Metrology in Chemistry and Traceability of Measurement Results

David Koech: BSc, MSc
koechdk@gmail.com
koechd@kebs.org

Index

- *Metrology*
  - need for measurement quality
- International Measurement System
- Traceability of measurement results

1

What is a Measurement ?

Process of experimentally obtaining one or more **quantity values**

Quantity is a property which has a magnitude that can be expressed as a number and a unit e.g.

- Quantity: ***Cadmium (mass)concentration***
- Quantity value: ***12 mg/l Cd***
- Measurement result: ***12 ± 2 mg/l Cd***

(VIM, 3rd edition)

2

What is Measurement Quality ?

- Results should be fit for purpose – regarding several parameters e.g uncertainty, price and comparability

Comparability - measurements need to be comparable over:

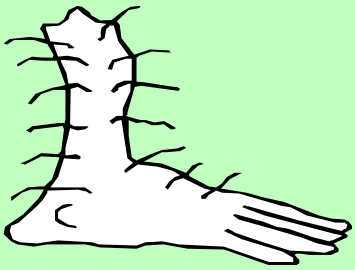
- Time 1900 2000 2100 year
- Between different laboratories
- Between different countries

measured once – accepted everywhere

3

… Lack of Standard …

King's foot



4

… Lack of Standard …
Variations of One Unit of Length (Ell)

- The "ell", a unit originating from the custom of measuring cloth using one's forearms, existed in many countries.
- In order to make trade possible at all in these days, conversion tables were used.
  (Buskes and van Gerven)

5

… Lack of Standard …

country	ell(m)	city	ell(m)
England	1.14	Vienna(A)	0.78
Scotland	0.94	Bruges (B)	0.70
Germany	0.6	Amsterdam (NL)	0.69
Russia	0.5		

(Buskes and van Gerven)

6

Meter Convention

- The lack of standards was resolved in the second half of 19th century with the signing of meter convention on 20th may 1875 in Paris by representatives of 17 nations
- This treaty established the international system of units (SI) for the signatory countries
- Currently there are 54 signatory countries and 37 associate members (as at 22/10/2012)

7

Aims of the meter convention

- Achieve international uniformity in measurement
- Establish common system of units
- Harmonise laws and regulations
- Achieve mutual recognition of measurements

8

Meter Convention

- The Convention of the Metre (*Convention du Mètre*) is a treaty that created :
  - International Bureau of Weights and Measures (BIPM)
  - Intergovernmental organization under the authority of the General Conference on Weights and Measures (CGPM) and
  - the supervision of the International Committee for Weights and Measures (CIPM).
- The BIPM acts in matters of world metrology

9

SI

International System of Units

10

SI Base Quantities

quantity	unit	symbol
Length	metre	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

11

SI Derived Quantities Examples

quantity	unit	symbol
▪ Speed, velocity	metre per second	m/s
▪ Density	kilogram per cubic metre	kg/m^3
▪ Concentration (of amount of substance)	mole per cubic metre	mol/m^3

12

Chemical measurements

Remember your dinner

- Raw meat
- Smoked salmon
- Chicken tandoori
- Rice curry
- New York Steak
- Cheese platter
- Fruit cocktail
- Great Wall red wine
- Non-alcoholic drinks
- Tea or coffee

Bon Appetit !

Are you sure ? Did you measure the quality values?

13

Remember recent Food scandals

- Growth hormones in beef
- BSE in beef
- Dioxine and melamine 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 and honey

We have to analyse/measure ! And results should be accurate and comparable

14

Trade, Health and Food Safety

Recent examples of temporary closure of markets due to the presence of residues

- Antibiotics in pork, Japan
- Antibiotics in meat, Korea
- Antibiotics in salmon, Japan
- Crystal violet in salmon, EU
- Leucomalachite green in salmon, Chinese Taipei
- Amphenicol in salmon, Canada
- Dioxin in pig meat, South Korea
- Melamine in milk
- Carbaryl in wine
- Cd in mussels
-

15

Chemical measurements used:

- Monitoring conformity assessment & product spec
- Protect consumers against fraud & counterfeit products
- Assist hospital physicians
- Support justice system
- Forensic evidence
- Revenue for govt
- Free movement of trade

16

Lack of Measurement Quality can Lead to:

- Duplication of measurements
- Use of extra resources
- Lack of trust
- Negative economic impact
- Disasters/accidents
- Loss of business & trade

17

Effect on Trade

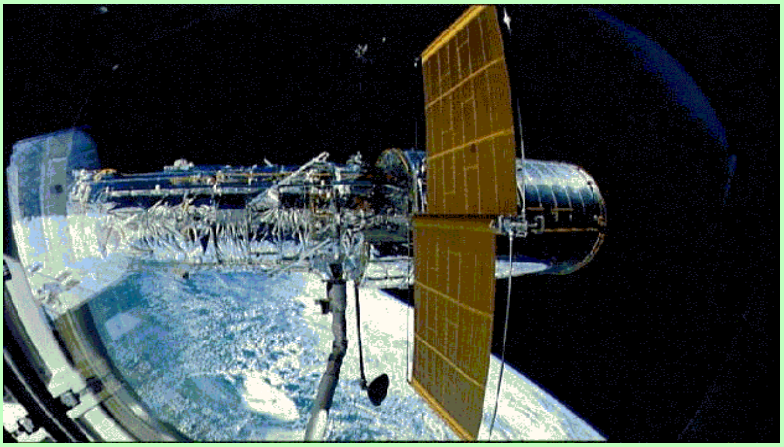
❖Lake Victoria fish (EU ban caused damage of 100 million US$ p.a. and 150 000 people jobless).

❖Sri Lanka tea export (90 billion Rs p.a. (800 million US$) hindered due to inability to measure pesticides and lack of international recognition).

❖Chilean export of marine, fish, meat, milk and agricultural products (10.5 billion USD p.a.) vulnerable due to lack of sufficient credible traceable testing

18

Disasters



19

Mars Climate Orbiter

...confusion about units leads to crash...

- On 23 September 1999 the Mars Climate Orbiter,one of the missions in a long-term program of Mars exploration, burned out completely.
- The accident was not due to a technical problem, but the result of the different measurement units used by the NASA teams.
- Flight system software used the metric unit newton while the ground software uses imperial measure pound force (ibf)other used the English units. The spacecraft encountered Mars at an improperly low altitude and led to the loss of the orbiter.

The fate of the Mars Climate Orbiter clearly shows the need for standardization of units

20

Loss of Revenue

- A subsidiary of an oil company in the Far East analysed a batch of petrol. Their local lab established that the gum content (components in the gasoline that polymerize during combustion) was much too high.
- On the basis of this analysis the company sold the batch to a trader for a much lower price.
- The trader asked a second lab to perform an analysis in order to find out what he could do with the off-spec petrol.
- He was very pleasantly surprised to find that the gasoline was actually on-spec and he was able to make a healthy profit selling the batch for the normal price.

The oil company only found out much later that the problem was not the petrol, but an error at their own lab. By then this error had already cost them $ 10 million.

(Buskes and van Gerven)

21

Wastage

- The 800-mile trans-Alaska pipeline pumps oil from the northern coast to the southern border of Alaska.
- Construction started in 1973 and was completed 4 years later.
- The pipeline was originally budgeted $ 900 million, but the cost escalated to exceed $ 1 billion.
- A steel manufacturer was awarded the multimillion dollar contract to supply steel for the pipeline with S content of less than 0.005%.
- When several of the joint welds in the pipeline began to fail, it became clear that the S content was much higher than specified.

The poor quality of the steel, in part due to inadequate or lack of measurements, set the project back several millions of dollars, once again emphasizing the need for accurate measurements.

(Buskes and van Gerven)

22

Save on cost

- A high measurements uncertainty for cholesterol can lead to an unnecessary costly treatment or a higher health risk.
- Reducing the measurement uncertainty from 23.7% in 1949 to 5% in 1995, saves to the Unites States alone $ 100 million every year in health care costs.

Standard reference materials played an important role in lowering the measurement uncertainty.

(W. May)

Note: Today other compounds (lipoproteins) are used for risk markers of myocardial diseases

23

Decisions on chemical measurements

- Means
  - Food can be eaten
  - Goods can be sold
  - Patients should be treated
  - Support health care, trade, production social problems

  But results from PT shows quality of results not satisfactory. Why???– Metrological aspects probably not considered

24

Are we really doing the right job ?

• Do we know what we really like/intend to measure
• Did we clearly define the measurand
• Are we really measuring what we intend to measure
• Are our measurement results comparable, traceable
• Do we use validated methods and procedures
• Do we use the right reference measurement standards; Certified Reference Materials
• Do we know the accuracy/measurement uncertainty
• Does a reliable (accredited) measurement and testing infrastructure exist.

If not, we have a problem !

25

Metrology – Science of Measurement

- Metrology includes all theoretical and practical aspects of measurement, whatever the **measurement uncertainty** and field of application.

(VIM, 3rd edition)

26

Before

Quality of chemical measurements based on:

- A quality management system
- Accreditation

Now:

• In addition, principle of measurement science (metrology)

• First applied in Physics but also applicable to chemistry as well

27

Metrological traceability

✓Property of a **measurement result** whereby the result can be related to a reference **through an unbroken chain of** calibrations, each contributing to the **measurement uncertainty .** *JCGM 200:2008 (VIM 3).*

✓Traceability to the SI, or if not (yet) possible to another internationally agreed reference (hardness, pH, WHO International Units)

"Once measured, accepted everywhere " requires Comparability through Traceability

28

Metrological Principles

- Uncertainty of measurements
- Traceability
- Validation of measurements procedures
- Statistical tools used for uncertainty evaluation.
- CRM
- Interlaboratory

29

Key players

- Measurement service providers
  - NMI
  - National labs
  - Reference labs
  - Quality control labs
- National accreditation bodies
- Organization for education & training

30

Metrology in chemistry

Comparison btw chemistry & phyiscs		
	Physics	**Chemistry**
Measurement	Quantity e.g tempt	Quantity of analyte, eg DDT in milk
Units	m, s, K	Mol/l, mg/Kg
Influenced by	Direct measurements	Various factors
Major Impact	Equipment calibrations	Chemical measurements
Depended on	Sample independent	Sample dependant
Example	Length of table	Conc. Pb (eg blood)

31

Chemistry in SI
It is quite new!

- Amount of substance (AoS)
- Agreed on 1971
- Mole (mol)

32

Progress in development of metrology in chemistry

- BIPM- CCQM (consultative committee on quality of materials)
- EURACHEM &CITAC- GUM
- ISO/IEC 17025:199

33

Consultative Committee for Amount of Substance CCQM - Metrology in Chemistry

- Established by the CIPM in 1993
- About 40 member and observer organizations (NMIs, Designated Institutes and others)

Functions:

- Primary methods for measuring amount of substances
- International comparisons
- Establishment of international equivalence between national laboratories
- Advice to CIPM on matters concerned with metrology in chemistry

34

CCQM – Metrology in Chemistry

CCQM Working Groups

• Key Comparisons and CMC Quality	NMIA	L. Mackay
• Organic Analysis	NIST	W. May
• Inorganic Analysis	LGC	M. Sargent
• Gas Analysis	NPL	M. Milton
• Electro-chemical Analysis	SMU	M. Mariassy
• Surface Analysis	BAM	W. Unger
• Bio-Analysis	LGC	H. Parkes

35

Traceability

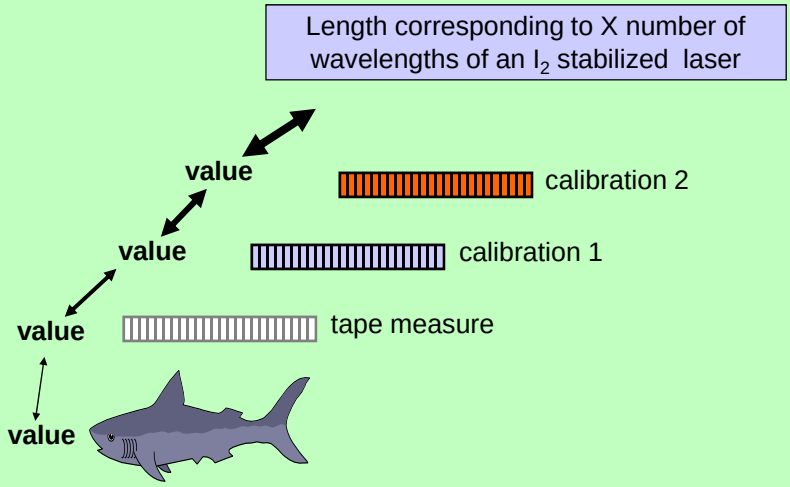
Key: Reliability of result to be traceable to stated reference through unbroken chain of comparisons all having stated uncertainties. *(VIM, 3rd edition)*

To establish & demonstrate traceability

- Specify measurand & model equation
- Choose measurement procedure
- Validate methods
- Choose reference standard
- Estimate uncertainty

36

Traceability of Length Measurements



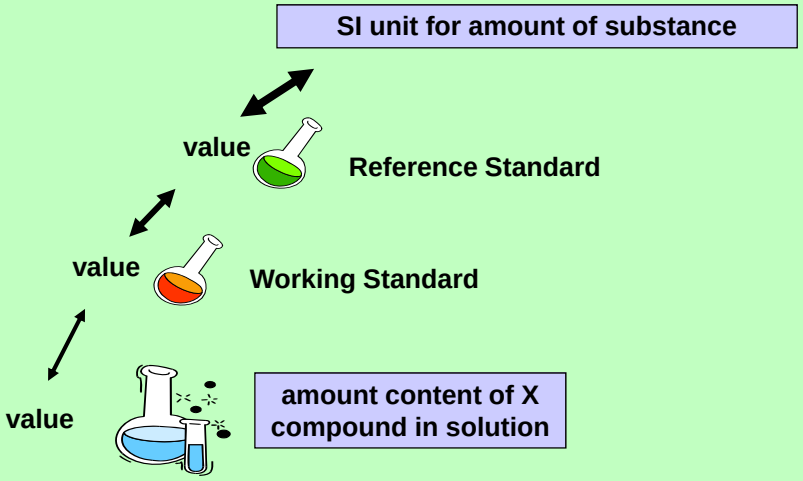
37

analytical measurements
need to be comparable
in time and space

traceability is the best
way to achieve this

38

Traceability of Chemical Measurements



39

Problems...

- Absence of reference standards
- Absence of links to common basis
- Appropriate use of standards by laboratories
- Appropriate use of uncertainty

40

stated references

stated uncertainty

41

Stated References – 3 different

- In VIM 3 examples of different stated references are given
  - A measurement unit (VIM 1.9), e.g. mol/l, °C
  - A measurement standard (VIM 5.1), e.g. the certified reference material SRM 2193, a $CaCO_3$ pH standard.
  - A measurement procedure (VIM 2.6), e.g. ISO 1736:2008 Dried milk … - Determination of fat content.
  - Determination of amount of substance requires in most cases measurements of different properties
    - Sample mass — mass reference – measurement unit
    - Analyte identity — pure material – measurement standard
    - Molar or Atomic weight — published data or measured

42

Several References for one measurand

*For **measurements** with more than one **input quantity in the measurement model,** each of the input **quantity values** should itself be metrologically traceable...*

NOTE 4 in VIM on Traceability

Example: Mercury in tuna fish (with a AAS after microwave digestion)

Measurement result: 4.03 ± 0.11 mg/kg, reported as total Hg on dry weight basis (105 ºC, 12 h)

Traceability has to be demonstrated for:

- Mass concentration of the Hg solution **1.00 g/l Hg** - a CRM certificate
- mass of sample **0.5 g** - calibration certificate of the balance
- volume of volumetric flask **100 ml** - calibration certificate
- drying temperature **105°C** - calibration of oven
- drying time **12 h** - ordinary clock or stopwatch
- Microwave digestion conditions **0.5 h at 180 ºC** - check according to specifications

(from Eurachem Traceability leaflet – www.eurachem.org)

43

Stated references

Quality	Analyte	Measurand	Unit	Stated reference
Conc	DDT	Conc. of DDT	ng/l	SI
Content	Pb	Conc	Mg/L	SI
pH	H^+	Conc. of H^+	pH unit	pH scale

44

Stated Uncertainty

- An interval around the measurement result
- The uncertainty budget including:
  - Uncertainties carried by the references
  - Uncertainties introduced by the measurement process

45

Stated Uncertainty

Usually the contribution of the uncertainties carried by the references to the total uncertainty is small relative to the contributions that originate from the measurement process

46

Reference Materials

- Values carried by reference materials should be traceable to other references
- The same features which are valid for the analytical laboratories are also valid for the reference materials producers

47

More Information

- www.bipm.org
- www.euramet.org
- www.citac.ws
- www.eurachem.org
- www.eurolab.org
- www.irmm.jrc.be
- www.nist.gov
- www.labnetwork.org

48

Things to Remember

- Metrology in chemistry is still "young"
- There is a lot to learn
- *Traceability is not an aim by itself but it helps achieving reliable results*
- *Traceability can only be claimed if uncertainty statement includes all the uncertainties from references and the measurement procedure*

49

What will you take for lunch?

- What will be the measurement quality of food?
  - -Color
  - - Raw meat
  - - bouquet, smell
  - - rare, medium, well cooked
  - - plain on your tongue, taste
  - - after-taste
- Need for “soft” metrology!!
  - - color
  - - taste
  - - smell
  - - glance

50

THANK YOU

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51