Counting and why it is different from amount of substance

CCU/CCQM Workshop on
"The metrology of quantities which can be counted"
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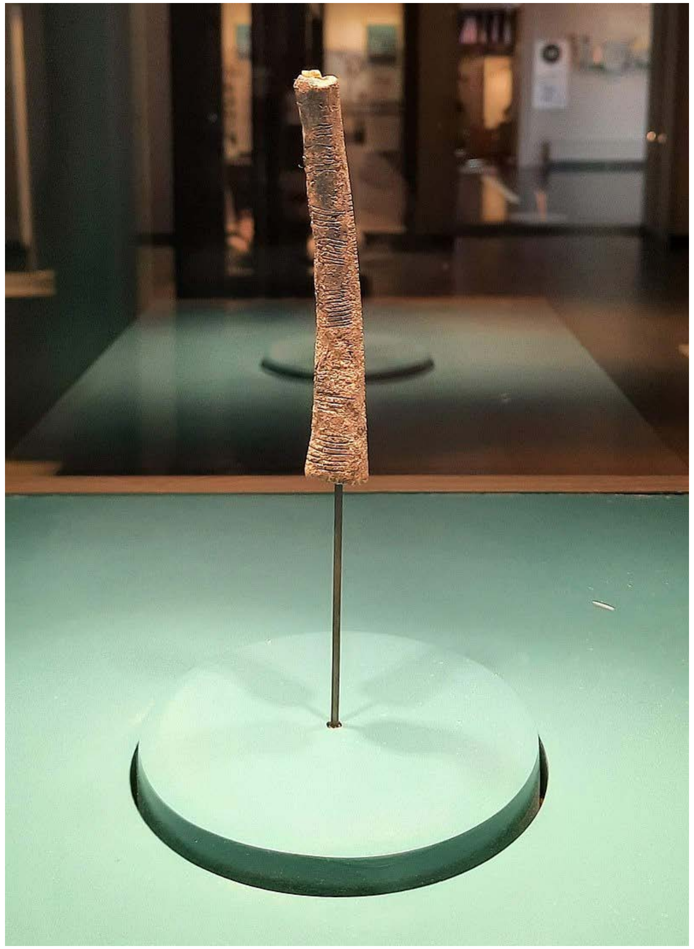
Counting

- Hugely important milestone in human development
- Arguably the first ‘measurement’ process

- Until recently outside formal metrology structures perhaps because of a distinction between:
  - Measurement as a process and a measurement result
  - Countable aggregates and continuous quantities

- Redefinition of the mole brought counting into sharper focus

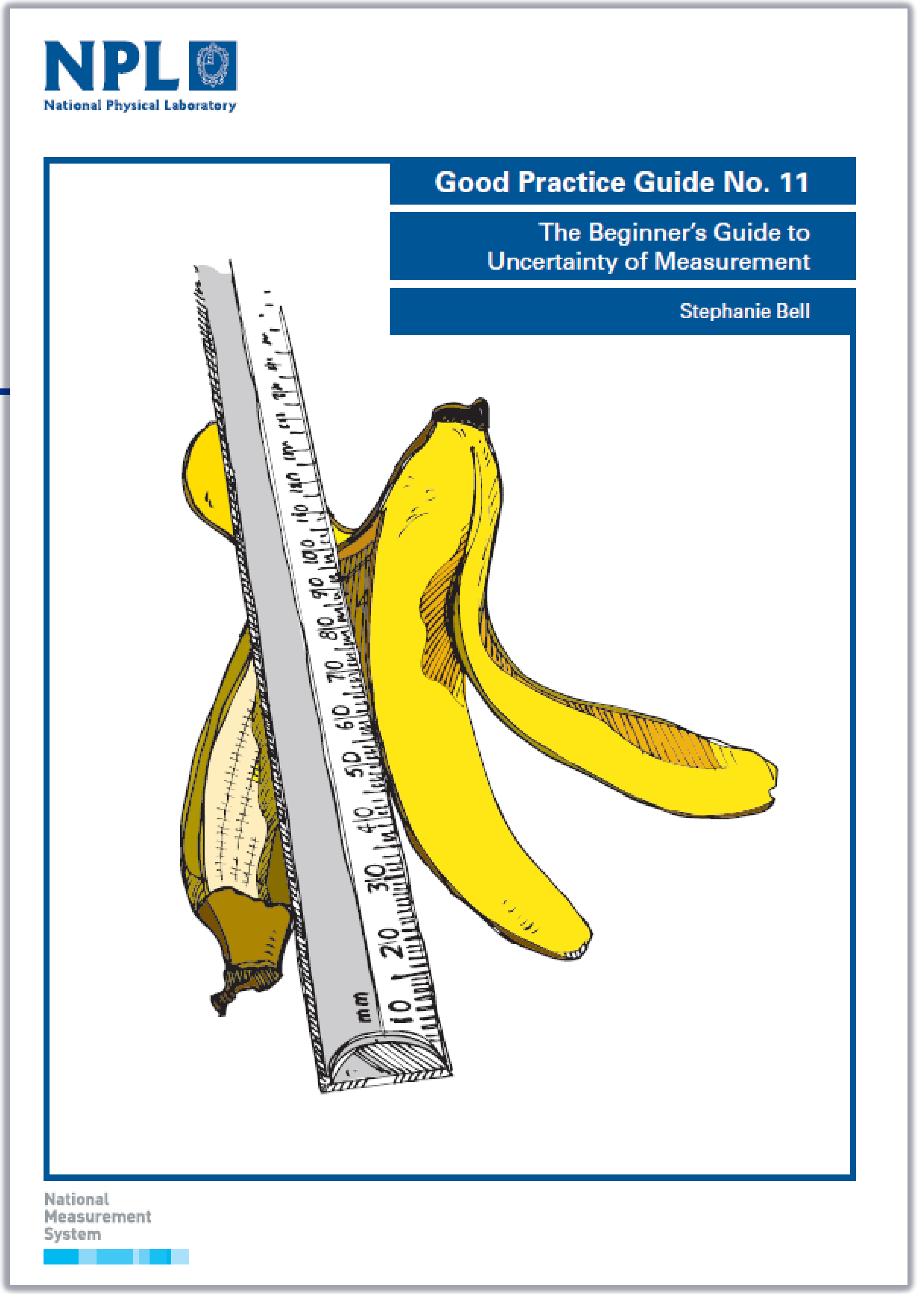


The 22 000 year-old Ishango bone

Thinking has developed since 2000

“What is not a measurement?
There are some processes that might seem to be measurements, but are not. […] Counting is not normally viewed as a measurement.”

- We now see counting as a measurement process & understand it can fit into the structures of metrology
- But we don’t have clear agreement on nomenclature
- Confusion between processes (counting) and quantities (number)
- The lack of descriptive ‘units’ remains a challenge, especially for digitalisation

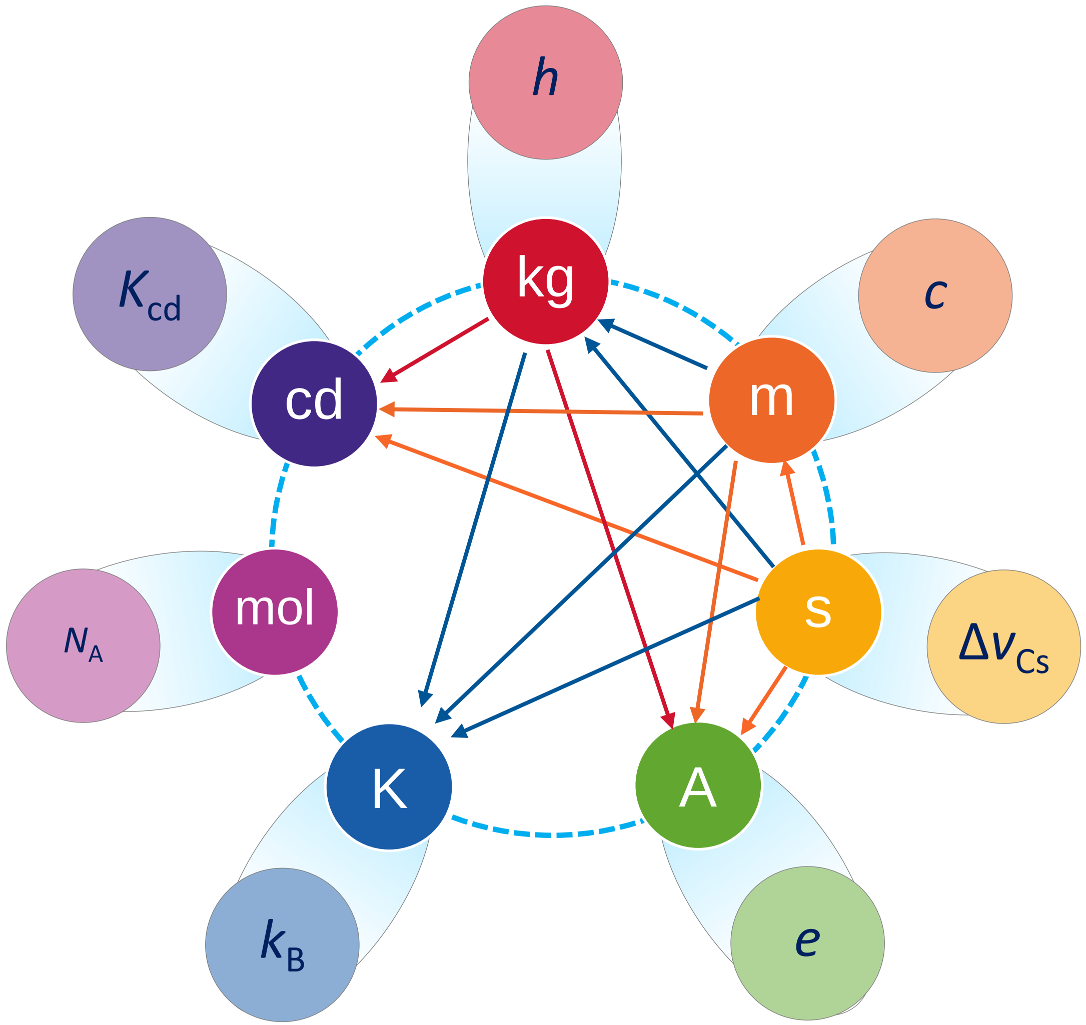


Counting / number is essential in the SI

- Counting / number underpins the definitions of the second and the mole
- The defining constant $\Delta\nu_{Cs}$ is the constant of proportionality (or 'concept synthesizer') between time and number (of transitions)
- Similarly, N_A is the constant of proportionality between amount of substance (AoS) and number (of elementary entities)

$$\boxed{n = N / N_A}$$

- It is <u>useful for practical measurement</u> that mol, K and cd have independent dimensions within the SI (and different from number)



XLIX. *Units and Dimensions* *.

By E. A. Guggenheim, M.A., Sc.D.‡

[Received March 24, 1942.]

1. *Preamble.*

There would be little point in referring to all the articles and books which I have read on the subject under discussion, and still less in referring to those which I have not read. The striking feature of the subject is that it has remained controversial for so long. I am convinced that the main reason for this is loose terminology, and my object is to indicate how the greater part of the controversial matter, if not all of it, can be eliminated by a carefully chosen terminology and notation.

One of the leading physicists of the nineteenth century is sometimes quoted as having said that one can multiply together only numbers and that the idea of multiplying one length by another length is nonsense. I have not troubled to check exactly what he said, since I consider it a matter of small importance. We are under no obligation to accept as valid today any statement, however eminent the author, dating from an epoch when Newton's ideas on the motion of matter were regarded as sacrosanct, while his ideas on the propagation of light were with equal conviction rejected out of hand as wrong.

I adopt the opposite attitude that we are entitled to muitiply together any two entities, provided our definition of multiplication is self-consistent and obeys the associative and distributive laws. Whether this extended conception of multiplication is useful or not is another question. In point of fact mathematicians find it profitable to multiply by one another, not only ordinary numbers, but also complex numbers, vectors, tensors, matrices, Dirac's q-numbers and various other entities §. It is likewise perfectly legitimate to multiply together any two physical entities, such as a length and a force. If the reader naïvely asks: "What, then, is the product of a foot and a pound?", I reply a "foot-pound". In case he suggests that this reply is unsatisfactory, I would point out that when a quarter is multiplied by three the product is "three-quarters", and when π is multiplied by $\sqrt{3}$ the product is $\sqrt{3}\pi$, and no simpler answer is possible.

* This article was written by request as the outcome of a discussion held by the Physical Society on February 6, 1942.

‡ Communicated by the Author.

§ The multiplication may or may not obey the commutative law. In the multiplication of physical scalar quantities in classical theory the commutative law is obeyed.

Early identification that amount of substance and number might be usefully distinguished

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"…for special problems it may be advantageous to increase the number of fundamental quantities above the usual number. It can sometimes be useful in dimensional analysis to regard the number of atoms as having dimensions different from a pure number"

E. A. Guggenheim (1942) Units and Dimensions, *Phil Mag*, **33**, 479-496

Why is counting a bit different?

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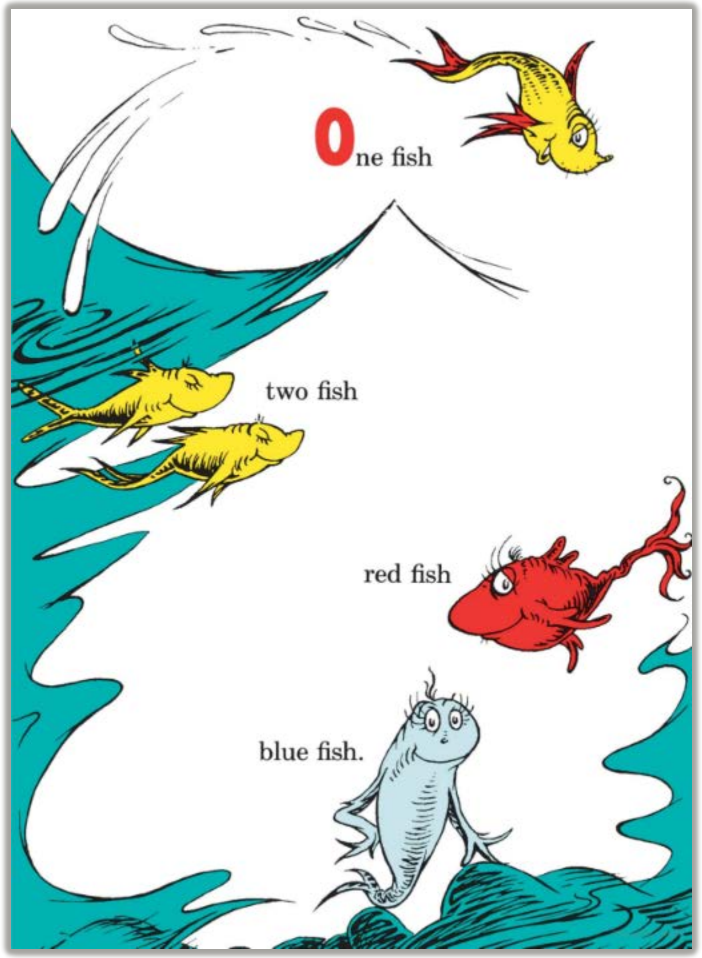
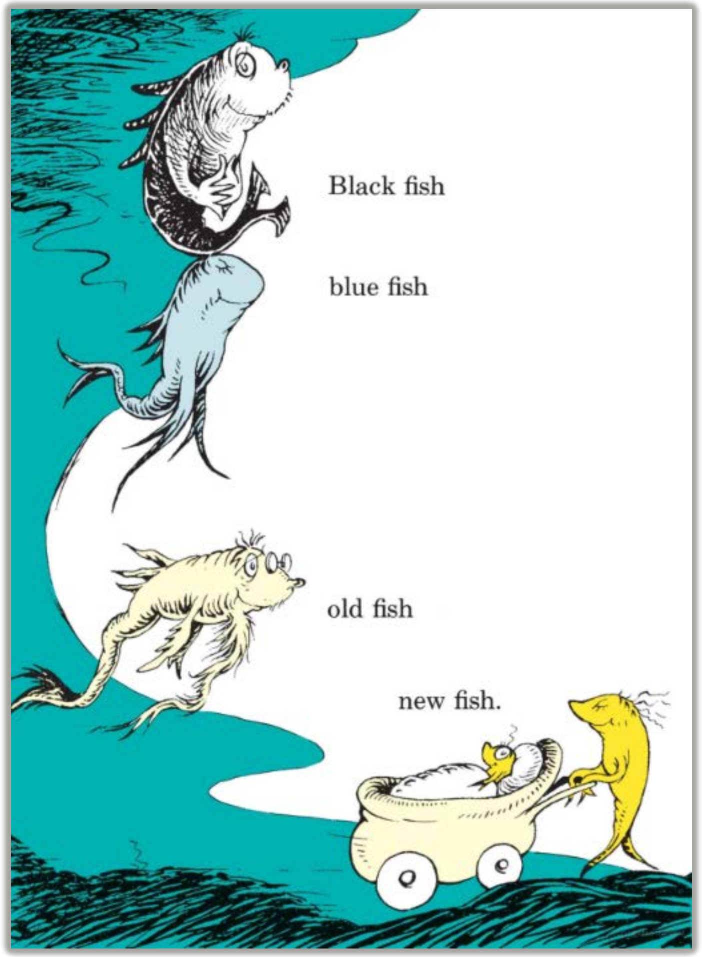
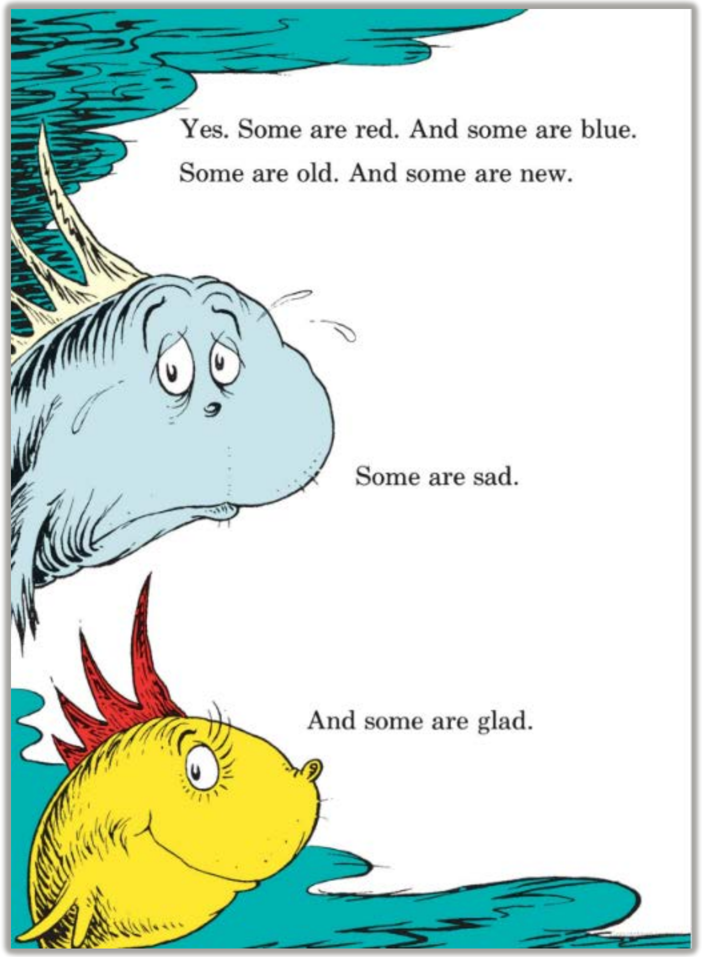






- Before we can count 'some things', we must decide what counts as 'something'!

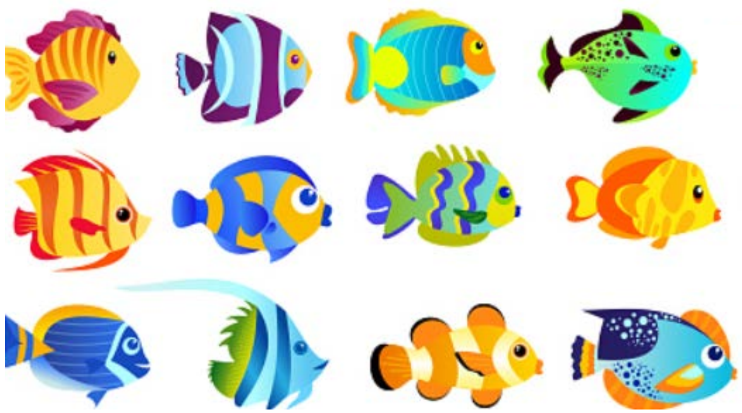
The problem of identity

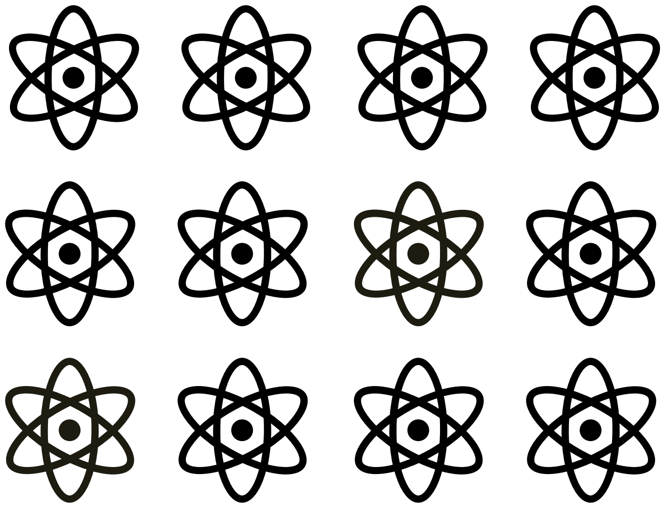
- A consideration for countable aggregates
- The generic ‘number’ and ‘amount of substance’ mean less than ‘length’

- Must sufficiently specify what is being counted
- ‘Number of fish’, ‘amount of substance of nickel’

- ‘Number of fish’ requires elaboration (sad, old, red…) in a way that ‘nickel’ does not
- Elaboration via <u>documentary standardization</u> (method-defined measurands)

number





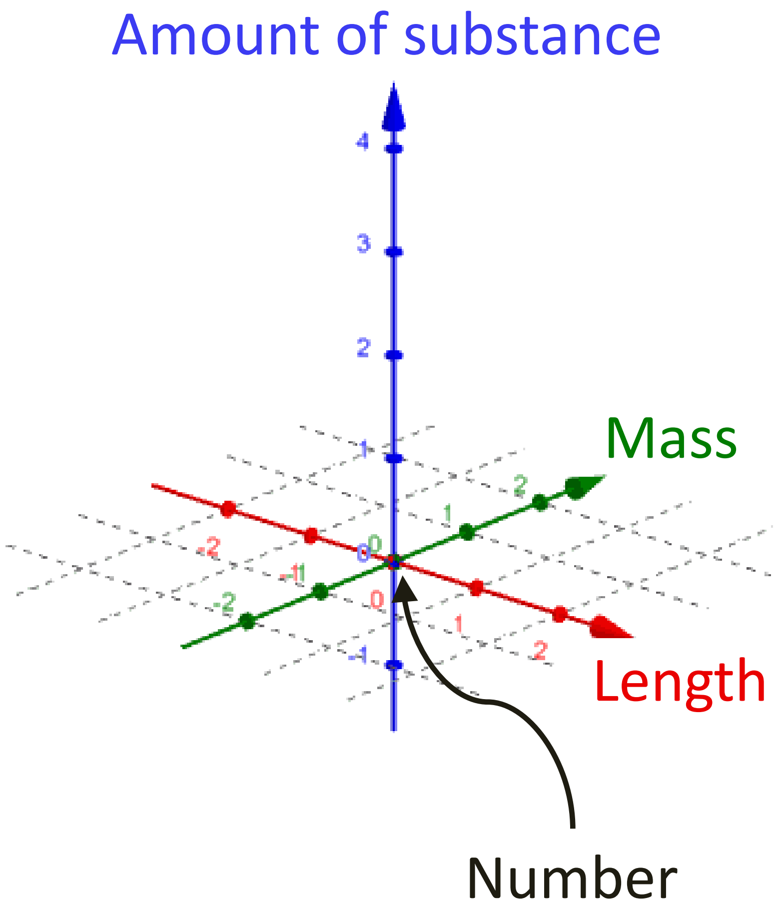
amount of substance

Why can we not have a mole of fish?

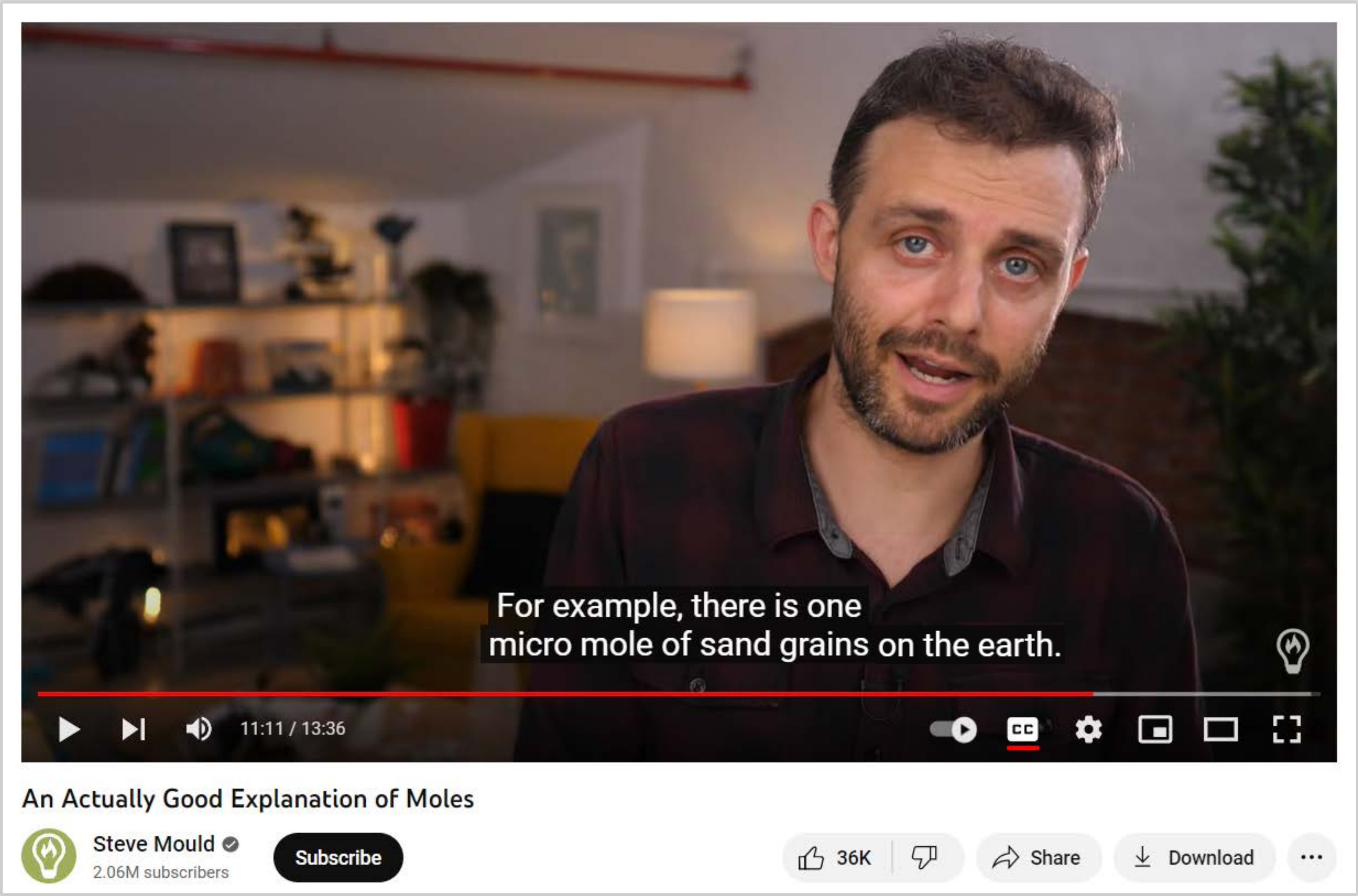
- 14th CGPM (1971) agreed the mole as the 7th SI base unit
- Distinguished intensive & extensive quantities in chemistry
- Brought chemistry formally within the SI – equating microscopic and macroscopic stoichiometry

- Gave amount of substance its own dimension
- Basis for distinguishing between AoS & number (of elementary entities)
- The mole is not just a name for a large number

- The redefinition of the mole was a reminder of these issues



We cannot have a mole of sand grains or eggs either…



We cannot have a mole of sand grains or eggs either…

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Metrology for Society's Challenges / SI redefinition / Countdown SI redefinition / The mole

UNIT OF THE MONTH APRIL 2019: MOLE

THE SI UNITS

[3] With 1 mol of eggs you could stack 100 layers of densely packed eggs on the sun. This is of course only a thought experiment! There would be many difficult boundary conditions for the actual implementation. And a huge amount of scrambled eggs.

We cannot have a mole of sand grains or eggs either…

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20 APRIL 2019

Countdown to the SI redefinition: How long would it take to eat a mole of Easter eggs?

In case you missed it, the redefinition of the International System of Units (SI) is going into effect next month on World Metrology Day, 20 May 2019. Each month we are bringing you a blog post featuring one of the units of the SI. This month we are focusing on a unit that has particular significance to chemists and therefore, our scientists at the [redacted] the mole, the unit used to measure the (usually very large) number of things, usually atoms or molecules.

The key characteristics of the mole

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- We use the mole, rather than a count of molecules, because it is useful & meaningful
- Two parts of the definition are salient to this distinction

The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly 6.022 140 76 × 10^{23} elementary entities. This number is the fixed numerical value of the Avogadro constant, N_A, when expressed in the unit mol^{-1} and is called the Avogadro number.

The amount of substance, symbol *n*, of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles.

SI Brochure, 9th Edition

Elementary entities

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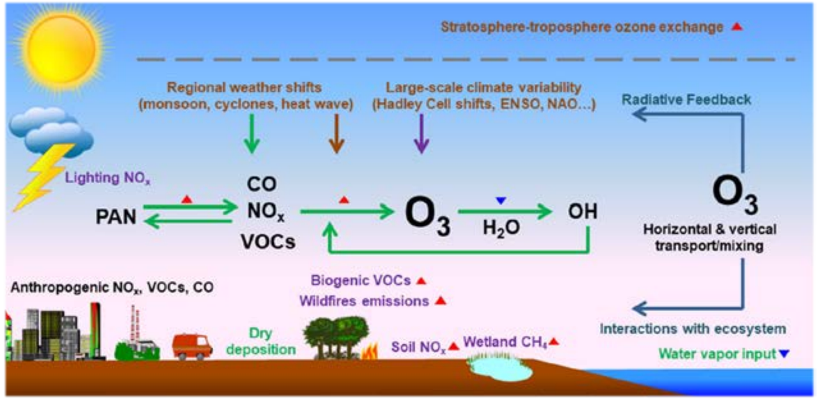
"Elementary entities": restricts the things that may be described to those that could take part in stoichiometric chemical reactions together and are sufficiently elementary that it is possible to define an identical set for the purpose of such a reaction

- Atoms, molecules, ions, electrons…
- <u>There is no identity consideration</u> – nickel atoms are identical (give or take isotopes, which may also be specified unambiguously)
- As molecules become larger, and chemistry moves into biology, there comes a point where it may be more expeditious to use number, mass or activity-based quantities

Of a system

“Of a system”: implies the elementary entities considered are located in close enough vicinity such that they could, in theory, react or interact with each other stoichiometrically

- A good example might be the gaseous composition of the troposphere
  - Reactions occur between these collections of molecules, relevant to state: the amount fraction of ozone is 30 nmol/mol



doi:10.1007/s40726-019-00118-3

- A bad example might be the presence of helium in the interstellar medium
  - Derives no benefit from the reasons the mole was introduced, better as: the number concentration of helium atoms is 100 m^{-3}

kipac.stanford.edu

Could we not still use a ‘count of molecules’?

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- A mole is used when it is <u>useful and meaningful</u> to consider elementary entities together, in a system
- Useful means that expression in amount of substance terms provides information or context to another property that is of interest
- Expressing as a count loses the benefits of the dimensionality of amount of substance
- Prefixes zepto and yocto were introduced to allow the mole to be used at very low amounts of substance rather than referring to molecules

5. Small numbers of entities

In cases where the number of entities being considered is small, quantities are commonly expressed as numbers of entities instead of amount of substance [5.1]. The Avogadro constant is the constant of proportionality that links amount of substance to the number of entities.

Mise en pratique for the definition of the mole in the SI, 2019

Considerations for counting / number

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communicate

- Number quantities have only one unit to express them ‘1’: we rely on a clear description of the quantity being described
- Standardizing nomenclature for number quantities & some ‘units’ downstream of the SI would be beneficial (especially for digitalization)

traceability

- Traceability does not require an etalon, established through appropriate, validated measurement procedures
- Problems with hierarchy as there is no ‘unit’ to curate and often no traceability to disseminate if ‘method defined’

ownership

- CIPM MRA can’t own all number quantities (unlike for all length quantities), but important number quantities should be identified for ownership
- The majority of these are likely to relate to chemical and biological measurement

What number quantities could the CIPM-MRA 'own' (c.f. CCQM discussion on 'method-defined' measurands)

- The measurand must be internationally agreed and specifically defined in the field of application
- The measurand must be a stable reference point in time and not dependent on a specific reference material
- The method, as applied at an NMI/DI, is considered the highest point of reference within a calibration hierarchy

R. J. C. Brown & H. Andres (2020)
Accred. Qual. Assur. **25**, 161-166


Accreditation and Quality Assurance (2020) 25:161–166
https://doi.org/10.1007/s00769-020-01424-w

DISCUSSION FORUM

How should metrology bodies treat method-defined measurands?

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Abstract
This discussion article explores how metrology bodies should approach method-defined measurands (also called operationally defined measurands). It begins by considering the different types of measurement that can be encountered and comparing their difference qualities, before discussing in more detail method-defined measurands and the nature of their current and future treatment by the global metrology system. The discussion highlights work performed within the Consultative Committee for Amount of Substance to address what should be within the scope of the International Committee for Weights and Measures Mutual Recognition Arrangement (CIPM-MRA) when method-defined measurands are considered and also how the metrology community can contribute to ensuring stability and comparability of these measurements outside the formal scope of the CIPM-MRA.

Keywords Method-defined · Measurand · Operationally defined · Metrology · Traceability

Introduction

Measurement types

The ISO 17034:2016 standard [1] defines a method-defined measurand (or operationally defined measurand) as a: "measurand that is defined by reference to a documented and widely accepted measurement procedure to which only results obtained by the same procedure can be compared". Sometimes these measurement procedures are referred to as empirical methods. This paper will consider the nature of these measurands and how they should be treated by our established metrology infrastructures, an aspect lacking from the few previous considerations of the topic [2, 3].

Method-defined measurands are almost exclusively considered in material, chemical and biological sciences, in part because of the very nature of these topics with analytes often contained within complex matrices requiring extraction, digestion or pre-concentration step prior to analysis. Indeed the complexity of these systems combined with the relatively recent (compared to physics) advent of formal metrology considerations in these area often leads to confusion between the SI traceability of results and the operationally defined nature of the measurands. In fact, these are almost entirely orthogonal considerations. Therefore, it is sensible first to consider the qualities of different quantities subject to measurement.

It is now widely accepted that a measurement result is not complete without an associated statement of uncertainty [4]. This estimate of uncertainty is important since it indicates the level of confidence in the measurement result produced and is an important indicator of whether the result is fit for purpose, meets quality guidelines or can be defensibly compared against limit or target values. Where possible, measurements should be traceable to the SI system of units and expressed in SI units with uncertainty statements generated from a well-understood measurement equation governing the measurement process, whose sensitivities to variations in the measurement process and other input parameters have been rigorously assessed. Under these conditions, measurement uncertainty estimates are relatively simple to produce and

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