Uncertainties in measurements using LSC Quench-curves

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Contents of this talk

- Introduction
- Method described by IAEA (Seibersdorf)
- Application to 4 nuclides
- Extended to quench index parameter (QIP or tSIE)

You get very limited information from the LSC manual on how the quench curve is fitted and on associated uncertainties.

This is an essential part of the calibration of a LS counter.
Uncertainty budget in LSC measurements

How do you do that thoroughly and nicely..?
Sometimes carried out very well...

GUM - Guide to the expression of Uncertainty in Measurements
IAEA TecDoc 1401 - Quantifying uncertainty in nuclear analytical measurements
ISO 11929 - (for the real die hards ....)
UKAS - M3003 (UK Accreditation Services)
NEN 7779 - Environment – measurement uncertainties (in Dutch)
DIN, French, Spanish....

That’s all very nice, thank you!
But please give us a practical example ...
IAEA TecDoc for several techniques!

IAEA TecDoc 1401 – July 2004

Quantifying uncertainty in nuclear analytical measurements

N.b. ! $^3$H determination using electrolytic enrichment
Very detailed on $^{90}$Sr LSC determination....
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/dm³ 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.
Basic formula for calculation of activity (Bq/l)

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

Where:

\( A \) = the current remaining activity, [Bq/L]
\( C \) = the Counts Rate in the region for tritium, [cpm]
\( \varepsilon \) = 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]

Uncertainty Sources in LS measurements (IAEA)

- Counts in the counting region
- Quench Curve or Counting Efficiency
- Sample Volume
- Recovery factor
- Measuring time
- Decay correction
Extend this IAEA uncertainty calculation...

More nuclides in ‘optimized’ window

• $^3\text{H}$ in 1-5 keV (usual...)
• $^{14}\text{C}$ in 4-50 keV (using trapping agent Carbosorb)
• $^{89}\text{Sr}$ in 220-500 keV
• $^{90}\text{Sr}$ in 500-900 keV (or 220-900 keV without $^{89}\text{Sr}$)

• Look at uncertainty of Quench Index Parameter too...
Quench curves: 3 main uncertainties...

- $S_{c+s}$: Counting of quench standards + Source uncertainty
- $S_{\text{curve-fit}}$: Curve fitting procedure: Quench index – efficiency
- $S_{\text{QIP}}$: Uncertainty of quench index measurement ($x$) leads to uncertainty in efficiency ($Y$)...

$$Y = A + Bx + Cx^2 + Dx^3 + Ex^4 + Fx^5 + Gx^6$$

But How?
Uncertainties and quench-curves....

Above 50 keV counts are lost....

N.B. in safe quench area with a flat Q-curve the uncertainty is much smaller than in region where the curve goes down steep...
Measured four quench curves

- $^3$H in Ultima Gold
- $^{14}$C Q-curves in toluene based cocktail
  
  (for use with Carbosorb trapping agent)
- $^{89}$Sr Q-curve in Ultima Gold
- $^{90}$Sr Q-curve in Ultima Gold

I apologize humbly for the next three slides....
Quench curve (1) : calculation of $S_{c+s}$

### Experimental data.

<table>
<thead>
<tr>
<th>No</th>
<th>time (min)</th>
<th>Specworks Countrate (cpm)</th>
<th>Ci Value</th>
<th>u(Ci)</th>
<th>u(Ci) Unc.</th>
<th>u(Ci) 2s</th>
<th>Theoretical activity A (dpm) @ 10-Jan-12</th>
<th>A_{std} Value</th>
<th>u(A_{std})</th>
<th>u(K)/K @ 10-Jan-12</th>
<th>u(K)/K Unc.</th>
<th>Counting Efficiency (%) and source uncertainty : Sc+s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.99</td>
<td>47546,73</td>
<td>0,65</td>
<td>154.6</td>
<td>237.4</td>
<td>129892</td>
<td>563</td>
<td>2.08E-07</td>
<td>36,60</td>
<td>0,20</td>
<td>0,005417</td>
<td></td>
</tr>
<tr>
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<td>0,65</td>
<td>237.4</td>
<td>129892</td>
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<td>2.08E-07</td>
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<td>63,65</td>
<td>0,34</td>
<td>0,005306</td>
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<td>94470,23</td>
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<td>268.5</td>
<td>129892</td>
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<td>129892</td>
<td>563</td>
<td>2.08E-07</td>
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<td>0,41</td>
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<td>93367,63</td>
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<td>59,29</td>
<td>0,31</td>
<td>0,005255</td>
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<td>59525,00</td>
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<td>2.08E-07</td>
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<td>113,9</td>
<td>129892</td>
<td>563</td>
<td>2.08E-07</td>
<td></td>
<td>19,17</td>
<td>0,12</td>
<td>0,0063</td>
<td></td>
</tr>
</tbody>
</table>

**sumsq** 0,000289  

**sqrt=Sc+s** 1,7%

Sorry, I really should be punished for this slide.  
I suggest beating with a stick...
Quench curve (2) : calculation of $S_{\text{curve-fit}}$

<table>
<thead>
<tr>
<th>No</th>
<th>Experimental data</th>
<th>Theoretical fit</th>
<th>Difference Theory - Experimental</th>
<th>$S_\varepsilon/\varepsilon_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>QIP</td>
<td>efficiency</td>
<td>$Y_{\text{fit,Excel}}$ 6th degree</td>
<td>$\Delta_{\text{Excel}}$ $\Delta_{\text{Excel}}^2$</td>
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<tr>
<td>1</td>
<td>1004.68</td>
<td>36.60</td>
<td>36.59</td>
<td>0.02            0.00032</td>
</tr>
<tr>
<td>2</td>
<td>858.95</td>
<td>55.98</td>
<td>56.30</td>
<td>-0.32           0.10037</td>
</tr>
<tr>
<td>3</td>
<td>727.79</td>
<td>63.65</td>
<td>62.90</td>
<td>0.75             0.55771</td>
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<tr>
<td>4</td>
<td>565.61</td>
<td>72.73</td>
<td>73.85</td>
<td>-1.13            1.26581</td>
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<tr>
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<td>432.22</td>
<td>80.71</td>
<td>79.92</td>
<td>0.79             0.61985</td>
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<td>6</td>
<td>309.05</td>
<td>80.62</td>
<td>80.14</td>
<td>0.48             0.22714</td>
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<tr>
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<td>206.98</td>
<td>71.88</td>
<td>73.18</td>
<td>-1.30            1.67963</td>
</tr>
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<td>137.49</td>
<td>59.29</td>
<td>59.14</td>
<td>0.15             0.02321</td>
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<td>98.61</td>
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<td>44.77</td>
<td>1.06             1.11780</td>
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<td>10</td>
<td>54.95</td>
<td>19.17</td>
<td>19.70</td>
<td>-0.53            0.28125</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>sum</th>
<th>sumsq</th>
<th>$S_\varepsilon$</th>
<th>sqrt</th>
<th>$S_{\text{curve-fit}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,873 sum</td>
<td></td>
<td>0,0018029</td>
<td>0,808 sqrt(sum)/(n)</td>
<td>0,042</td>
<td>4,2%</td>
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</tbody>
</table>

This is an example of a 6th degree polynomial in Excel

$$y = -4.79555E-15x_6 + 1.55968E-11x_5 - 2.04166E-08x_4 + 1.39933E-05x_3 - 5.51124E-03x_2 + 1.20322E+00x - 3.19178E+01$$

When is a fit close enough?  
6th or 7th degree polynomial? Origin or Excel?  

A bull whip punishment...
Quench curve (3) : calculation of $S_{QIP}$

Uncertainty in quench index parameter estimated as 0.4 %

<table>
<thead>
<tr>
<th>No</th>
<th>Experimental data</th>
<th>Theoretical fit</th>
<th>Difference</th>
<th>$S_{c}/\varepsilon_{i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
<td>Y-exp</td>
<td>Y_{fit, Excel}</td>
<td>tSIE+0.4% X+dx</td>
</tr>
<tr>
<td>1</td>
<td>1004.68</td>
<td>36.60</td>
<td>36.59</td>
<td>1008.70</td>
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<tr>
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<td>858.95</td>
<td>55.98</td>
<td>56.30</td>
<td>862.39</td>
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<td>727.79</td>
<td>63.65</td>
<td>62.90</td>
<td>730.70</td>
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<td>4</td>
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<td>72.73</td>
<td>73.85</td>
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<tr>
<td>5</td>
<td>432.22</td>
<td>80.71</td>
<td>79.92</td>
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<tr>
<td>6</td>
<td>309.05</td>
<td>80.62</td>
<td>80.14</td>
<td>310.29</td>
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<tr>
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<td>71.88</td>
<td>73.18</td>
<td>207.81</td>
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<td>137.49</td>
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<td>59.14</td>
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<tr>
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<td>98.61</td>
<td>45.83</td>
<td>44.77</td>
<td>99.00</td>
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<tr>
<td>10</td>
<td>54.95</td>
<td>19.17</td>
<td>19.70</td>
<td>55.17</td>
</tr>
</tbody>
</table>

Uncertainty in tSIE determination = 0.4 %

$y = -4.79555E-15x6 + 1.55968E-11x5 - 2.04166E-08x4 + 1.39933E-05x3 - 5.51124E-03x2 + 1.20322E+00x - 3.19178E+01$

Last punishment : with stones around my neck in the lake...

“Asterix and Obelix in Helvetia”
The total uncertainty is then calculated as follows:

\[ S_{total} = \sqrt{S_{c+s}^2 + S_{curve-fit}^2 + S_{QIP}^2} \]

<table>
<thead>
<tr>
<th>Radionuclide (window)</th>
<th>( S_{c+s} ) (%)</th>
<th>( S_{Curve-fit} ) (%)</th>
<th>( S_{QIP} ) (%)</th>
<th>( S_{total} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^3 )H (1-5 keV)</td>
<td>2.0</td>
<td>2.3</td>
<td>2.7</td>
<td>4.1</td>
</tr>
<tr>
<td>( ^{14} )C (4-50 keV; carbosorb)</td>
<td>1.7</td>
<td>4.4</td>
<td>3.4</td>
<td>5.8</td>
</tr>
<tr>
<td>( ^{89} )Sr (220-500 keV)</td>
<td>3.8</td>
<td>2.1</td>
<td>3.0</td>
<td>5.3</td>
</tr>
<tr>
<td>( ^{90} )Sr/Y (500-900 keV)</td>
<td>3.6</td>
<td>4.8</td>
<td>4.1</td>
<td>7.3</td>
</tr>
</tbody>
</table>
Please remember…

• Each lab should establish all these uncertainties for itself!

• Depends on LS counter
• On analytical method:
  distillation
  $^{14}\text{CO}_2$ trapping agents
  $\text{BaCO}_3$
  cocktail
  window setting (single/dual lable, high energy window)
  quench level
• *So, don’t quote me on these numbers!*
Conclusions  *Uncertainty in quench curves*

• General mathematical procedure has been shown... (I hope some labs will give it a try...)

• Uncertainty in quench curve not only counting + source
• Curve fit and quench index also play a role

• Uncertainties in some Q-curves for $^3$H, $^{14}$C, $^{89}$Sr and $^{90}$Sr in the range of 4-7 %, depending on application
Uncertainty budgets…

_in science, nothing is certain, except that it is uncertain…_

Thank you for your attention