Methods exist to reduce/eliminate correlation between variables

Suggested reading

IOP Publishing | Bureau International des Poids et Mesures Metrologia
Metrologia 52 (2015) S172–S190 doi:10.1088/0026-1394/52/3/S172

Uncertainty determination for activity measurements by means of the TDCR method and the CIEMAT/NIST efficiency tracing technique

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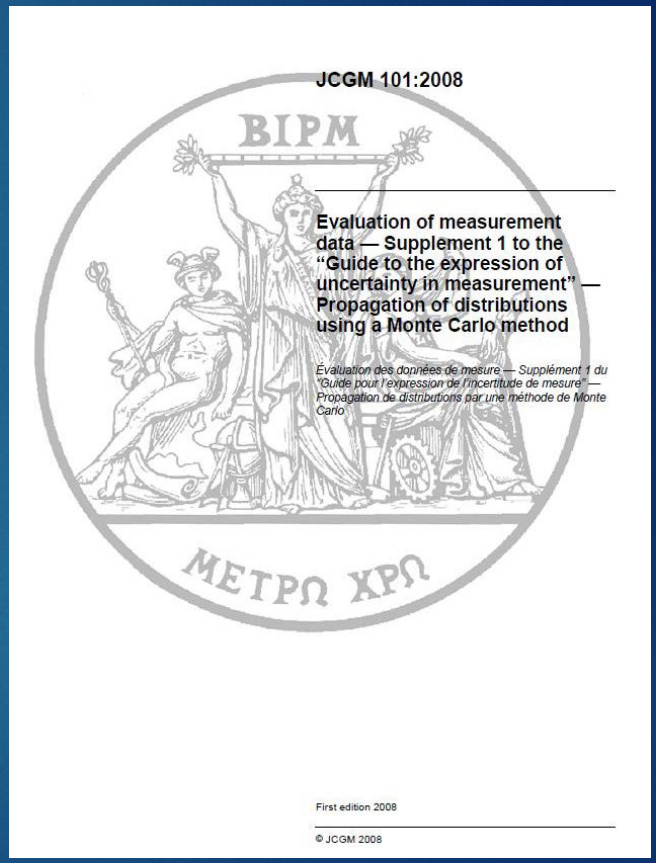
Abstract

Liquid scintillation counting is a very powerful technique for the activity determination of a number of radionuclides. In radionuclide metrology, the TDCR method and the CIEMAT/NIST efficiency tracing technique are widely used in many laboratories.

Both methods require rather complex calculation techniques to derive the counting efficiency of the nuclide under study.

This article explores the various sources of uncertainty that should be considered when applying these two techniques, and focuses on possible ways to evaluate them. Concrete examples are provided within the paper.



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