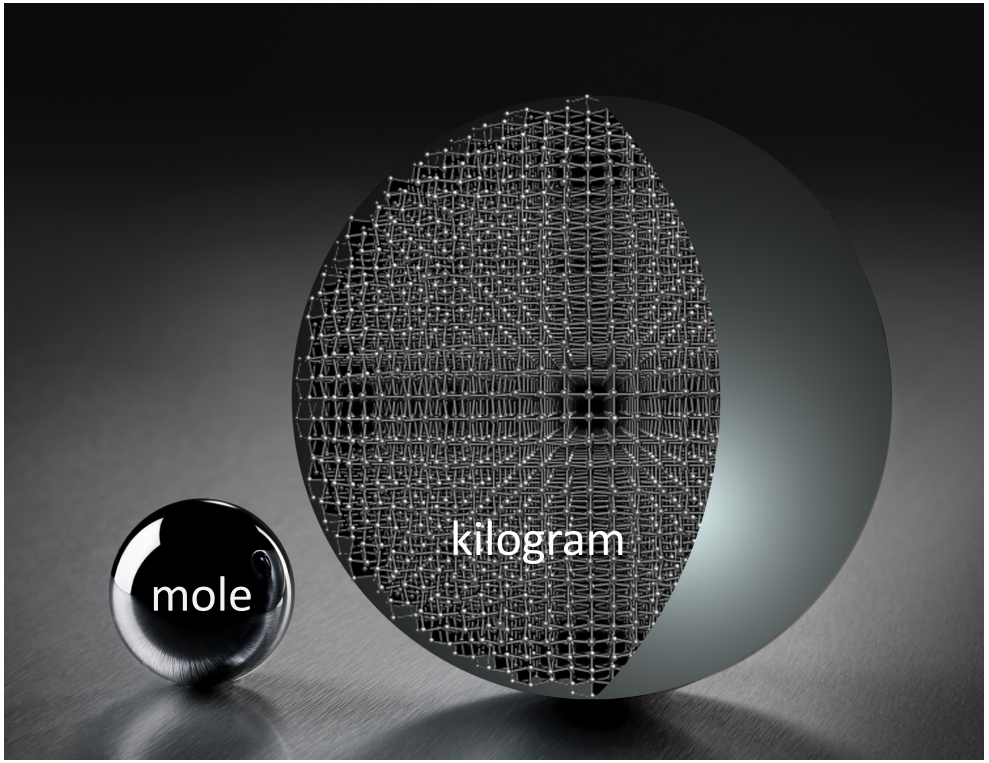
The metrology of quantities which can be counted

What questions is the workshop addressing:



What is counting?

Why do we count?

What do we count?

How do we count?

(How) can counting and measuring be equated?

Dr. B. Güttler
Physikalisch-Technische Bundesanstalt
Chair ad-hoc WG on the mole (CCQM, C[illegible])

CCU
CCQM

Why do we count (in metrology) **?**

Counting, either of single entities or of quantized processes and other phenomena, is of increasing importance in metrology, because:

- scientific and technical progress requires measurements to be made with an ever-increasing accuracy and sensitivity at very fine spatial resolutions or on extremely short timescales.
- Quantum- and nanotechnologies are approaching and, the needs of industry, health care, and the environment are requiring ever lower detection limits in chemical and biological measurement.
- the specific aspect of the new definition of the mole that has attracted great attention is its definition in terms of a number of entities – new for a definition of an SI base unit.

What is counting ?

Counting is the *process of determining the number of elements* of a finite set of objects.

Wikipedia

In a collection (or set) of objects (or elements), the *act of determining the number of objects present* is called counting.

Encyclopedia Britannica

The traditional way of counting consists of continually increasing a ..counter by a unit for every element of the set ...while marking (or displacing) those elements to avoid visiting the same element more than once, until no unmarked elements are left;

Wikipedia

What do we count?

Counting is increasingly applied whenever it comes to quantifying quantized measurands:

Entities: electrons, atoms, molecules
Processes: vibrations, radioactive decay,...

Counting may also be an appropriate tool for quantifying analogue quantities such as time and length

Essential (in metrology):
When the mole is used, the elementary entities must be specified.

When counting is used, it must be specified what is counted.

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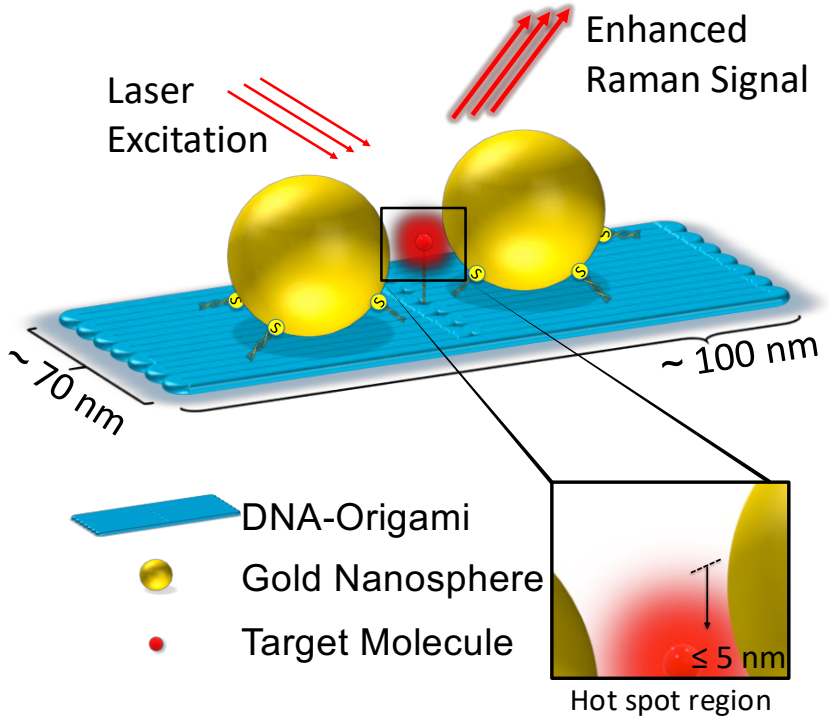
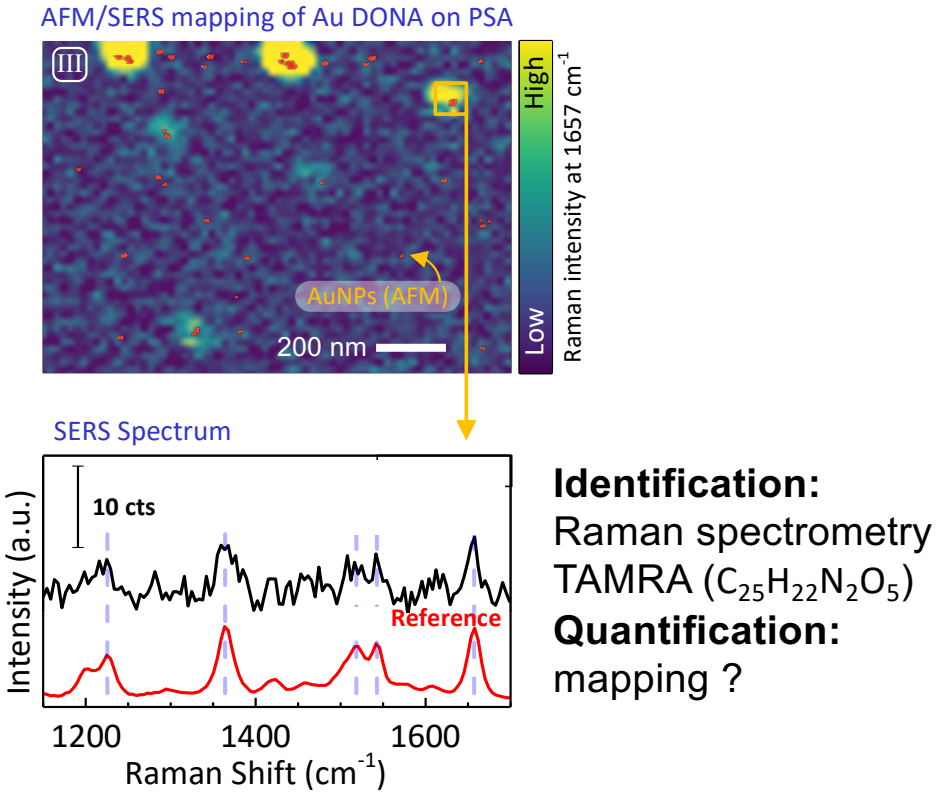
What *can* we count?





Identification:
Raman spectrometry
TAMRA ($C_{25}H_{22}N_2O_5$)
Quantification:
mapping ?

Spectral identification of a TAMRA molecule (on a Au sphere dimer) using SERS.
Ph.D. thesis Zunhao Wang, Laboratory of Emerging Nanometrology (PTB/Univ. Braunschweig)

How do we count?

Counting in mathematics

Infinite sets cannot be counted in the usual sense; for one thing, the mathematical theorems which underlie this usual sense for finite sets are false for infinite sets.

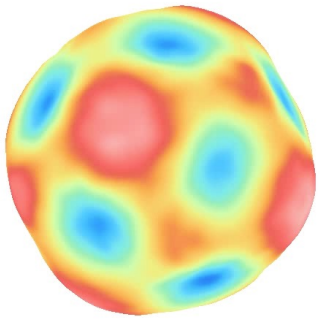
In practise:
Often, the number of entities/processes/phenomena to be counted is not infinte but very large (electrons, atoms, molecules,...)
...or distributed in very small numbers in a large compartment
...or have to be counted in a very short period of time

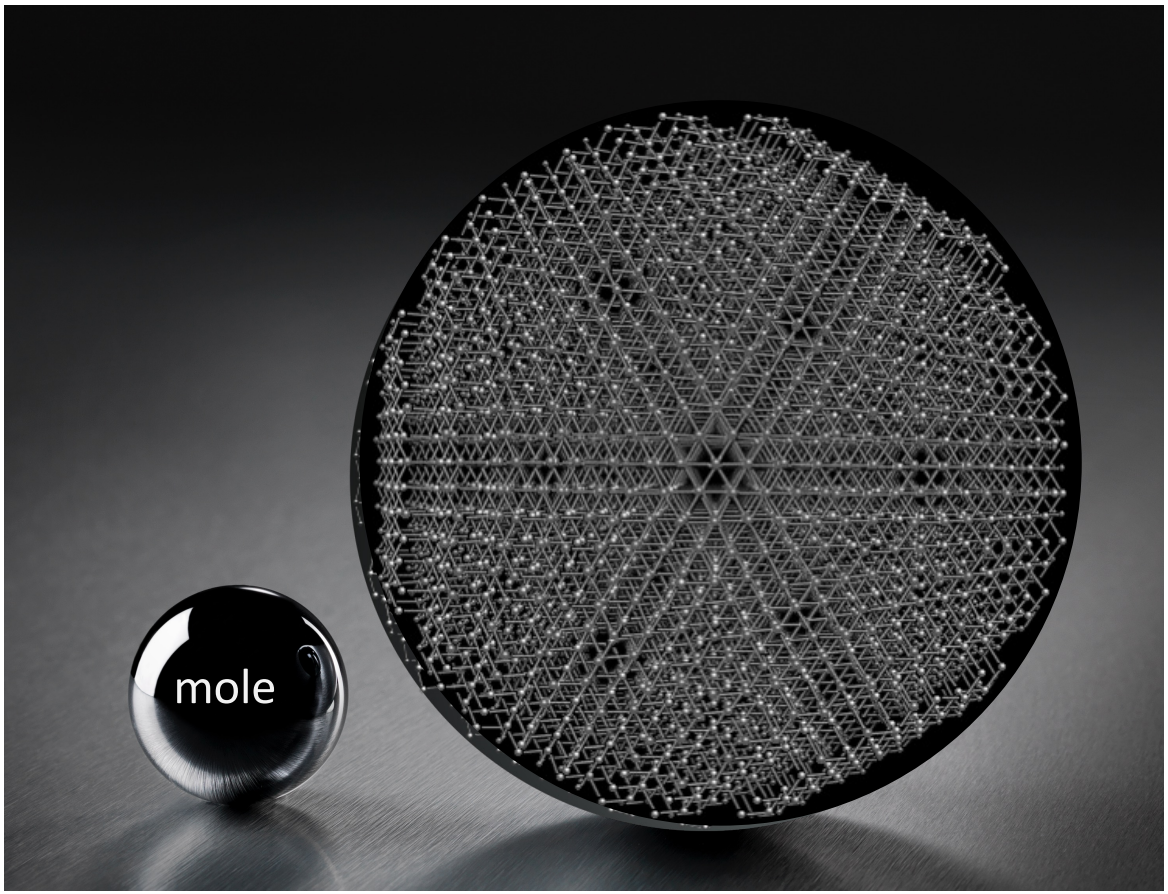
➜ intelligent procedures have to be used to count with an appropriate accuracy that is „fit-for-purpose“

How do we count (atoms)?

Identification:
mass spectrometry (^{28}Si atoms)

Quantification:
by counting *via*
$N = 8V_S/a(^{28}\mathrm{Si})^3$





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How do we count (atoms)?

- the specific aspect of the new definition of the mole that has attracted great attention is its definition in terms of a number of entities – new for a definition of an SI base unit.

  "Naturally, one might ask also in the case of the mole would it not be preferable to replace the definition of the mole given here by a molecular one; but as in the cases of the unit of mass and of electric current this would require determinations such as the absolute counting of molecules or the measurement of the mass of molecules that are not possible with the required precision."

  Jan de Boer, Secretary of the CIPM, 1971

  With the recent advances in science ..., our ability to determine the value of the Avogadro constant has now reached a level of relative uncertainty that allows a redefinition of the mole in terms of the explicit number of elementary entities. ..it realigns the definition of the mole with the way most chemists understand it."

  (R. Marquardt et al., draft IUPAC Recommendation 2017)

How can counting & measuring be equated?

SI-Brochure

There are also some quantities that cannot be described in terms of the seven base quantities of the SI, but have the nature of a count. Examples are a number of molecules, a number of cellular or biomolecular entities (for example copies of a particular nucleic acid sequence), or degeneracy in quantum mechanics. Counting quantities are also quantities with the associated unit one.

Mise-en-pratique of the mole

5. Small numbers of entities

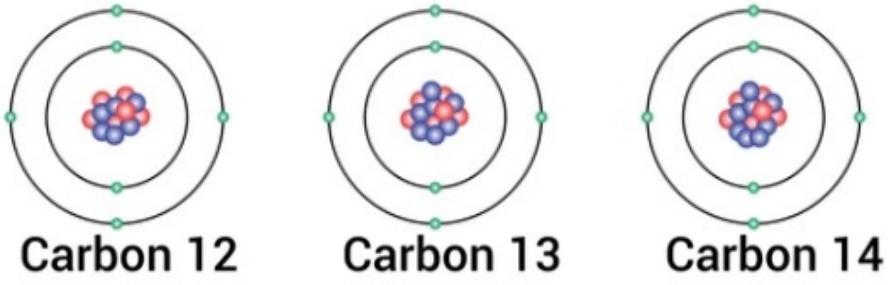
...The Avogadro constant is the constant of proportionality that links amount of substance to the number of entities. However, the number of entities and amount of substance may only be equated in this way if the entities considered in both quantities are elementary entities of the same type.

How can counting & measuring be equated?

When the mole is used, the elementary entities must be specified.

When counting is used, it must be specified what is counted.

...they can be, but must not be identical!
-> groups of entities with a common denominator: *example isotopes*



What if the entities are NOT exactly specified, but still require counting (f.e. by law)?

Which CC is dealing with entities/events/processes that cannot be simply attributed to one of the CCs?

Workshop questions for speakers

- What are the quantities within your technical discipline that relate to counting?
- What are the technical challenges for measuring these quantities, for instance: identifying/defining what is being counted, dealing with very small numbers, uncertainty?
- Do you express your measurement results using the unit one or one of the seven SI base units? What are the reasons? What improvements could be made to clarify the status and traceability of the unit one within the SI?

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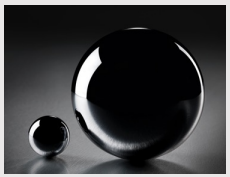

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