Uncertainty Assessment and Analytical Quality Specification

fighting Conceptual Barriers to

(intercontinental) Understanding, CBU{s

the International Vocabulary of Metrology - VIM edition 3

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The revision of "VIM2" (yielding "VIM3")

1. VIM2 (1993) was written for physics and engineering by physicists and engineers

2. For the first time in history, chemical measurement is covered by VIM3

3. Important change of title:
   from
   “International Vocabulary of basic and general Terms in Metrology” (VIM2)
   to
   “International Vocabulary of Metrology - basic and general Concepts and associated Terms – VIM (VIM3)
Condition for a consistent translation of a term in other languages used on the “intercontinental” scene:

one must **understand** the concept **behind the term** before being able **to translate the term** (!)
Penalties for not using VIM: fog!

- in 1998 EU Directive on IVD
- in future Directives
- in ISO Standards and Guides such as
  - ISO Guides 30, 31, 33, 34, 35, 17025
  - e.g. when used in accreditation
- in 1998 EC Directive on Drinking Water
- in the Certification of quantity values and associated uncertainties in
  - IRMM, NIST, LGC, BAM, PTB, ERM, NMIJ, NMLA,
- in Documents produced by EURACHEM, CITAC, ISO-REMCO,
- in programmes like IMEP, REIMEP, NUSIMEP
Some key definitions of the revised VIM:

2.3 *measurand*

*quantity* intended to be measured

introduces the *intention* of the analyst ("*intended* to be measured")

similarly,

"fitness for *intended* use" is used rather than "fitness for purpose"
2.9 **measurement result**
set of *quantity values* being attributed to a *measurand* together with any other available information

Note 2: A measurement result is generally expressed as a single *measured quantity value* and a *measurement uncertainty*

2.36 **measurement uncertainty**
non-negative parameter characterizing the dispersion of the *quantity values* being attributed to a *measurand*, based on the information used
DISCREPANCY PROBLEMS ARE MOSTLY CAUSED, NOT SO MUCH BECAUSE OF THE EFFECTS OF UNKNOWN BIAS, BUT BECAUSE OF THE LACK OF A FULL (= ‘GUM’) EVALUATION OF MEASUREMENT UNCERTAINTY
2.34 target measurement uncertainty

measurement uncertainty specified as an upper limit and decided on the basis of the intended use of measurement results

- a target measurement uncertainty can be used as a measure of the “fitness for intended use” of a measurement result
- a target measurement uncertainty is derived from external requirements (not from performance specifications of the measuring system) such as regulatory authorities
2.6 measurement procedure
detailed description of a measurement according to one or more measurement principles and to a given measurement method, based on a measurement model and including any calculation to obtain a measurement result

Note 2: A measurement procedure can include a statement concerning a target measurement uncertainty
5.1 **measurement standard**
realization of the definition of a given **quantity**, with stated **quantity value** and associated **measurement uncertainty**, used as a reference

Note 7: The word “embodiment” is sometimes used in the English language instead of “realization”

5.12 **calibrator**
**measurement standard** used in **calibration**

5.4 **primary measurement standard**
**measurement standard** established using a **primary reference measurement procedure**, or created as an artifact, chosen by convention
2.40 calibration hierarchy
sequence of calibrations from a reference to the final measuring system, where the outcome of each calibration depends on the outcome of the previous calibration.

Note 1: Measurement uncertainty necessarily increases along the sequence of calibrations.

2.41 metrological traceability
property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty.

Note 2: Metrological traceability requires an established calibration hierarchy.
metrological traceability is a prerequisite to evaluation of the measurement uncertainty of the end user’s measurement result
2.7 reference measurement procedure
measurement procedure accepted as providing measurement results fit for their intended use in
- assessing measurement trueness of measured quantity values obtained from other measurement procedures for quantities of the same kind,
  - in calibration, or
  - in characterizing reference materials

2.8 primary reference measurement procedure
reference measurement procedure used to obtain a measurement result without relation to a measurement standard for a quantity of the same kind

Note 1: The Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM) uses the term “primary method of measurement” for this concept
this definition prevents to use “primary” for

• “prestige” reasons
• political reasons
• commercial reasons
interlaboratory comparisons (ILC)

- Operation of having two or more laboratories carry out measurements and compare measurement results for the same quantity embodied in samples of the same material.

- The operation enables the determination of the metrological equivalence of pairs of measurement results of the participants but does not, by itself, establish metrological traceability.
interlaboratory comparisons (ILC)

- **purposes:**
  - assessment of participant’s measurement performance
    - proficiency testing PT
    - external quality assurance scheme EQAS
    - interlaboratory measurement bias study
  - **IMEP**

- **measurement capability**
  - Ability to measure a specified *quantity* of a given *kind*, in a specified interval of *quantity values*, embodied in a specified material, as demonstrated by a *measurement uncertainty*

- all of these are tools for quality assurance
IMEP- 17: Trace and minor constituents in human serum
Certified value : 4.412 ± 0.033 mmol·L\(^{-1}\) \([U=k\cdot u_c \ (k=2)]\)

<table>
<thead>
<tr>
<th>Glucose Material 1</th>
<th>Photometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values above 50%</td>
<td></td>
</tr>
<tr>
<td>c (mmol L(^{-1}))</td>
<td>Uncertainty(mmol L(^{-1}))</td>
</tr>
<tr>
<td>7.8</td>
<td>0</td>
</tr>
</tbody>
</table>

All reported results (1011) arranged in method groups:
Photometry; Amperometry; Vitros 250-950 and Other/No info
IMEP-17: Trace and minor constituents in human serum
Certified value: 2.334 2 ± 0.006 9 mmol·L$^{-1}$ [$U=k \cdot u_c (k=2)$]

### Results from all participants (983 laboratories)

#### Calcium Material 1

<table>
<thead>
<tr>
<th>Values above 20%</th>
<th>c (mmol/L)</th>
<th>Uncertainty (mmol/L)</th>
<th>Dev. (%)</th>
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</thead>
<tbody>
<tr>
<td>3</td>
<td>0.00</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.00</td>
<td>29</td>
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<tr>
<td>3.45</td>
<td>0.12</td>
<td>48</td>
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<tr>
<td>4.41</td>
<td>0.09</td>
<td>89</td>
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<td>4.64</td>
<td>0.00</td>
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<td>4.7</td>
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<td>101</td>
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<tr>
<td>4.75</td>
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<td>4.8</td>
<td>0.06</td>
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<td></td>
</tr>
<tr>
<td>4.81</td>
<td>0.00</td>
<td>106</td>
<td></td>
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</table>

#### Values below -20%

<table>
<thead>
<tr>
<th>c (mmol/L)</th>
<th>Uncertainty (mmol/L)</th>
<th>Dev. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9500</td>
<td>0.00</td>
<td>-59</td>
</tr>
<tr>
<td>1.19</td>
<td>0.04</td>
<td>-49</td>
</tr>
<tr>
<td>1.27</td>
<td>0.00</td>
<td>-46</td>
</tr>
<tr>
<td>1.51</td>
<td>0.06</td>
<td>-35</td>
</tr>
</tbody>
</table>
A hunter fired both barrels of a shotgun at a duck. The first hit two feet in front, the second hit two feet behind.

**ON THE AVERAGE THE DUCK WAS DEAD**

In duck hunting one wants to keep trying until a *single shot* hits the mark.

*Source: J Ruzicka 1980 (at the habilitation of Kai Heydorn KØBENHAVN)*

*It is cheaper to perform less measurements, but have sufficiently small uncertainty every time, than making many measurements and use the average*
2.28 **Type A evaluation of measurement uncertainty** evaluation of a component of measurement uncertainty by a statistical analysis of *measured quantity values* obtained under defined measurement conditions.

2.29 **Type B evaluation of measurement uncertainty**

evaluation of a component of *measurement uncertainty* determined by means other than a statistical analysis of **Type A evaluation of measurement uncertainty**

(sometimes the basis of Type B evaluation is called “subjective information” - GUM 3.3.5)
- Prevents to state that a measurement method has a fixed (constant) measurement uncertainty, independent of whether it is carried out carefully or sloppily.

- A measurement procedure contains a detailed description and therefore obliges to decide a priori on its intended use as a
  - “reference measurement procedure”, or as a
  - “primary measurement procedure”

- A measurement method does not have a fixed (i.e. constant) measurement uncertainty, but a given measurement procedure has.

- Introduces the concept of “target measurement uncertainty” as a measure of “fitness for intended use”
These very important definitions put the ultimate task and responsibility for the measurement result (back) to the analyst responsible; this is absolutely correct because his/her professional skill and judgement is essential:

GUM 3.4.8: “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”

GUM 4.3.2: “Type B evaluation of standard uncertainty ... calls for insight based on experience and general knowledge, and is a skill to be learned with practice”
2.46 metrological comparability of measurement results

comparability of measurement results, for quantities of a given kind, that are metrologically traceable to the same reference

Note 1: A metrological traceability chain is defined through a calibration hierarchy

Note 2: Metrological comparability of measurement results does not necessitate that the measured quantity values and associated measurement uncertainties compared be of the same magnitude
2.43 **metrological compatibility of measurement results**

property of a set of measurement results for a specified *measurand*, such that the absolute value of the difference of any pair of *measured quantity values* from two different measurement results is smaller than some chosen multiple of the *standard measurement uncertainty* of that difference.
- metrological comparability of measurement results is caused by metrological traceability to the same reference.

- metrological compatibility is related to metrological equivalence of measurement results.

- metrological comparability of measurement results is “vertical” in the same metrological traceability chain because it has to do with metrological traceability, whereas

- metrological equivalence of measurement results is “horizontal” because it compares measurement results each belonging to a different metrological traceability chain.
Measurements of mass use the *property of ‘inertia’* of matter. This property is *not* *substance-specific*.

Measurements of amount use the *property of ‘numerosity’* (*numerousness, countability*) of matter. This property is *substance-specific*.

In addition:

Most of our analytical measurement equipment is based on the use of the *property of ‘numerosity’* or *‘countability’* of matter.
many chemical measurements are:

- limited in Quality
- non comparable
- non reliable
with sincere wishes
to all
for a
good discussion