

COMPARABILITY OF OUT AND INDOOR OZONE MEASUREMENTS

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Content

Measurement Quality

Traceability

Ozone international intercalibration – CCQM P28

Uncertainty

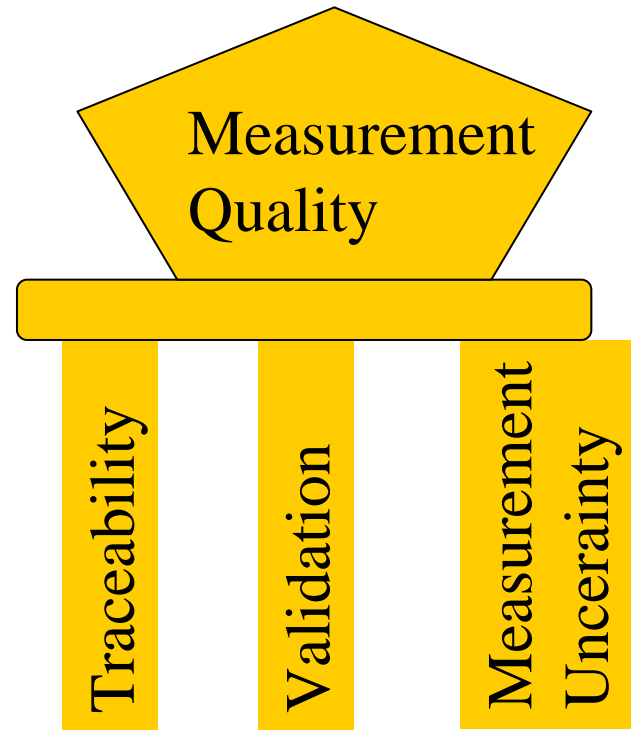
Comparison of two results

Comparability



What is measurement quality?

Measurement quality
*Measurements are solving
the client issue – fit for
intended purpose*



Quality Control
Internal and External

The four parts of measurement quality

1. Method **validation** demonstrates that the method (set of conditions) used in this laboratory at a certain time was fit for purpose and all significant effects were identified.
2. Calibration of critical equipment completes the metrological **traceability** chains.
3. **Measurement uncertainty** is estimated from the method validation and the traceability.

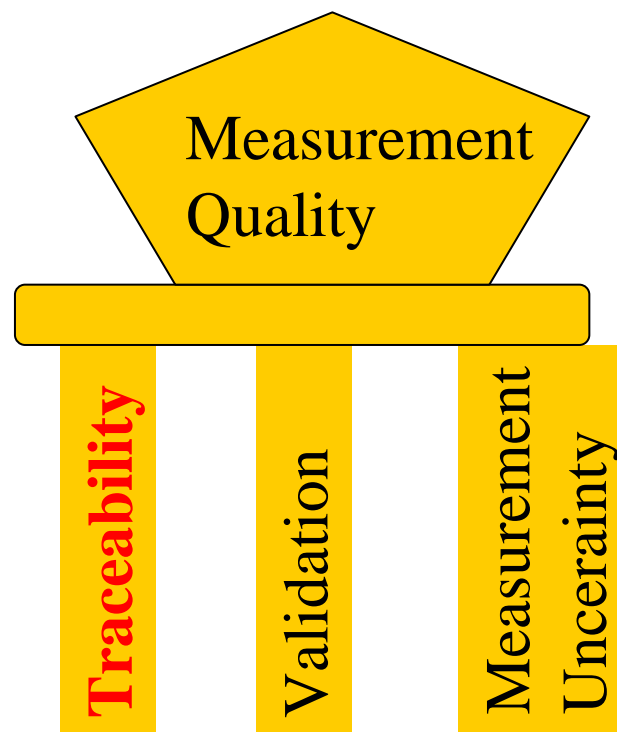
4. **Quality control** (internal and external) assures that the measurement results (including uncertainty) are of the same quality as at the time of validation.

Source: Eurachem Traceability leaflet
www.eurachem.org



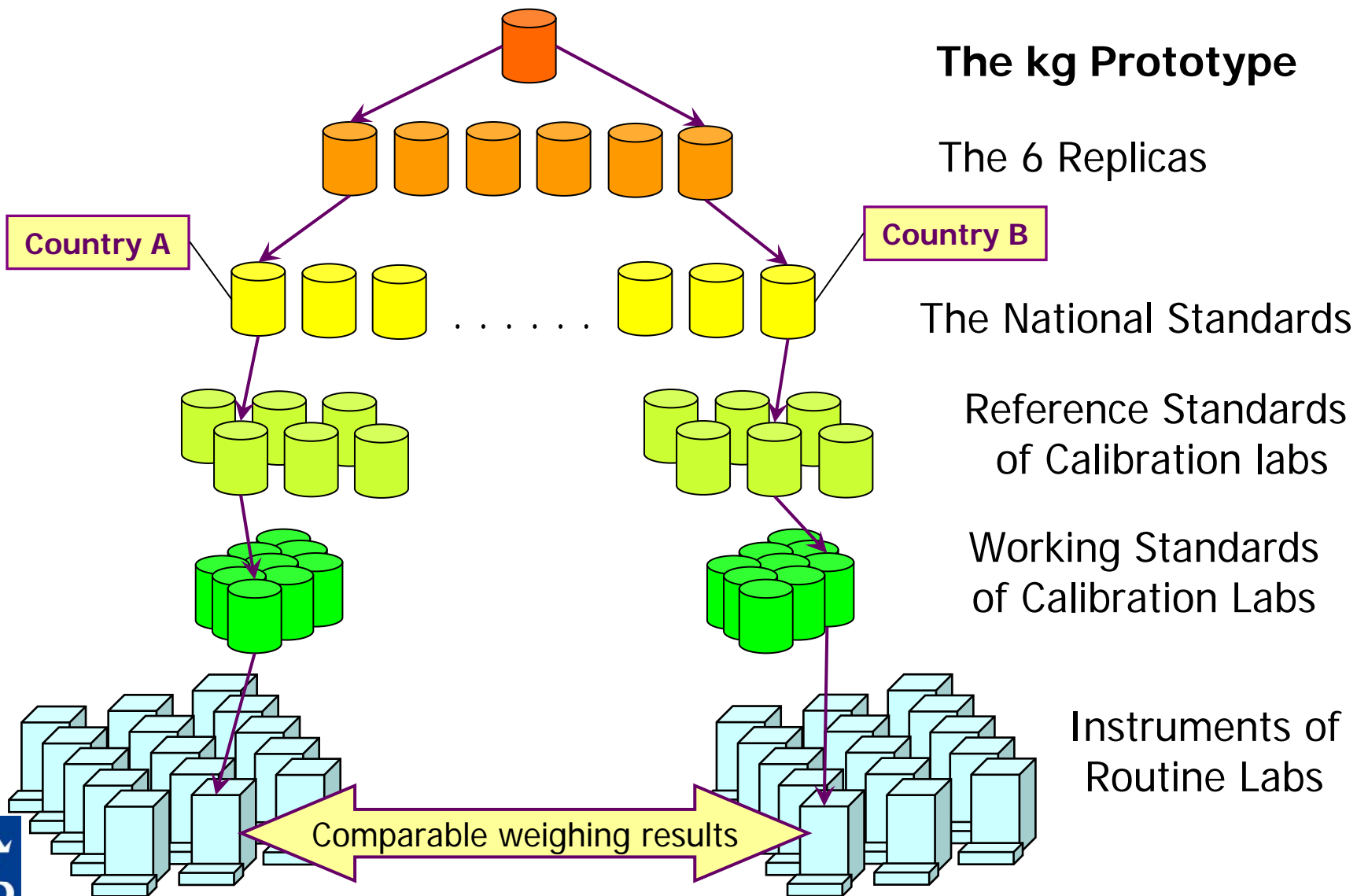
Measurement quality for Ozone measurement?

- 1 Traceability - No ozone standards available
 - 2 Internal Quality Control
 - No reliable ozone generators available
- Iodide titration not robust
ASTM; D5011-92



Quality Control
Internal and External

Traceability of mass measurement



Traceability for ozone measurement

No traceable measurement standard available

One major method of analyses – ISO 13964:1998*

Spectrophotometry – light absorption at 253,7 nm –
Beer Lambert law

The mole fraction of ozone, c is traceable to:

1. L – cell length
2. α - absorption coefficient at 1 atm (P_0) and 0 °C (T_0)

$$A = \ln \frac{I_0}{I} = a \cdot L \cdot c$$

*Air quality -- Determination of ozone in ambient air -- Ultraviolet photometric method

Traceability for ozone measurement - spectrophotometry

$$C_{O_3} = 10^6 \cdot \frac{1}{\alpha L} \cdot \ln \frac{I_0}{I} \cdot \frac{P_0}{P} \cdot \frac{T}{T_0}$$

C = molfraction of ozone (ppm)

α = absorption coefficient of ozone at 253,7 nm

I = light intensity

P_0 = pressure - 1 atmosphere (101,325 kPa)

T_0 = temperature - temperature 0 °C (273,15 K)

Results are traceable to:

- 1.Length – cell length
- 2.Absorption coefficient
- 3.Pressure
- 4.Temperature



National and international networks for atmospheric ozone measurements

NIST-EPA Standard Reference Photometer (SRP)

- US ambient O₃ measurements under EPA regulations
- an increasing number of worldwide National Metrology Institutes maintain SRPs

Joint BIPM-NIST programme to maintain the comparability of the worldwide network of ozone reference standards

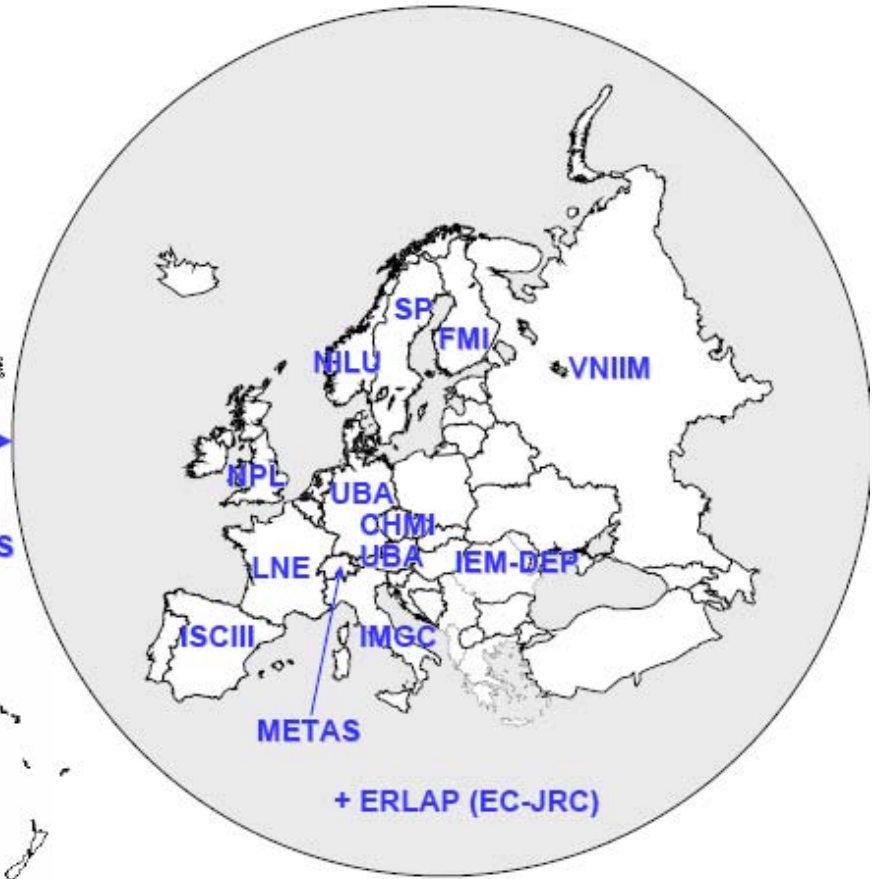
NIST



CCQM-P28 Participating institutes

+ BIPM - GPT

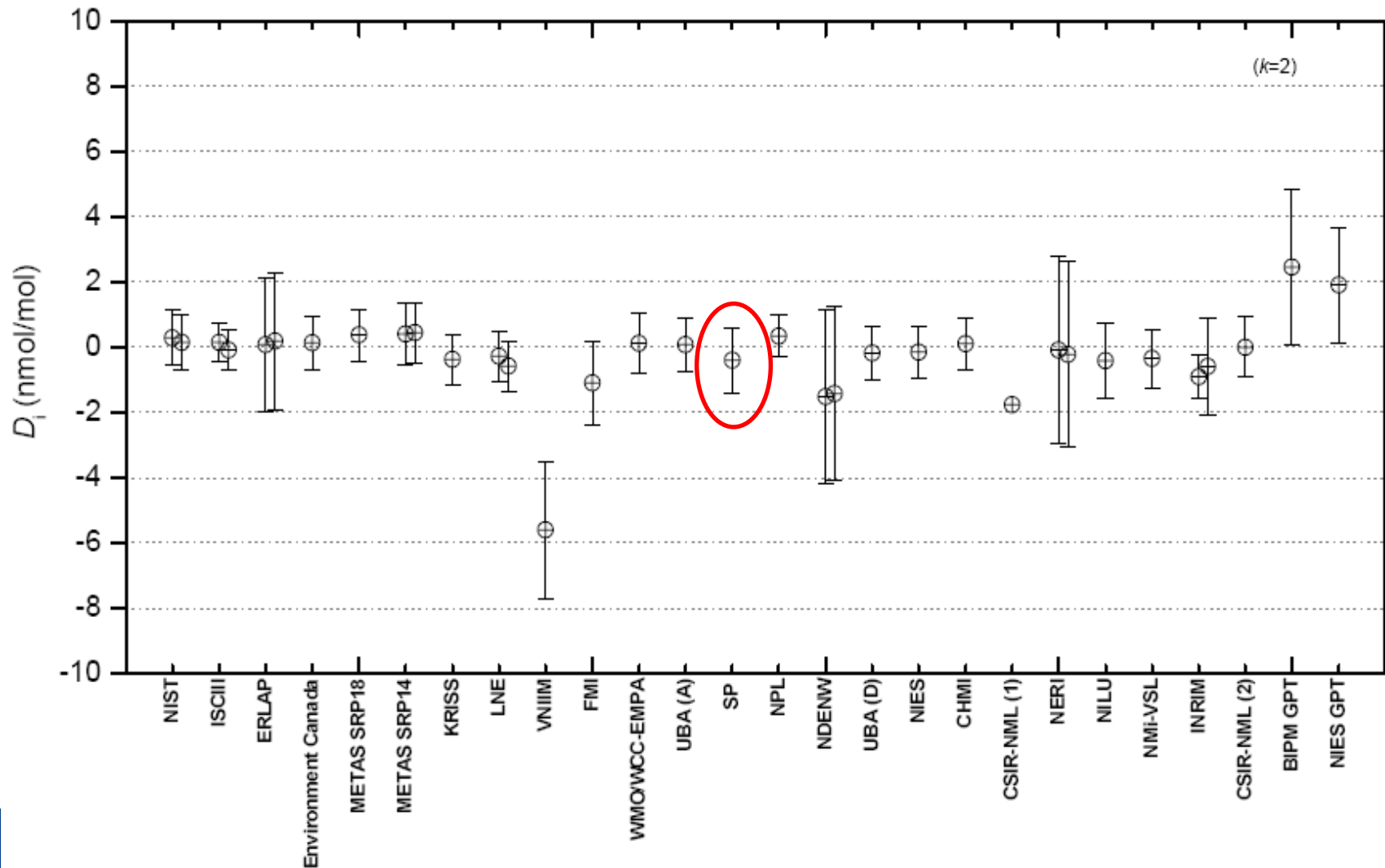
+ WMO - EMPA



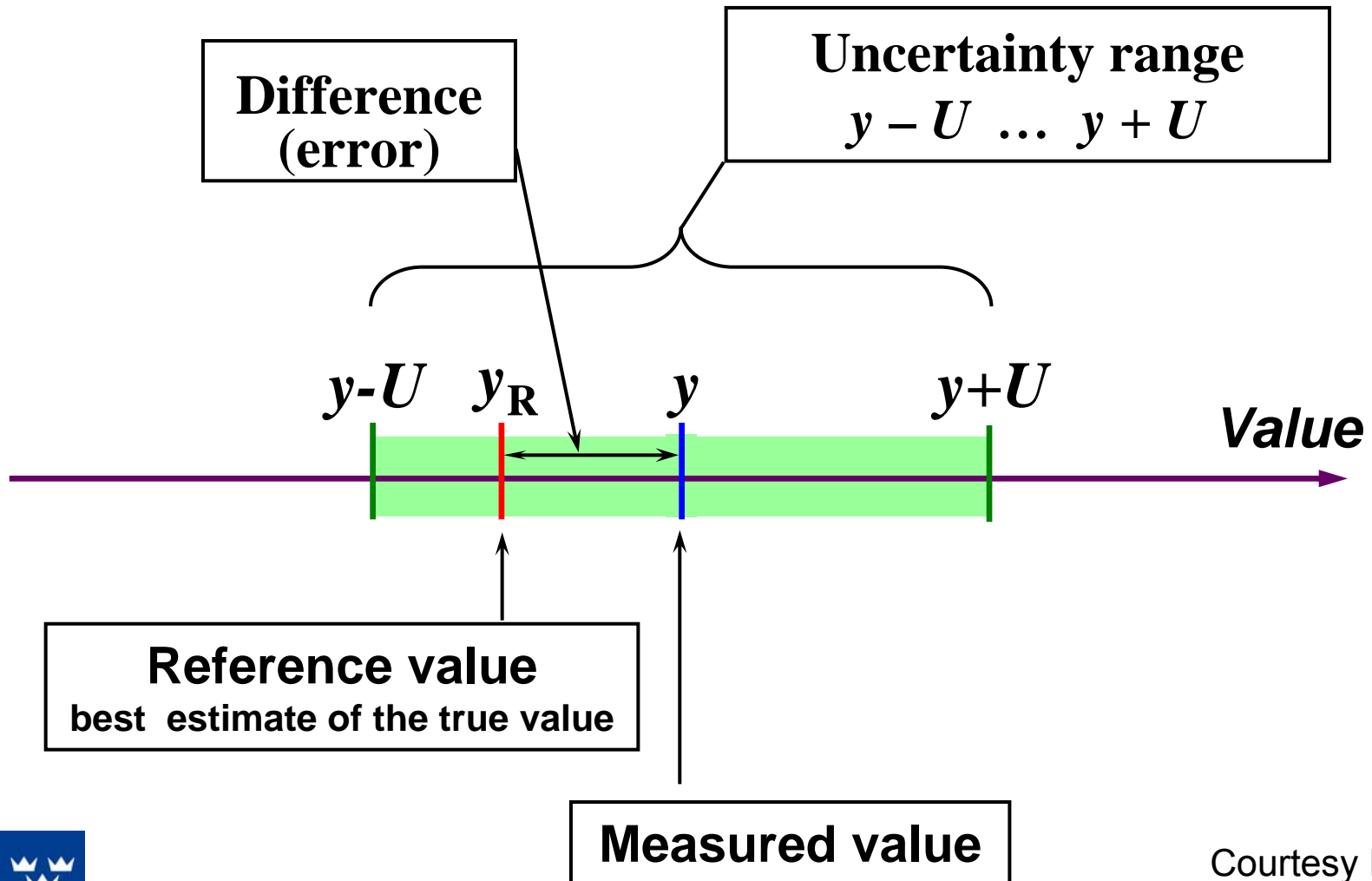
Reference : BIPM-SRP27



CCQM P28 – Comparison at 80 nmol/mol



Value (y); Difference; Uncertainty (U)



Uncertainty: symbols

y – measured value

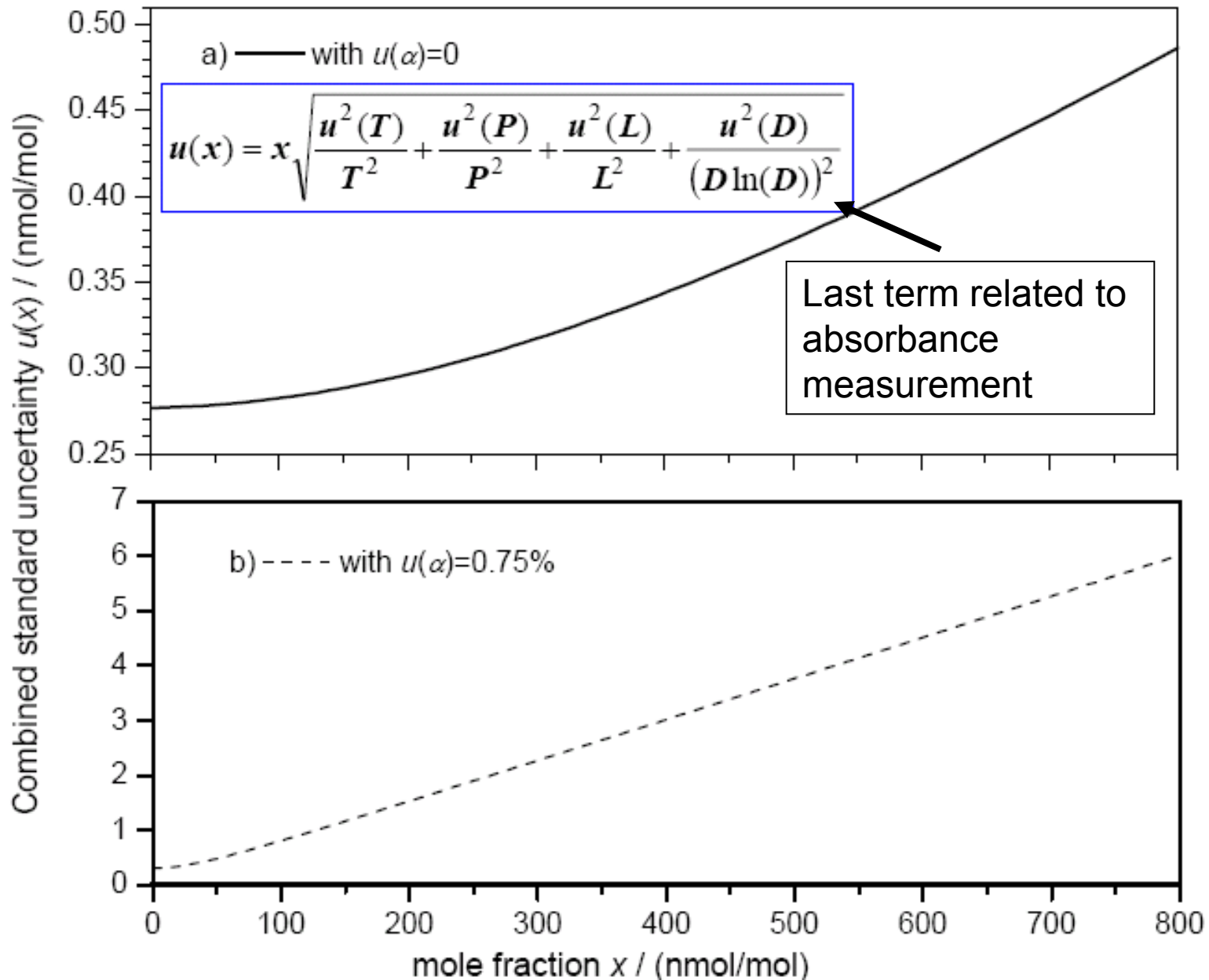
u – standard uncertainty (of type A and B) – similar to a standard deviation

u_c – combined uncertainty (root sum of the squares of individuals $u(y)$)

$U = u_c \cdot k$ – expanded uncertainty

k – coverage factor (gives a particular confidence level for the expanded uncertainty)

Uncertainty as a function of ozone mole fraction



Is there a difference?

Ozone results

Lab 1 - mole fraction 80 nmol/mol \pm 3 nmol/mol

Lab 2 - mole fraction 85 nmol/mol \pm 3 nmol/mol

Where \pm 2 nmol/mol is the expanded uncertainty given at a confidence level of 95 %

The uncertainty intervals overlap! Is there no difference?

$$\Delta = y_1 - y_2$$

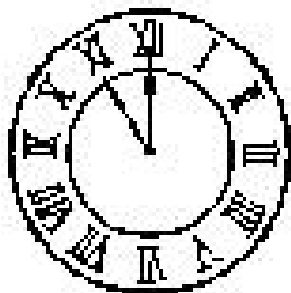
$$U_{\Delta} = \sqrt{U_{y1}^2 + U_{y2}^2} = \sqrt{2 \cdot U_y^2} =$$

$$= \sqrt{2} \cdot U_y = 1,4 \cdot 3 = 4,2$$

The difference is 5 - there is probably a real difference

Measurement quality in place – what do we get?

comparability: property of measurement results enabling them to be compared because they are metrologically traceable to the same stated metrological reference; independent of:



Time



Place



Laboratory/operator/procedure