Securing the basis for making the right decision:

the correct understanding of measurement results in chemistry

Prof Dr Paul De Bièvre
Independent Consultant on Metrology in Chemistry
IUPAC Delegate to JCGM, and to JCGM – WG 2 (VIM)
IUPAC Delegate to CCQM

EURACHEM - EUROLAB DANMARK - LABQUALITY
KØBENHAVN-KØGE (DK)
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CENTRAL BUREAU
FOR
NUCLEAR
MEASUREMENTS
(now EC - IRMM)

COMPARABILITY
TRACE

IN MEASUREMENTS
OF AMOUNT OF SUBSTANCE

A WORKSHOP FOR EURACHEM COMMITTEE MEMBERS AND INVITEES

11 AND 12 NOVEMBER 1992

Organised at the request of
EURACHEM
A focus for analytical chemistry in Europe

Some replies to the request submitted by the organizers:

“right decisions”
based on measurement results in chemistry
require a “correct basis” for
measurement results

a “correct basis” for measurement results requires
“correct understanding” of
measurement results as well as of all essential
concepts related to the measurement concerned

“correct understanding “ of
measurement results in chemistry
requires *clearly defined concepts* in measurement
[i.e. it requires the elimination of CBUs
Conceptual Barriers to Understanding]

the 2008 International Vocabulary of Metrology -
Basic and General Concepts and associated terms
(VIM) edition 3
Guide JCGM 200:2008
[ISO / IEC Guide 99:2007]
www.bipm.org / en / publications / guides / vim.html

the 2010 IUPAC Recommendations on
“Metrological Traceability of Measurement Results in Chemistry

consistent translation of a term from one language into other languages used on the intercontinental scene is only possible under a basic condition:

one must
understand the concept behind the term
before
being able to translate the term

= justification for VIM 2008

One never gets the “truth” when measuring
(it requires a ‘reference’ to call something “true”)

but we can make a “model” of our best knowledge of what we think is “close to the truth” :

it is a quantity equation $Y = f(X_1, X_2, X_3, \ldots)$
called ‘measurement function’ (VIM3, entry 2.49) ;

simple example: $n = I \cdot t$

it relates an output quantity Y (the ‘measurand’) we intend to measure (2008 VIM definition), to one or more input quantities X_i which are subject to measurement (1993 definition of ‘measurand’)

The 19th / 20th century concepts 'true value' and 'error' are being abandoned

in the period 2 000 ± 10

in favour of

- the 'metrological traceability' of these results, and
- their 'measurement uncertainty'

'Metrological traceability' reveals us where the measurement result comes from by revealing the "trace" along which it comes to us

the times that we could "declare" a measurement result as a number times a unit without further explanation, are over

- **A measurement result now contains by definition the associated measurement uncertainty as a "measure of doubt" about that result**
- **the times that we could "declare" a measurement result without a measurement uncertainty, are over**

Metrological traceability is *decided* by the analyst before the measurement

thatt logically puts the analyst (back) in full charge -and responsibility- of the measured quantity value (not the statistician)

metrological traceability is a prerequisite to measurement uncertainty
hence, measurement uncertainty is dependent on a variety of *decisions*

measurement uncertainty is evaluated by the analyst after the measurement
(evaluation includes decisions because choices are involved)

it logically puts the analyst (back) in full charge -and responsibility- of the measurement uncertainty
(not the statistician)
because decisions must be made

There is news !

- **The good news:**
  there is now a new
  International Vocabulary of Metrology (“VIM”)
  which covers chemical measurement
  (that was not the case in 1984 (“VIM1”) and 1993 (“VIM2”)

- **The bad news:**
  everybody will have to go back to the workbench and study

- **But … the VIM is extremely helpful by clarifying and simplifying our thinking and our language**

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)

The revision of VIM2 (yielding VIM3):

4. uses the “substitution principle”:
   any concept used in the definition of another concept must be replaceable by the definition of that concept given elsewhere in VIM3
   (to make that clear, it is printed in bold)

5. uses GUM, even if the definition of some GUM concepts are already up for refinement in “GUM2”
   (which may be planned)

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The revision of VIM2 (yielding VIM3):

6. leads to improved internal consistency
7. will lead to improved consistency within and between ISO Guides and Standards
8. generates more clarity

   therefore better understanding

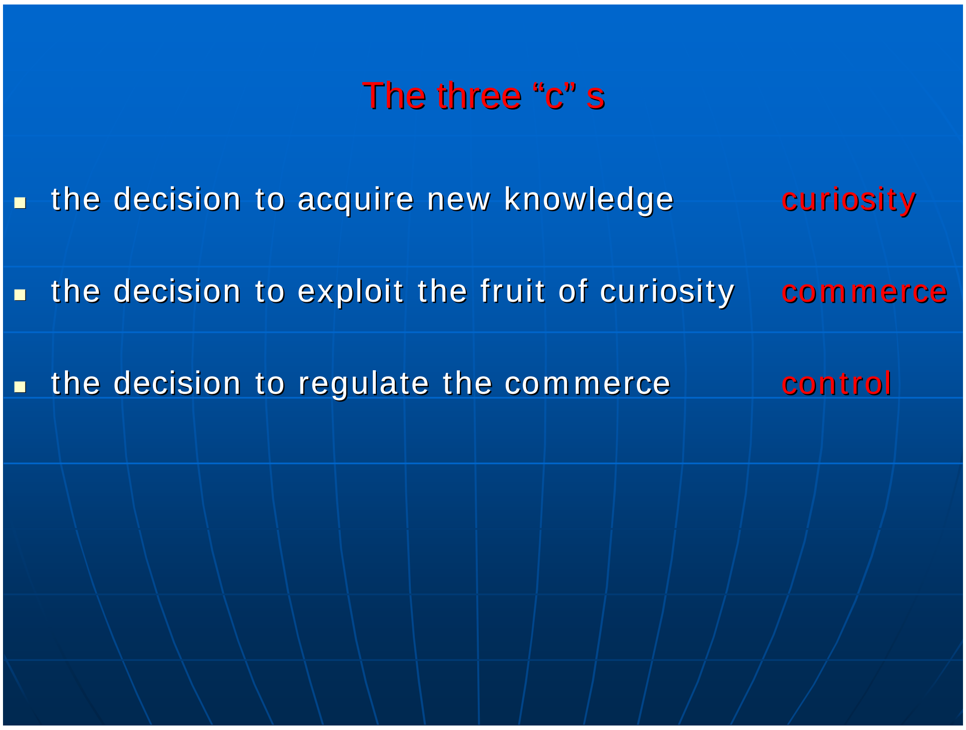
   ↓

   hence makes agreements possible

   in trade
   in implementation of EC Directives
   in mutual acceptance of measurement results

PDB2003043


Metrological principles
must be practicable:
there is no metrology
but
practical metrology
Paul De Bièvre
PDB00030
© P De Bièvre GEEL MAR 1999 2009: BANGKOK Mar


The three "c" s
the decision to acquire new knowledge
curiosity
the decision to exploit the fruit of curiosity
commerce
the decision to regulate the commerce
control

with sincere wishes
to all

for
good discussions!

2.2 metrology

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

2.3 measurand

2.3 **measurand**
quantity intended to be measured

- the English "quantity" is not the translation (anymore) from the French "quantite"
- "quantity" in English has become the translation of the French "grandeur de mesure"

- "amount" has become the translation of the French "quantite"
- the French "quantite" has now to be translated into the English "amount"

realizing an 'intention' implies taking a *decision*

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

similarly,
"fitness for *intended* use"
is henceforth used rather than
"fitness for purpose"

the choice of the measurand is a *decision*

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.
Examples : see VIM3

- Note 2 A reference can be a **measurement unit**, a **measurement procedure**, a **reference material**, or a combination of such

a decision

Warning:

don't confuse quantity and carrier of quantity

quantity	carrier
mass, diameter, height, density	metal cilinder, tree
velocity, wavelength, frequency, colour	electromagnetic wavelength (in the range 400-800 nm)
amount-of-substance, mass, density, pH value	NaCl solution, water in a container

Ref: U Feller METAS

PDB99122

2.3 measurand

- quantity we measure:
  e.g, length, mass, temperature, volume, pressure, amount concentration, mass concentration, mass fraction, electric current, …
- the specification of the measurand results from the intention of the analyst about what (s)he is going to measure
- **it is a *decision* made *before* the measurement**
- the measurand can be operationally defined, e.g.,
  leachable Cd concentration in a ceramic plate, measured according to a specified procedure

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

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)

Type B evaluation implies *decisions* by the analyst

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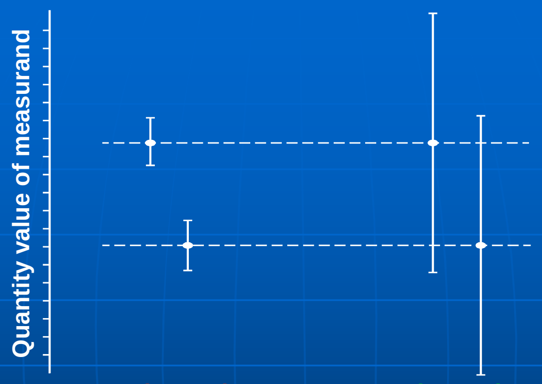
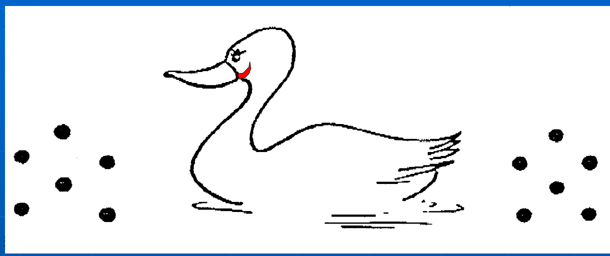


SAME MEASURAND IN SAME SAMPLE

Lab 1 and 2: DISCREPANCY PROBLEM

Lab 1 and 2: NO DISCREPANCY NO PROBLEM

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



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 to keep trying until a ***single shot*** hits the mark.

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

It is cheaper to perform less measurements,
fix a target measurement uncertainty, and
then have sufficiently small measurement uncertainty every time,

than making many measurements and use the average

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”

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The “culture” of statistics in chemical measurement, especially in Type A evaluation:

“culturing” the description of results
a posteriori

does only describe a result in terms of a distribution of a set of values
a posteriori

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“Life can only be
understood BACKWARDS
but it must be
lived FORWARDS”

S. Kierkegaard, Danish philosopher, 1813 – 1855

generating quality can only be done by the
analyst making *decisions*
before the measurement

this is a matter of logics, even chrono-logics

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**

A quantity value obtained by an operationally defined measurement procedure can be designated as a metrological ‘reference’

A designation implies *decisions* by the analyst

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
non-metrological reason such as:
- prestige
- politics
- commerce

this also applies to the (mis-) use of the concept
'**primary measurement standard**' (see further)

measurement procedure
"accepted" as a reference measurement procedure,
requires an agreement, hence a *decision*

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A measurement is almost never "absolute";
in extremely simplified terms, we could say that

it is a comparison of an unknown 'quantity value'
(embodied in a sample)
to a known 'quantity value'
(embodied in a 'measurement standard'):

the first link of a 'metrological traceability chain' is thereby born

we use the known 'quantity value' carried by
(embodied in) the 'measurement standard'
(usually called 'CRM' in common parlance)
to calibrate our 'measuring system'
hence a better term for this 'measurement standard' is 'calibrator'

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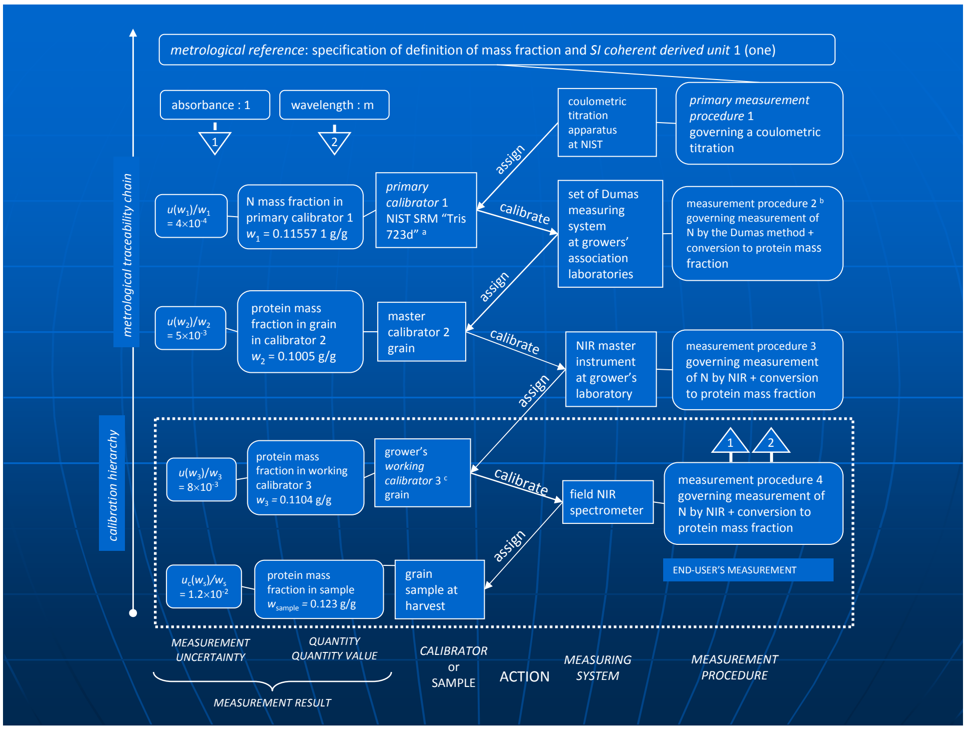

- a measurement method has no fixed, i.e. constant, measurement uncertainty, but a specified reference measurement procedure has

- a measurement procedure contains a detailed description depending on its *intended use* as a:
  - "reference measurement procedure", or as a
  - "primary measurement procedure" (see further)

- a measurement procedure enables to introduce the concept of "target measurement uncertainty" (tmu) as a measure of "*fitness for intended* use" of the measurement result

a target measurement uncertainty is *decided*

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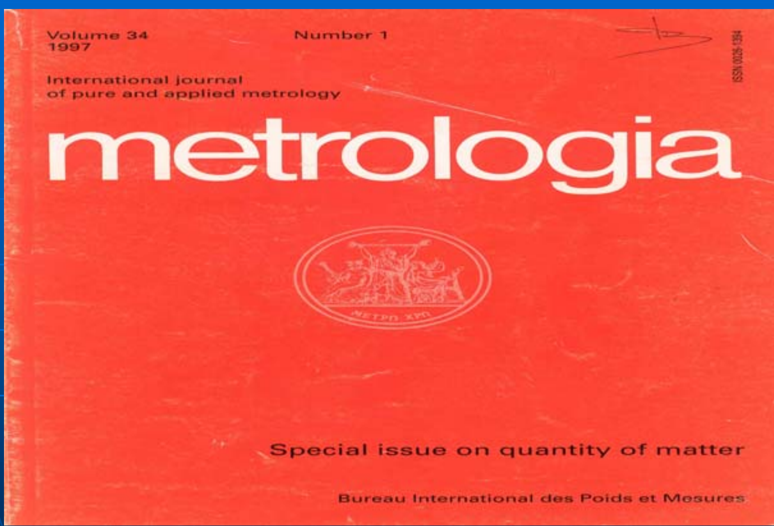
- **Impressive example of ambiguous terminology**



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1.9 measurement unit

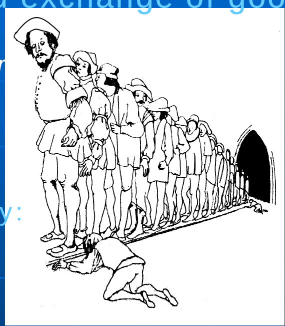
real scalar quantity, defined and adopted by convention, with which any other quantity of the same **kind** can be compared to express the ratio of the two quantities as a number

- …
- …
- Note 3 Measurement units of quantities of dimension one are numbers. In some cases these measurement units … are expressed by quotients such as millimole per mole equal to 10-3 and microgram per kilogram equal to 10-9.

…

the choice of a measurement unit is a *decision*

Units for measurement used to take man as "reference" and were created for commerce and exchange of goods



"Es sollen sechtzehn Mann, klein und grosz, wie sie so ungefehrlich aus der Kirchen gehen, ein jeder vor den anderen seinen Schuch stellen. Dieselbigen Lenge ist, und soll seyn, ein gerecht gemyn Messrute" (Konventionalfestlegung).
Jacob Klögel, Staatsschreiber in Oppenheim, 1575.

Grand Duchy of Baden, end of the 18th century:

- 112 different ells
- 163 different grain masses
- 80 different weights

→ chaos, fraud → Governments, in science and commerce demanded a unified measurement system in the 18th century

"Es ist bey uns nicht so wie in grossen Königreichen, wo die weite entfernung der provinzen alle neuen einrichtungen fast unmöglich machet: Mit geringer mühe könnte in unseren gränzen nur eine Maass, eine Elle, ein Gewicht, eingefürt werden".
"Beschreibung der Gewichten und Maassen der Stadt Bern", 1770.
source: U Feller EAM

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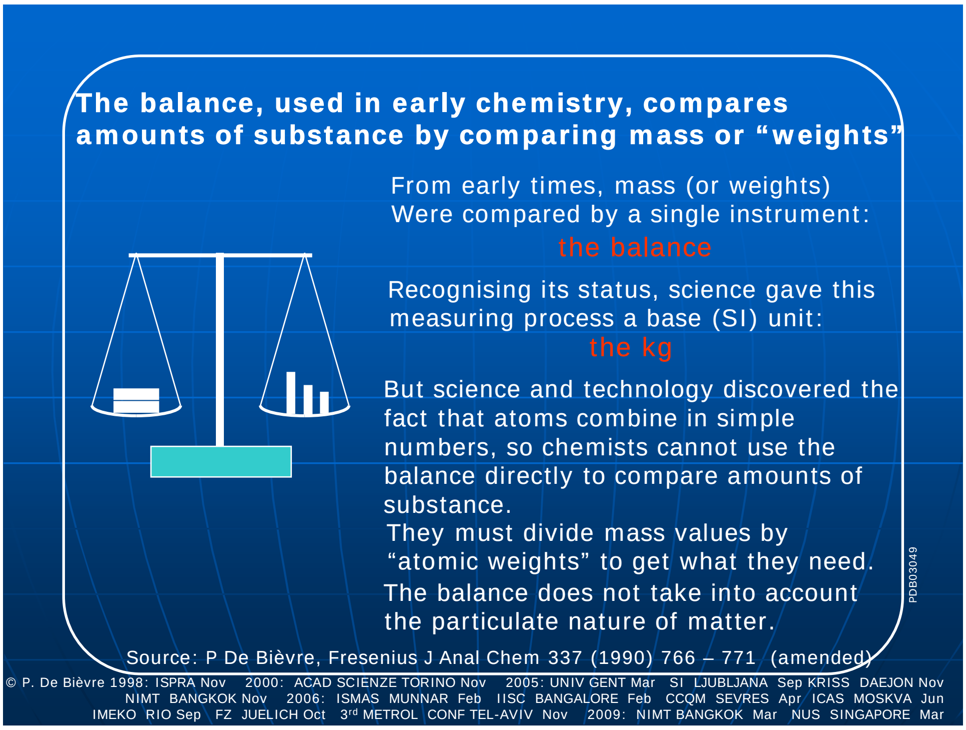
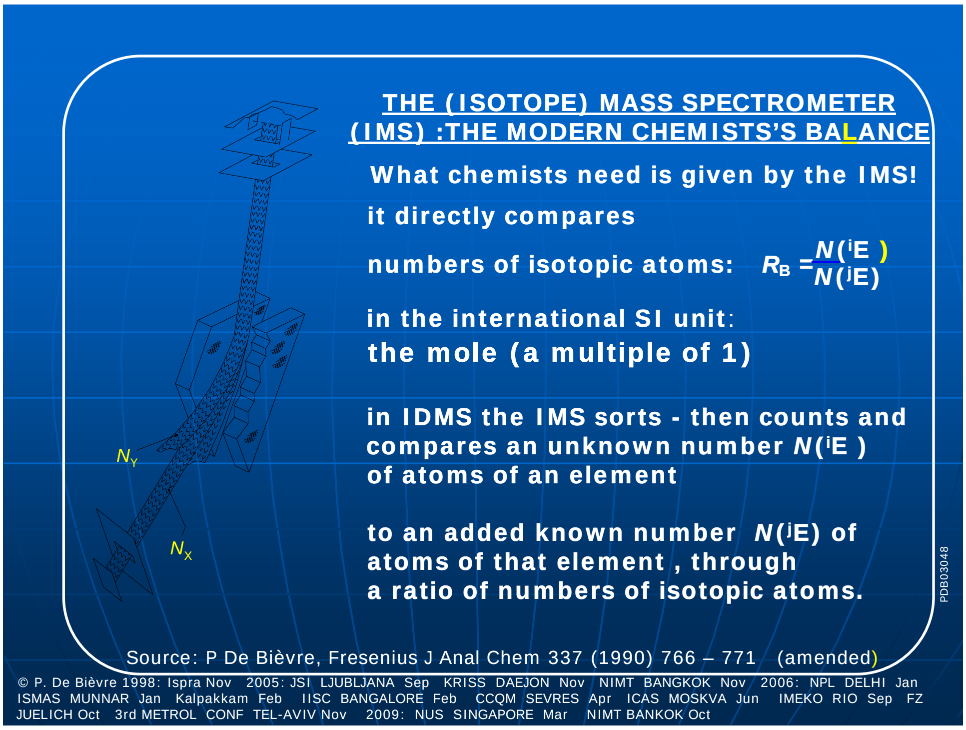

The balance, used in early chemistry, compares amounts of substance by comparing mass or "weights"
From early times, mass (or weights)
Were compared by a single instrument:
the balance
Recognising its status, science gave this measuring process a base (SI) unit:
the kg
But science and technology discovered the fact that atoms combine in simple numbers, so chemists cannot use the balance directly to compare amounts of substance.
They must divide mass values by "atomic weights" to get what they need.
The balance does not take into account the particulate nature of matter.
PDB03049
Source: P De Bièvre, Fresenius J Anal Chem 337 (1990) 766 – 771 (amended)
© P. De Bièvre 1998: ISPRA Nov 2000: ACAD SCIENZE TORINO Nov 2005: UNIV GENT Mar SI LJUBLJANA Sep KRISS DAEJON Nov NIMT BANGKOK Nov 2006: ISMAS MUNNAR Feb IISC BANGALORE Feb CCQM SEVRES Apr ICAS MOSKVA Jun IMEKO RIO Sep FZ JUELICH Oct 3rd METROL CONF TEL-AVIV Nov 2009: NIMT BANGKOK Mar NUS SINGAPORE Mar


THE (ISOTOPE) MASS SPECTROMETER
(IMS) :THE MODERN CHEMISTS'S BALANCE
What chemists need is given by the IMS!
it directly compares
numbers of isotopic atoms: $R_B = \frac{N(^iE)}{N(^jE)}$
in the international SI unit:
the mole (a multiple of 1)
in IDMS the IMS sorts - then counts and compares an unknown number $N(^iE)$ of atoms of an element
to an added known number $N(^jE)$ of atoms of that element , through a ratio of numbers of isotopic atoms.
N_Y
N_X
PDB03048
Source: P De Bièvre, Fresenius J Anal Chem 337 (1990) 766 – 771 (amended)
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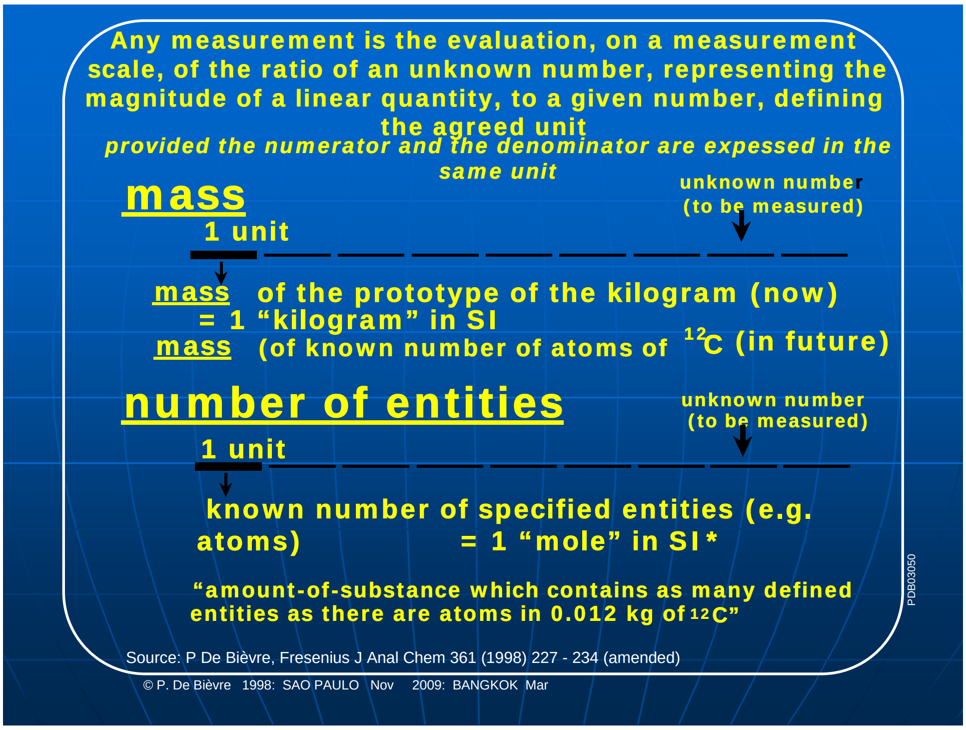
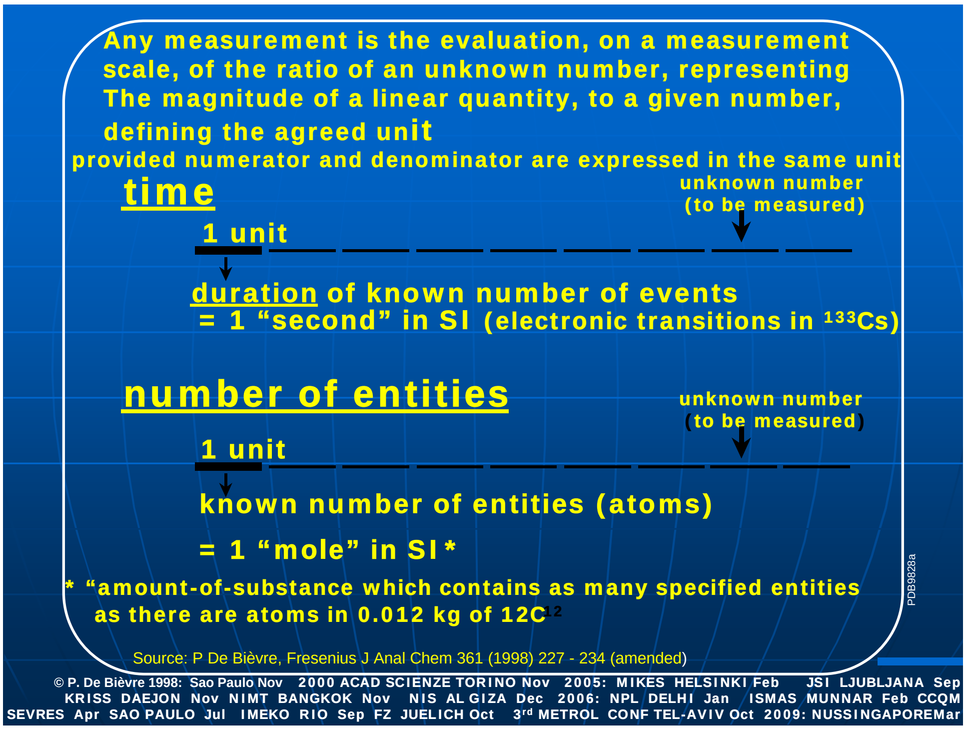

Any measurement is the evaluation, on a measurement scale, of the ratio of an unknown number, representing the magnitude of a linear quantity, to a given number, defining the agreed unit
provided the numerator and the denominator are expessed in the same unit
mass
unknown number (to be measured)
1 unit
mass of the prototype of the kilogram (now) = 1 “kilogram” in SI
mass (of known number of atoms of 12C (in future)
number of entities
unknown number (to be measured)
1 unit
known number of specified entities (e.g. atoms) = 1 “mole” in SI *
“amount-of-substance which contains as many defined entities as there are atoms in 0.012 kg of 12C”
PDB03050
Source: P De Bièvre, Fresenius J Anal Chem 361 (1998) 227 - 234 (amended)
© P. De Bièvre 1998: SAO PAULO Nov 2009: BANGKOK Mar


Any measurement is the evaluation, on a measurement scale, of the ratio of an unknown number, representing The magnitude of a linear quantity, to a given number, defining the agreed unit
provided numerator and denominator are expressed in the same unit
time
unknown number (to be measured)
1 unit
duration of known number of events = 1 “second” in SI (electronic transitions in 133Cs)
number of entities
unknown number (to be measured)
1 unit
known number of entities (atoms)
= 1 “mole” in SI *
* “amount-of-substance which contains as many specified entities as there are atoms in 0.012 kg of 12C12
PDB9828a
Source: P De Bièvre, Fresenius J Anal Chem 361 (1998) 227 - 234 (amended)
© P. De Bièvre 1998: Sao Paulo Nov 2000 ACAD SCIENZE TORINO Nov 2005: MIKES HELSINKI Feb JSI LJUBLJANA Sep
KRISS DAEJON Nov NIMT BANGKOK Nov NIS AL GIZA Dec 2006: NPL DELHI Jan ISMAS MUNNAR Feb CCQM
SEVRES Apr SAO PAULO Jul IMEKO RIO Sep FZ JUELICH Oct 3rd METROL CONF TEL-AVIV Oct 2009: NUSSINGAPOREMar

$$\frac{m\,(A)\,/\,m\,(kg)}{m\,(B)\,/\,m\,(kg)} = \frac{m\,(A)}{m\,(B)}$$

mass values of samples of material X and Y are comparable because measured in the same unit

kg

[note that numerator and denominator being ratio-ed to the same unit, leads to a numerical value with unit one]

$$\frac{N\,(E,A)}{N\,(E,B)} = \frac{N\,(E,A)\,/\,N_A}{N\,(E,B)\,/\,N_A} = \frac{n\,(E,A)}{n\,(E,B)}$$

numbers of a specified entity, here of element E, in materials A and B, are comparable because measured in number *N* of specified entity (same unit one) or in same “bunch” of entities (same unit mol)

Source: P De Bièvre, Fresenius J Anal Chem 361 (1998) 227 - 234

Elements (symbol E) :

$$\frac{N\,({}_iE)}{N\,({}_jE)} = \frac{K\,({}_iE^+)}{K\,({}_jE^+)} \cdot \frac{I\,({}_iE^+)}{I\,({}_jE^+)} = K\,({}_iE^+, {}_jE^+) \cdot r\,({}_iE^+, {}_jE^+)$$

$$R_{i,j} = K_{i,j} \cdot r_{i,j}$$

Compounds (symbol Cp) :

$$\frac{N\,({}_iCp)}{N\,({}_jCp)} = \frac{K\,({}_iCp^+)}{K\,({}_jCp^+)} \cdot \frac{I\,({}_iCp^+)}{I\,({}_jCp^+)} = K\,({}_iCp^+, {}_jCp^+) \cdot J\,({}_iCp^+, {}_jCp^+)$$

$$R_{i,j} = K_{i,j} \cdot r_{i,j}$$

Isotopes (symbol ${}^iE$) :

$$\frac{N\,({}^iE)}{N\,({}^jE)} = \frac{K\,({}^iE^+)}{K\,({}^jE^+)} \cdot \frac{I\,({}^iE^+)}{I\,({}^jE^+)} = K\,({}^iE^+, {}^jE^+) \cdot J\,({}^iE^+, {}^jE^+)$$

$$R_{i,j} = K_{i,j} \cdot r_{i,j}$$

We transform the problem of the measurement of a difficult-to-measure quantity (a number ratio) into the measurement of an easy-to-measure quantity (an electric current ratio); the conversion factor *K* must be measured and its measurement uncertainty evaluated.

measurements of mass use
a property of matter called '*inertia*'
this property is *not substance-specific*

measurements of amount use
a property of matter called '*numerosity*'
this property is *substance-specific*

in addition:

most of our analytical measurement procedures and measurement equipment , is based on the use of the property of matter called '*numerosity'*
this property is *substance specific*

The choice of the property of matter (inertia or numerosity) which we will use as basis for our choosing the measurement unit for a measurement,
is a *decision*

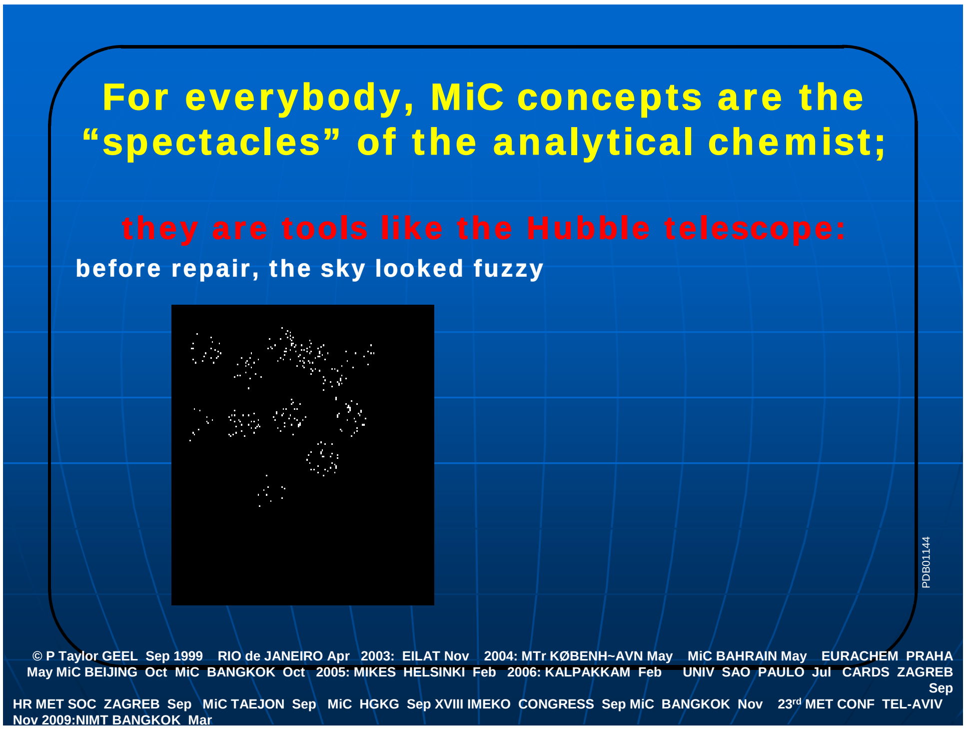
All these *decisions* are to be made

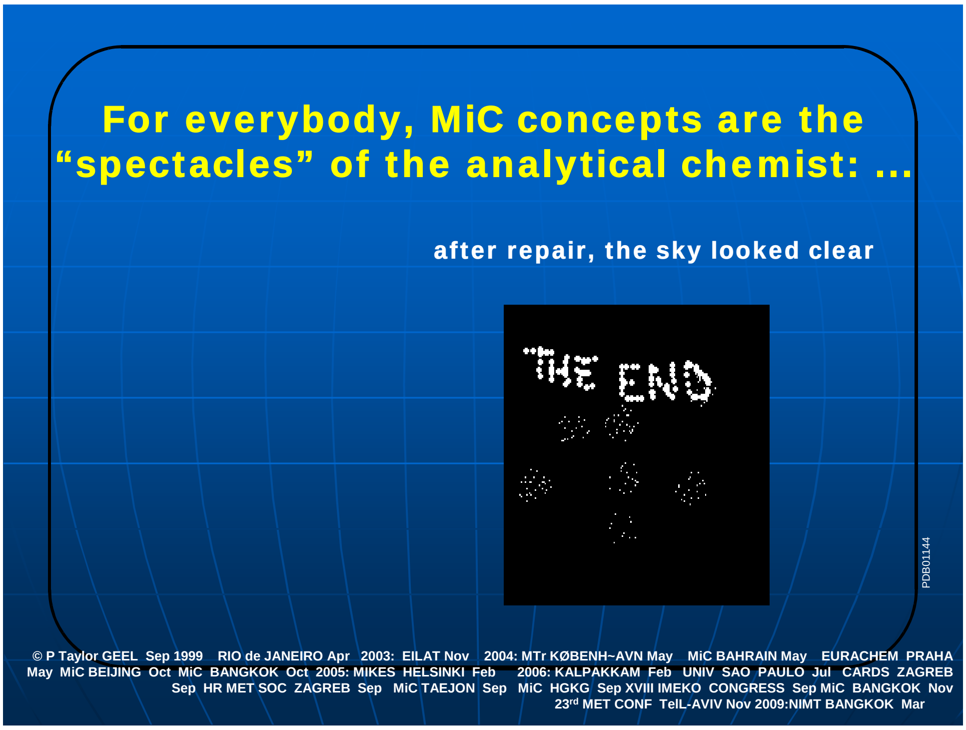
in function of the intended use of the measurement result

this intended use follows from

- **the identification of the needs we decide to investigate**

- **the identification of the problems we set ourselves to solve**


For everybody, MiC concepts are the “spectacles” of the analytical chemist;
they are tools like the Hubble telescope:
before repair, the sky looked fuzzy
PDB01144
© P Taylor GEEL Sep 1999 RIO de JANEIRO Apr 2003: EILAT Nov 2004: MTr KØBENH~AVN May MiC BAHRAIN May EURACHEM PRAHA May MiC BEIJING Oct MiC BANGKOK Oct 2005: MIKES HELSINKI Feb 2006: KALPAKKAM Feb UNIV SAO PAULO Jul CARDS ZAGREB Sep HR MET SOC ZAGREB Sep MiC TAEJON Sep MiC HGKG Sep XVIII IMEKO CONGRESS Sep MiC BANGKOK Nov 23rd MET CONF TEL-AVIV Nov 2009:NIMT BANGKOK Mar


For everybody, MiC concepts are the “spectacles” of the analytical chemist: …
after repair, the sky looked clear
THE END
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