# Internationally understood **concepts** and **associated terms**… & some other vocabulary as defined in the VIM and the GUM

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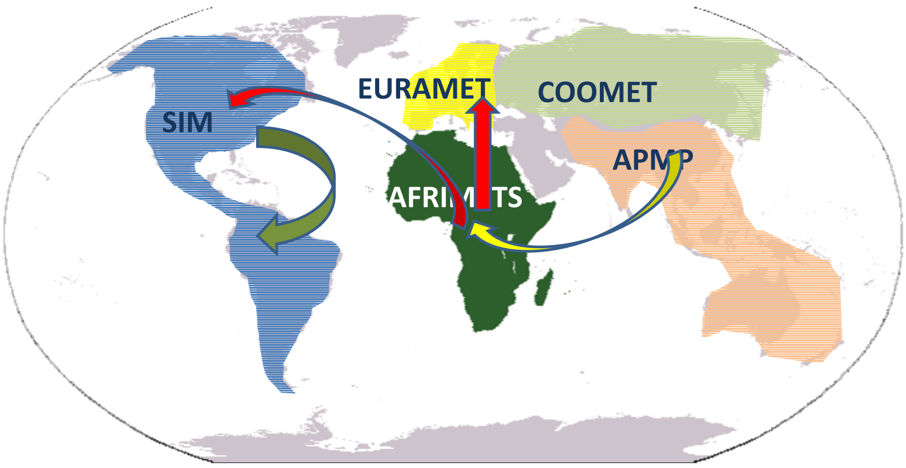
Chair: MiC (Afrimets)

## Measure once, accepted everywhere




**Overcome technical barriers to trade**
**Measurement security in you own country…**

## Transactional Efficiency in National and International Trade

- **Import/Export Requirements**
- **Pricing of Commodities**
- **Authentification/ Source of Origin**
- **GMO**
- **Emissions Trading**

## Food Scandals…

- Growth hormones in beef
- BSE in beef
- Dioxine in milk
- Salmonella in eggs
- Heavy metals in rice and wine
- Glycol in wine, diesel oil in olive oil
- Toxic residues in fish, oyster, shrimp (from all waste water)
- Pesticides in fruits
- Nitrates and nitrites
- GMO's in soya, rice, grains

We have to analyse/measure !

~~Technical Barriers to Trade (TBTs)~~

**Conceptual Barriers to Trade (CBTs)**

**Intercontinental Barriers to Trade**

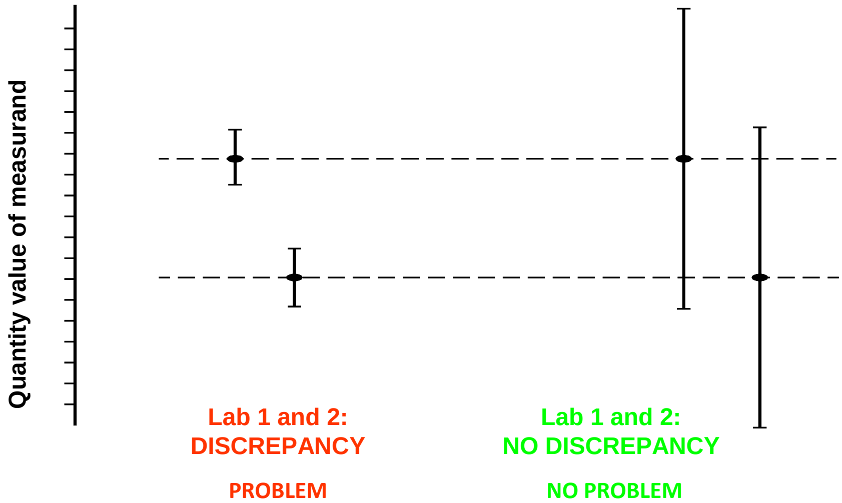
**Intracontinentual barriers to Trade**

**Understand the terminology first**

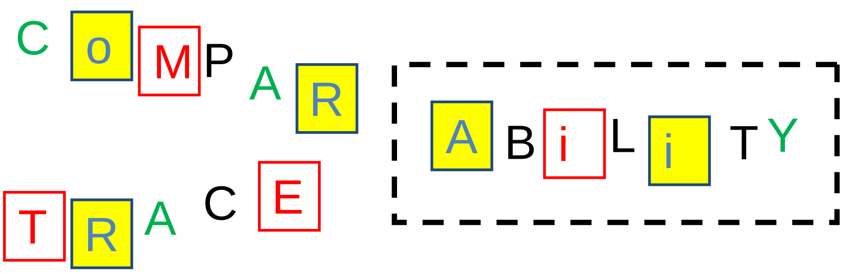
# The Cost of Non-Conformance

- For over 200 years, the leading nation in global economy, the USA, has resisted adopting the metric system. This has exacted a cost, as the loss of the Mars Climate Orbiter in 1999 illustrates. A NASA investigation revealed that **one team used American measures while another team used metric units** leading to a trajectory error of 60 miles – a $125-million disappearing act
- American experts have calculated that if gasoline pumps in the U.S. were found to be set just to the limit of the maximum negative tolerance (-96 mL) it would result in U.S. consumers being overcharged more than $1 Billion dollars per year, which is far greater than the annual cost of all U.S. weights and measures programs combined.

# Chemical measurements




# So you are ‘able’??



# Chemical Measurements

- According to a study released by the Council for Chemical Research, **chemistry is core or important to virtually all industrial sectors and technology areas**
  - *"Measuring Up: Chemical R&D Counts for Everyone", CCR, 2006*

- **For metrology in chemistry** the task is to determine the quantity of a **specific chemical entity** and not merely "amount of substance"

- **Chemical measurements are multidimensional**
  - a large number of chemical entities ($>10^5$)
  - in a broad range of matrices ($10^?$)
  - and mass fractions ranging from $<10^{-12}$ to 1

# 2.3 Measurand

2.3 **measurand**

**quantity** intended to be measured

1.1 **quantity**

property of a phenomenon, body or substance, where the property has a magnitude that can be expressed as a number and a reference

1.10 **base unit**

**measurement unit** that is adopted by convention for a **base quantity**

Note 3 : For number of entities, the number one, symbol 1, can be regarded as a **base unit** in any **system of units**

# What is the measurand?

It is a well defined quantity:

- carbon monoxide in nitrogen or air for amount-of-substance fractions equal to or greater than 5 µmol/mol
- Total Se (~20 mg $kg^{-1}$) and selenomethionine (~ 10 mg $kg^{-1}$) in a wheat flour sample.
- Determination of the mass fraction of a peptide in solution (µg/g)
- Quantitation of a linearised plasmid DNA, based on a matched standard in a
- matrix of non target DNA
- The volume of a vessel / flask
- The potential difference between the terminals of a battery

# 2.6 Measurement Procedure

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**

## Measurement Procedure

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**

## Measurement Procedure

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

Gravimetry

Tritrimetry

Isotope Dilution-ICP

Neutron Activation Analysis

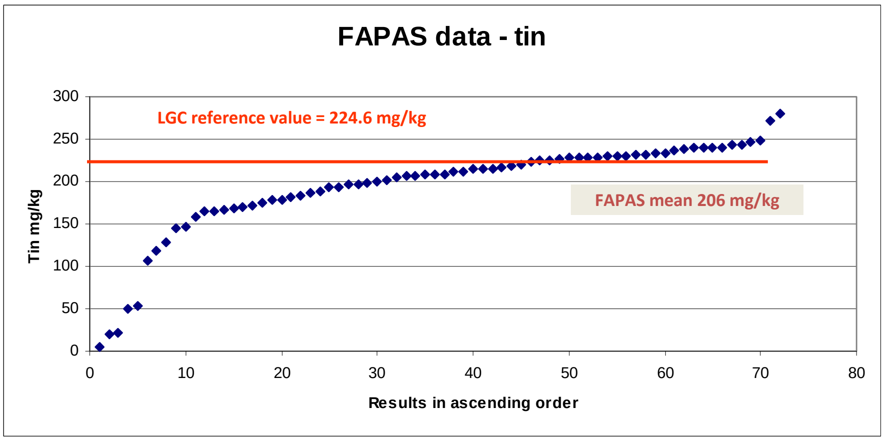
# Measurement Result

**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**

# Measurement Result



## Change in Sn performance using reference instead of consensus value

| Effect on Rating | Number of Labs. | Percent |
|---|---|---|
| 'Acceptable' **>>** 'Unacceptable' | 17 | 37 |
| 'Unacceptable' **>>** 'Acceptable' | 9 | 20 |
| No change to rating | 20 | 43 |

## 2.36 Measurement Uncertainty (MU)

2.36 **measurement uncertainty**

non-negative parameter characterizing the dispersion of the **quantity values** being attributed to a **measurand**, based on the information used

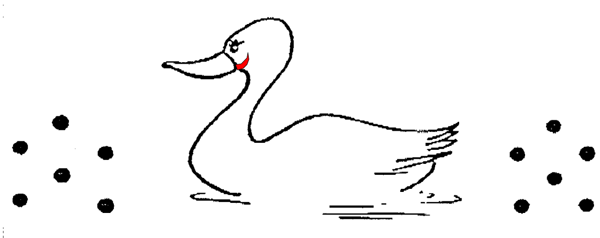
"A parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand"

- GUM
- EURACHEM/CITAC

*Note: metrological traceability is a prerequisite for measurement uncertainty*

# Measurement Uncertainty

- Measurement uncertainty can be used to help judge the consistency of experiment and theory, of different measurement procedures, and of different laboratories.
- As the tolerances applied in industrial production become more demanding, the role of measurement uncertainty becomes more important when assessing conformity to these tolerances.
- Measurement uncertainty is a concept central to quality standards [18, 20].



**ON THE AVERAGE THE DUCK WAS DEAD**

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 a ***single shot to*** hit the mark.

*Source: J Ruzicka 1980 (at the habilitaion of K Heydorn KØBENHAVN)*

***It is cheaper to perform less measurements,***
***but have sufficiently small uncertainty,***
***meeting a pre-set "target measurement uncertainty"***

***than making many measurements and use the average***

# 2.28 Type evaluation of MU

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**

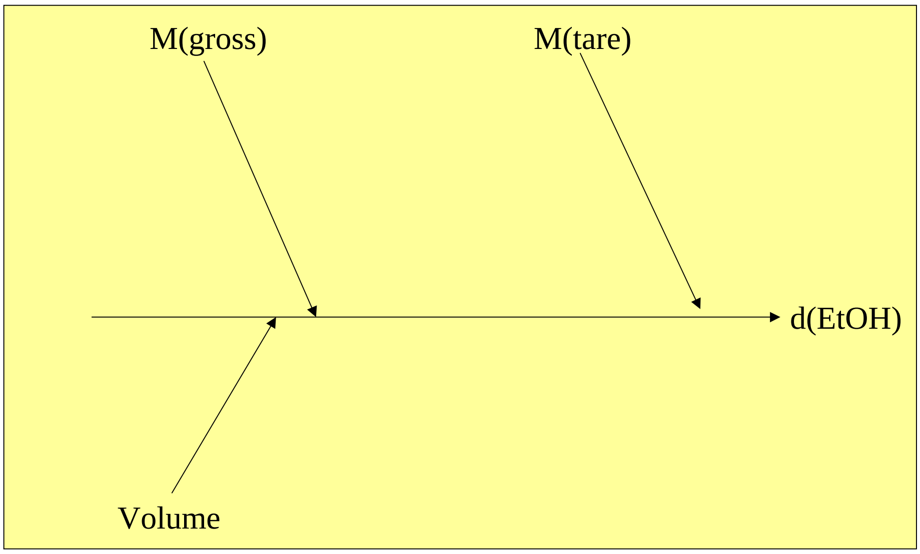
(sometimes the basis of Type B evaluation is called "subjective information" - GUM 3.3.5)

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:

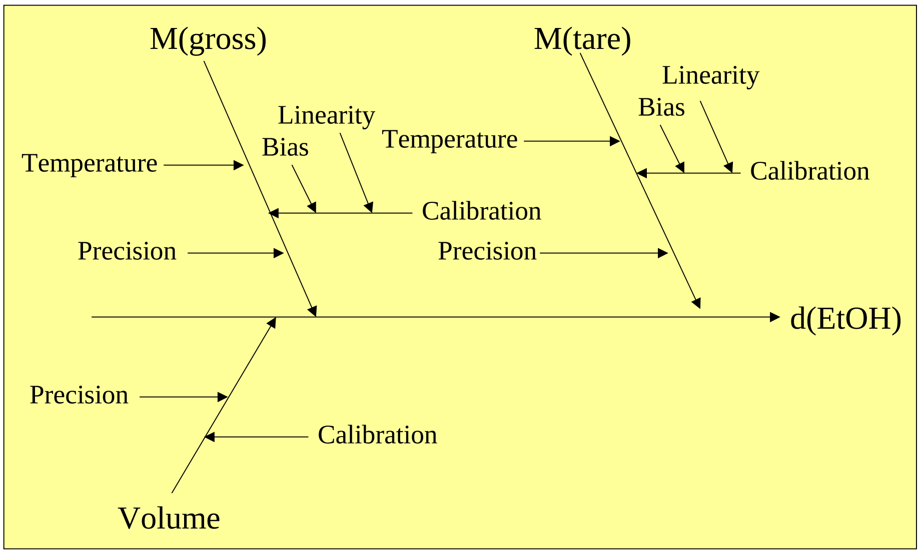
GUM 3.4.8: "The evaluation of uncertainty is neither a routine task nor a purely mathematical one; it depends on detailed knowledge of the nature of the measurand and of the measurement"

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"

## Measurement Uncertainty: Initial list: Main branches




## Initial list



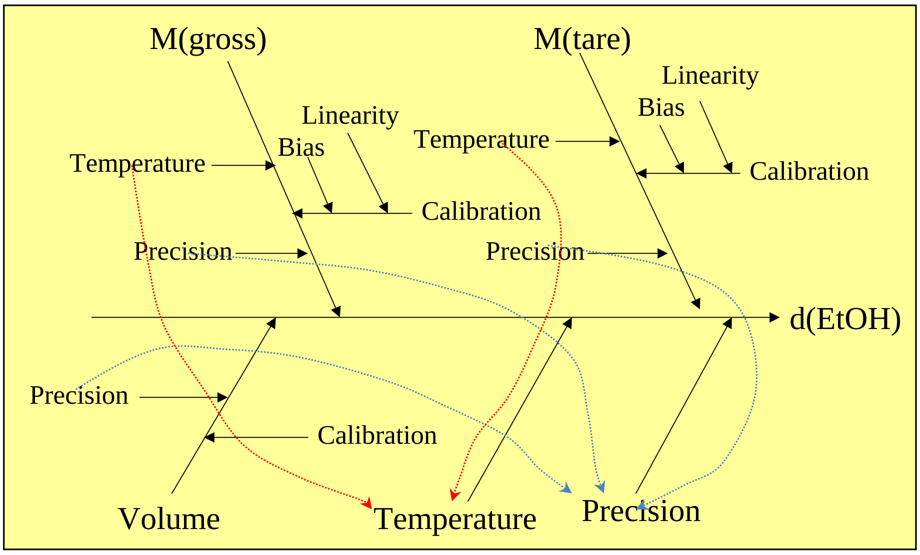
## Cause and effect analysis (cont.)

- ✓ Step 1: Write the complete equation for the result.
- ✓ Step 2: Consider each step of the method and add additional main branches.
- ✓ Step 3: For each branch, add factors until their effect on the result becomes negligible.
- ✓ Step 4: Resolve duplications, re-arrange, group related causes.

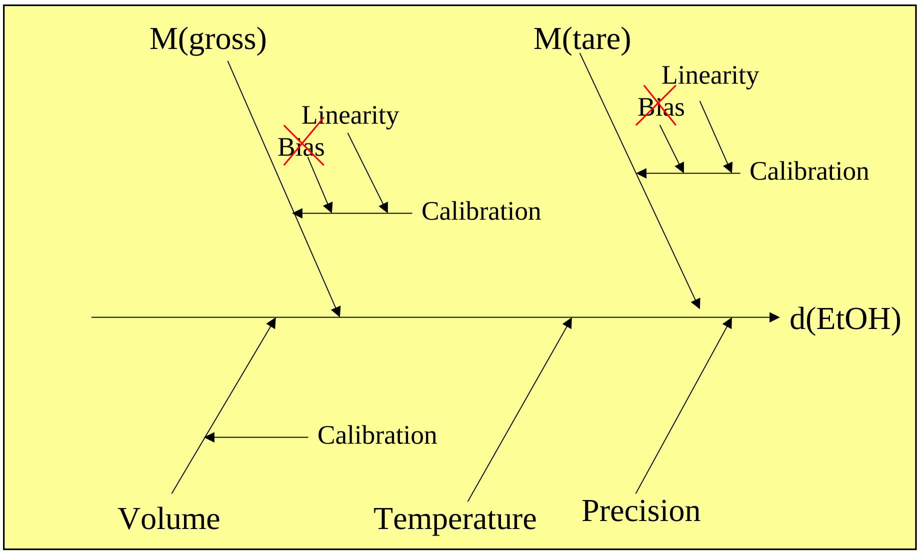
## Cause and effect analysis (cont.)

- ✓ RULE 1: Cancelling effects: remove both.
- ✓ RULE 2: Similar effects, same time: combine into a single input.
- ✓ RULE 3: Different instances: re-label.

## Combination of similar effects




## Cancellation




**Same balance: bias cancels**

## Measurement Uncertainty

- ✓ Two categories
  - ✓ Those whose estimate and associated uncertainty are directly determined by the current measurement
  - ✓ Those whose estimate and associated uncertainty are brought into the measurement from external sources
- ✓ Their uncertainties require different ways of evaluation

## Type A Evaluation

- ✓ For component of uncertainty arising from random effect
- ✓ Applied when multiple independent observations are made under the same (repeatability) conditions
- ✓ Data can be from repeated measurements, control charts, curve fit by least-squares method, etc.
- ✓ Obtained from a probability density function derived from an observed frequency distribution (usually Gaussian)

## Type A Evaluation (cont)

- Best estimate of the expected value of an input quantity – arithmetic mean

$$\bar{q} = \frac{1}{n}\sum_{k=1}^{n} q_k$$

- Distribution of the quantity – experimental standard deviation

$$s(q_k) = \sqrt{\frac{1}{n-1}\sum_{k=1}^{n}(q_k - \bar{q})^2}$$

- Spread of the distribution of the means – experimental standard deviation of the mean

$$s(\bar{q}) = \frac{s(q_k)}{\sqrt{n}}$$

- Type A standard uncertainty

$$u(x_i) = s(\bar{q})$$

- Degrees of freedom

$$\nu_i = n - 1$$

## Type B Evaluation

- Evaluated by scientific/professional judgment
- Based on all available information
  - Previous measurement data
  - Experience of the behaviour of instruments or materials
  - Calibration certificates
  - Manufacturer's specifications
  - Reference data from textbooks
- Can be as reliable as type A components
- Can sometimes be verified by experiment

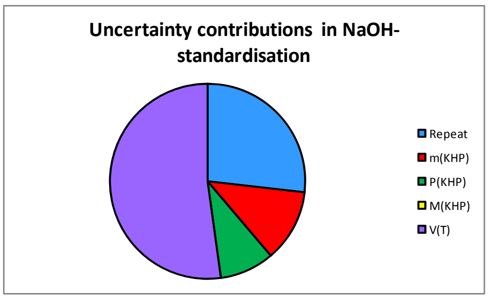
## Combining Uncertainties

- ✓ All uncertainty components must be converted to be in the same unit of measurement (speak the same “language”).
- ✓ To combine standard uncertainties, they must all be converted to standard variances (squared).
- ✓ They can then be combined linearly (summed).
- ✓ To obtain a combined standard uncertainty, the resulting variance must be converted to a deviation (positive square root).

## Measurement Uncertainty

- Useful tool to evaluate and improve method’s performance

$$c_{NaOH} = \frac{1000 \cdot m_{KHP} \cdot P_{KHP}}{M_{KHP} \cdot V_T}$$



# Traceability

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: M**easurement 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 uncertainy**

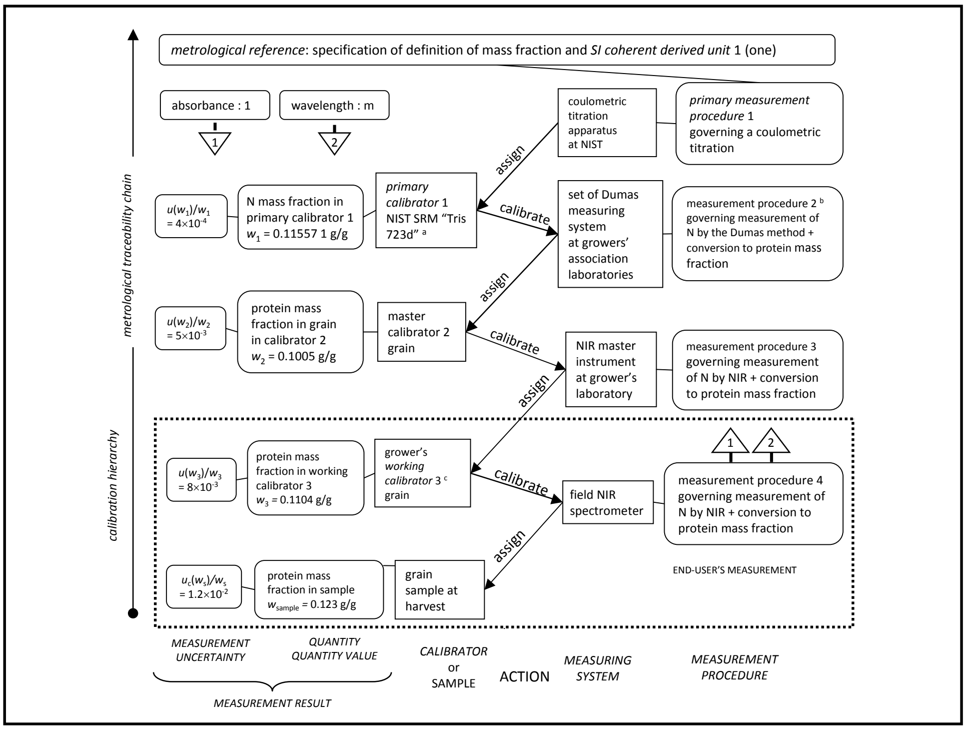
Note 2: **Metrological traceability** requires an established **calibration hierarchy**

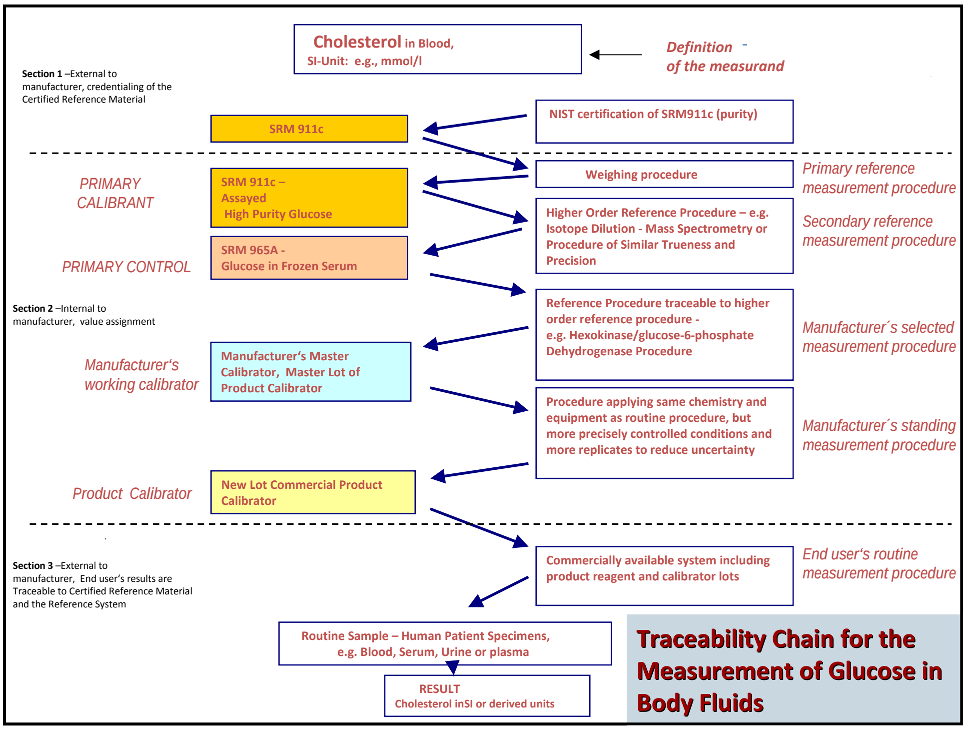
- strictly speaking, ultimate metrological traceability is not to the measurement unit chosen, but to the definition of that measurement unit, nor is it -ultimately- to a practical realization of that measurement unit but

  ***to the definition of that measurement unit through its practical realization***

- metrological traceability is a

  ***prerequisite*** **to evaluation of measurement uncertainty**


metrological reference: specification of definition of mass fraction and SI coherent derived unit 1 (one)
absorbance : 1
wavelength : m
1
2
coulometric titration apparatus at NIST
primary measurement procedure 1 governing a coulometric titration
metrological traceability chain
calibration hierarchy
u(w1)/w1 = 4×10-4
N mass fraction in primary calibrator 1 w1 = 0.11557 1 g/g
primary calibrator 1 NIST SRM "Tris 723d" a
assign
calibrate
set of Dumas measuring system at growers' association laboratories
measurement procedure 2 b governing measurement of N by the Dumas method + conversion to protein mass fraction
u(w2)/w2 = 5×10-3
protein mass fraction in grain in calibrator 2 w2 = 0.1005 g/g
master calibrator 2 grain
assign
calibrate
NIR master instrument at grower's laboratory
measurement procedure 3 governing measurement of N by NIR + conversion to protein mass fraction
assign
u(w3)/w3 = 8×10-3
protein mass fraction in working calibrator 3 w3 = 0.1104 g/g
grower's working calibrator 3 c grain
calibrate
field NIR spectrometer
measurement procedure 4 governing measurement of N by NIR + conversion to protein mass fraction
assign
uc(ws)/ws = 1.2×10-2
protein mass fraction in sample wsample = 0.123 g/g
grain sample at harvest
END-USER'S MEASUREMENT
MEASUREMENT UNCERTAINTY
QUANTITY QUANTITY VALUE
MEASUREMENT RESULT
CALIBRATOR or SAMPLE
ACTION
MEASURING SYSTEM
MEASUREMENT PROCEDURE


Cholesterol in Blood, SI-Unit: e.g., mmol/l
Definition of the measurand
Section 1 –External to manufacturer, credentialing of the Certified Reference Material
SRM 911c
NIST certification of SRM911c (purity)
PRIMARY CALIBRANT
SRM 911c – Assayed High Purity Glucose
Weighing procedure
Primary reference measurement procedure
PRIMARY CONTROL
SRM 965A - Glucose in Frozen Serum
Higher Order Reference Procedure – e.g. Isotope Dilution - Mass Spectrometry or Procedure of Similar Trueness and Precision
Secondary reference measurement procedure
Section 2 –Internal to manufacturer, value assignment
Reference Procedure traceable to higher order reference procedure - e.g. Hexokinase/glucose-6-phosphate Dehydrogenase Procedure
Manufacturer´s selected measurement procedure
Manufacturer's working calibrator
Manufacturer's Master Calibrator, Master Lot of Product Calibrator
Procedure applying same chemistry and equipment as routine procedure, but more precisely controlled conditions and more replicates to reduce uncertainty
Manufacturer´s standing measurement procedure
Product Calibrator
New Lot Commercial Product Calibrator
Section 3 –External to manufacturer, End user's results are Traceable to Certified Reference Material and the Reference System
Commercially available system including product reagent and calibrator lots
End user's routine measurement procedure
Routine Sample – Human Patient Specimens, e.g. Blood, Serum, Urine or plasma
RESULT Cholesterol inSI or derived units
Traceability Chain for the Measurement of Glucose in Body Fluids

## Metrological Traceability

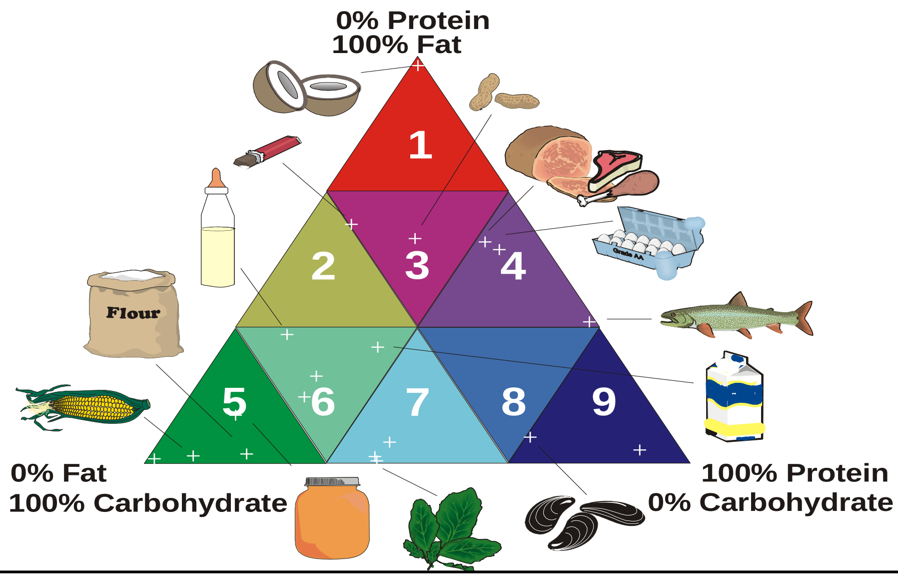
- ✓ Traceability to the SI or if not (yet) possible to another internationally agreed reference
  (e.g. hardness, pH, WHO International Units)
- ✓ Globally recognized, reliable and comparable measurement values with a stated measurement uncertainty, traceable to long term stable measurement standards (Trueness)
- ✓ Applicable to all fields of measurements, analysis and testing

## Traceability

Establish traceability of the result of the complete analytical procedure by

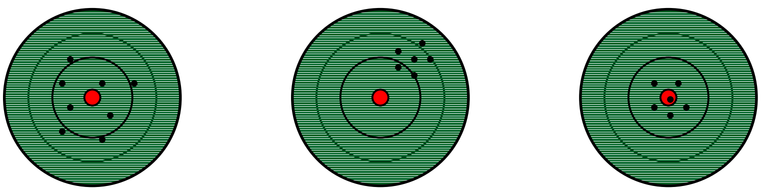
- ✓ **Using a primary method.**
- ✓ **Using the analytical procedure to make measurements on a quantified pure sample of the analyte.**
- ✓ **Using the analytical procedure to make measurements on an appropriate CRM.**
- ✓ **Making measurements using a defined procedure.**

# The Food Triangle for CRMs




# Accuracy and Precision

- Accuracy: Closeness of the measured value to the "true" value
- Precision: Describes the scatter / spread of results typically achieved for multiple analyses of a homogeneous sample



# Precision

- Instrument precision
  - Replicate analyses
- Method Precision
  - Repeatability
    - One analyst, one instrument, short period of time
  - Intra-laboratory repeatability (intermediate value)
    - Different analysts, one or more instruments, within one laboratory, over period of time
  - Reproducibility (largest)
    - Different laboratories
- Measure SD / RSD
  - 10 x measurements
  - Dependent on Concentration

# Accuracy / 'True' Value

Demonstrated through:

- Analysis of Certified Reference Material (CRM)
  - Certified (traceable to SI)
  - Matrix material similar to sample's matrix
- Analysis by another accurate & traceable method (preferably primary)
- *Analysis of Reference Material (RM)*
- *In-house Quality Control Sample (QCS)*
- *Standard Addition*
- *Interlaboratory comparison / Bi-lateral comparison*
- *Proficiency Testing (PT) Scheme*

## Fit for purpose

- Fitness for 'intended use/purpose'
- Specify the use/purpose for it to have any meaning whatsoever
- The same technique/method/procedure, applied with different carefulness/detail/attention can produce results over a wide spectrum – apply your method for your intended purpose

## NB to take note:

Traceability and MU:

- MU does not imply you have traceability
- For complete MU you have to consider the full traceability chain, each step

VIM III [JCGM200:2008]

**Conceptual barriers to understanding**

thank you