Horwitz Equation as Quality Benchmark in ISO/IEC 17025 Testing Laboratory

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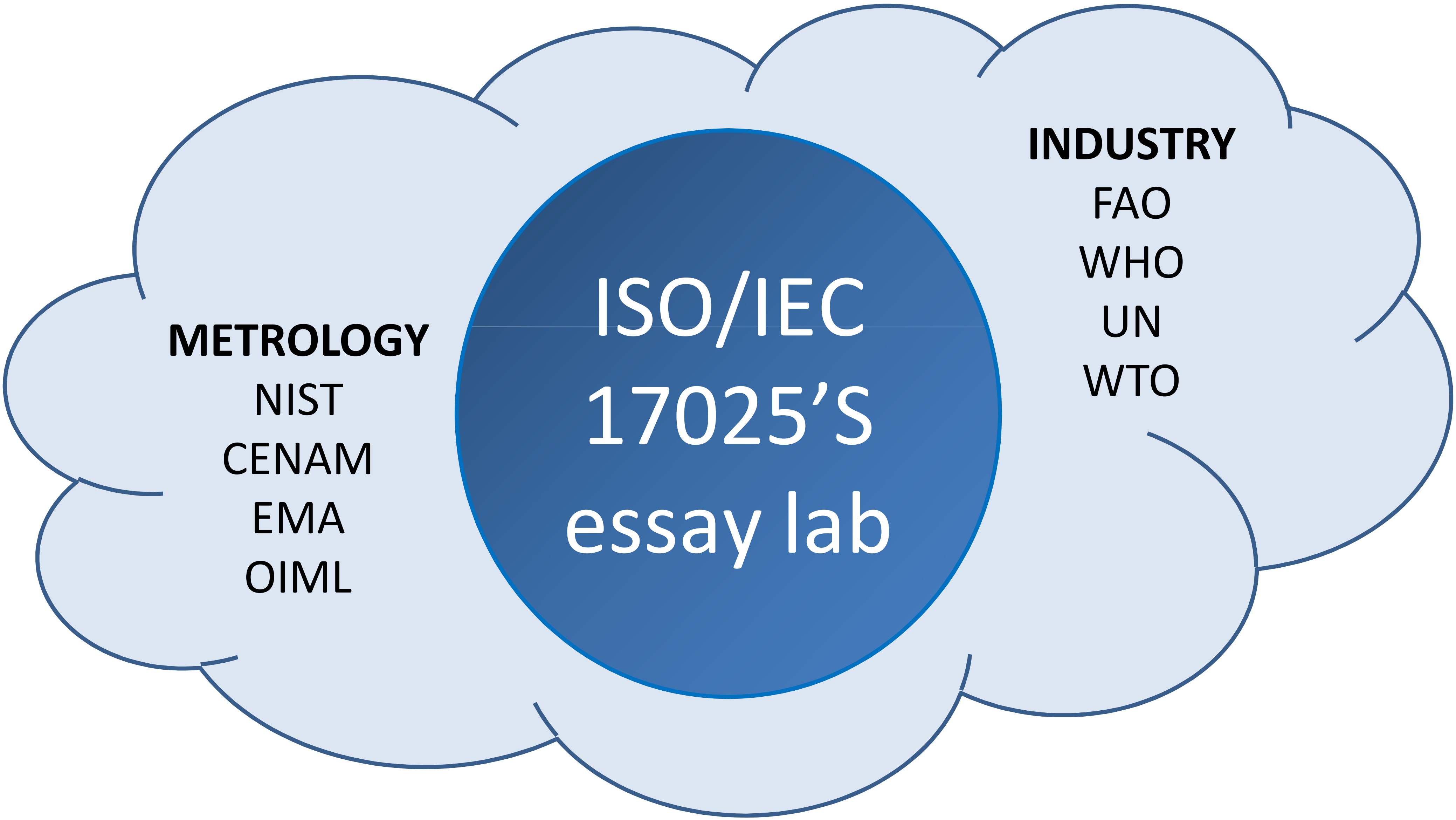
Preface

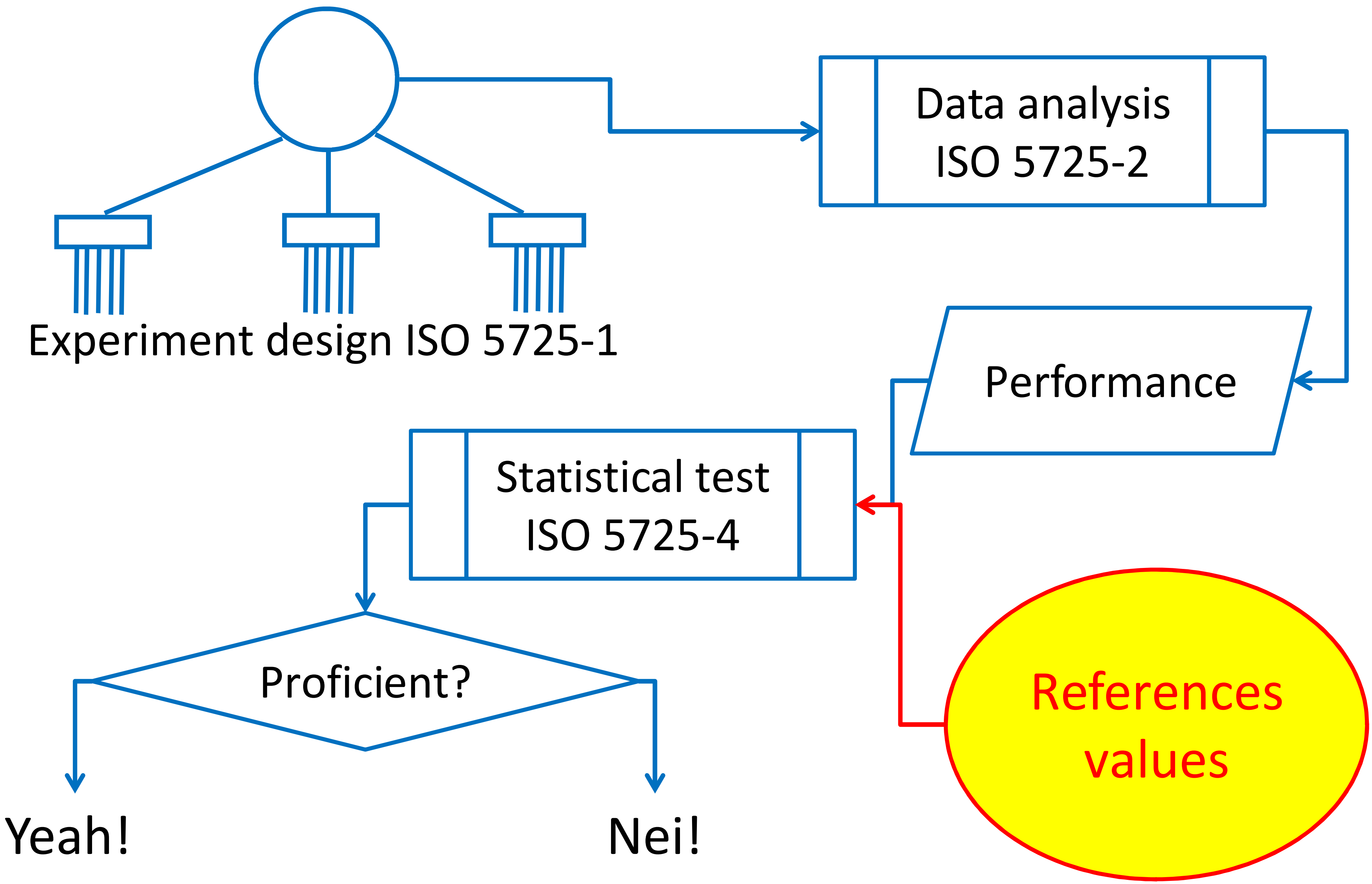
ISO/IEC 17025 **accredited** Testing Labs:

- ✓ Keep **quality controls** of their processes.
- ✓ Express **uncertainty** of measurements.

Accreditation Requirements



17025 Lab's Quality Assurance



The core question

Which reference values should be used to validate ISO 5725's results

Acknowledgment

- Authors express gratitude to **Mr. Javier Vargas** for his allowance to use **Oil Reclaiming's** control charts to show applications of Horwitz Equation.

Objectives

1. **Reproducibility** and **Uncertainty** of measurement?
2. Scope of testing laboratories **quality control**?
3. **Horwitz** equation as quality benchmark?
4. Uncertainty **accreditation policies**?

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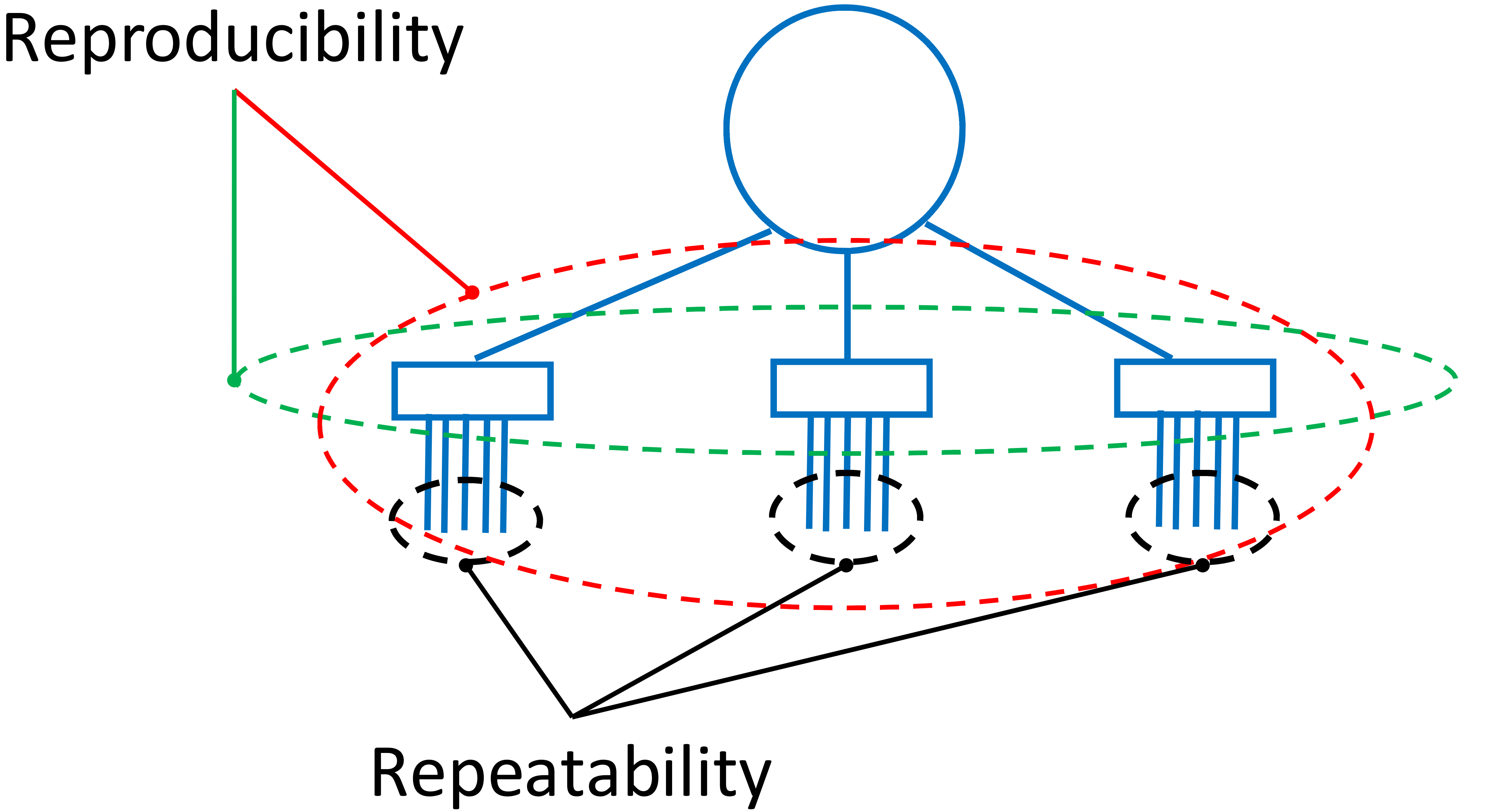
International Vocabulary of Metrology
VIM



VIM terms

2.24 reproducibility condition of measurement

…different locations, operators, **measuring systems**, and replicate measurements on the same or similar objects

VIM terms

2.25 measurement reproducibility

reproducibility **measurement precision** under **reproducibility conditions of measurement**

NOTE Relevant statistical terms are given in ISO 5725-1:1994 and ISO 5725-2:1994.

VIM terms

2.21 measurement repeatability

repeatability **measurement precision** under a set of **repeatability conditions of measurement**

VIM terms

2.20 repeatability condition of measurement

…same **measurement procedure**, same operators, same **measuring system**, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time.

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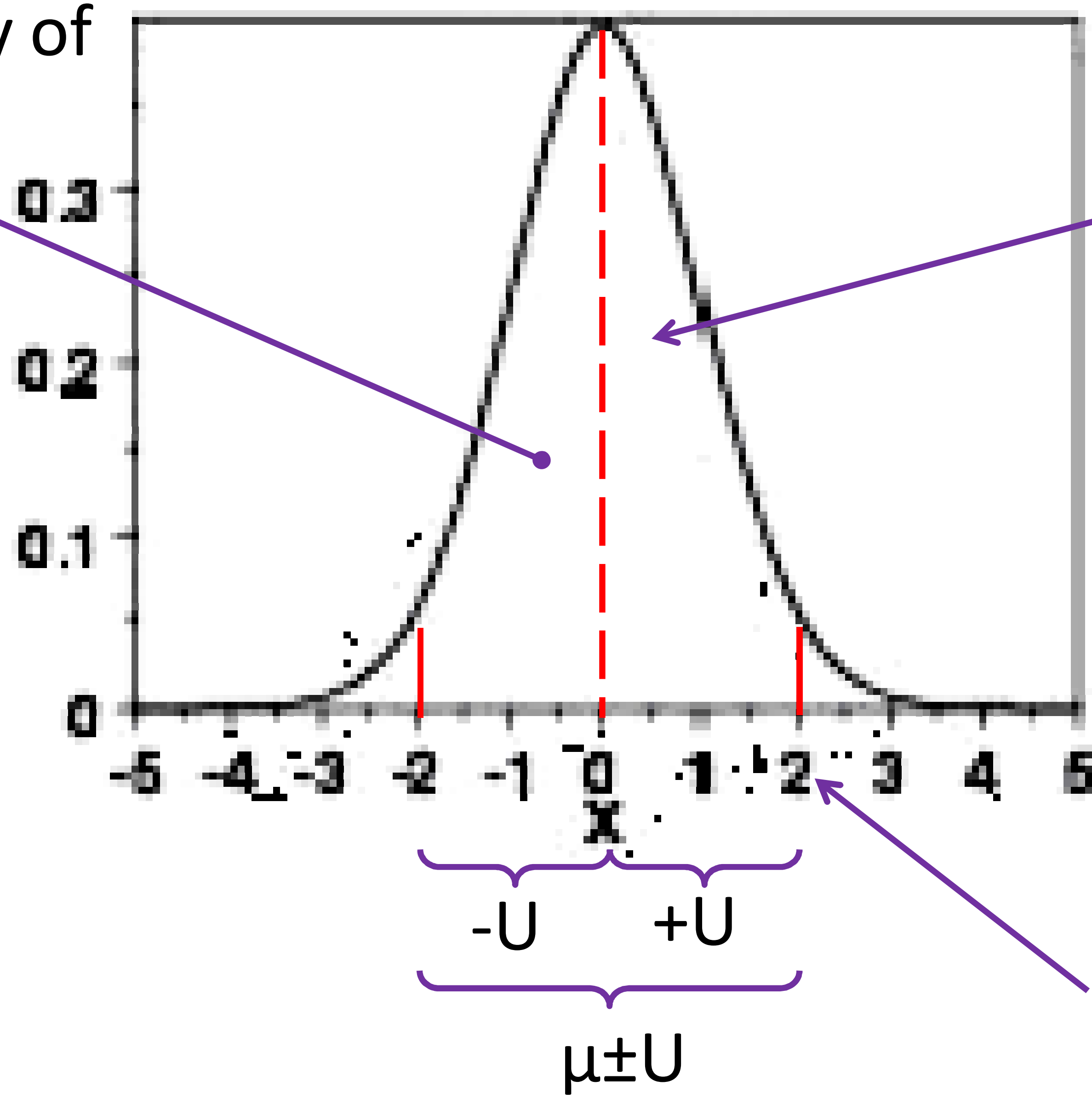
Uncertainty

Probability of 95% ; k=2

Mean μ MEASURAND



U=k·u
k=2

Uncertainty is to measurement…

what **control limits** are to standardized **production processes**. Nevertheless…

there are some **experimental conditions** that should be complied to estimate the **useful value**; **GUM** explains the general criteria.

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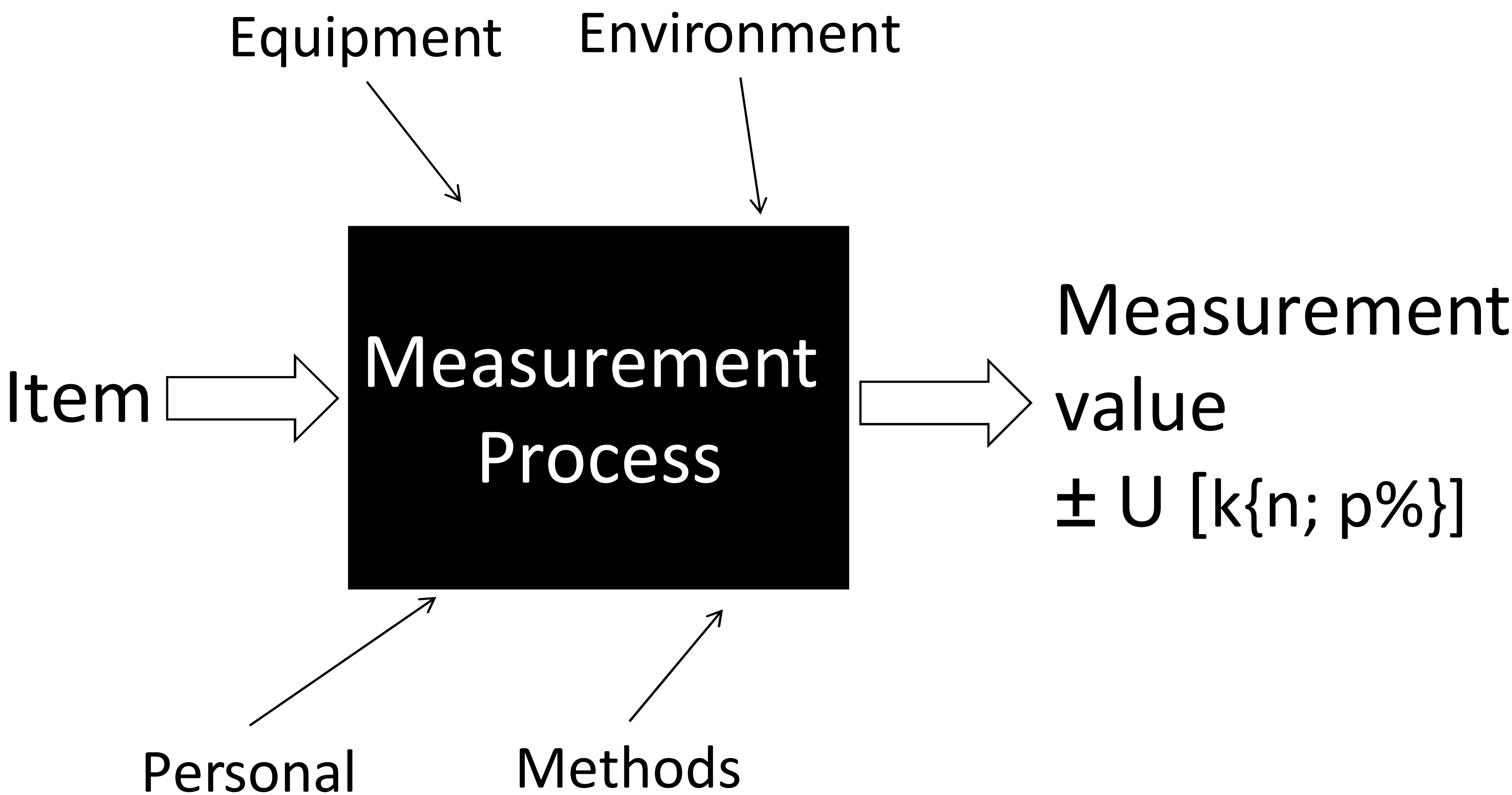
17025's Quality Control

5.9.1. The laboratory shall have quality control procedures for monitoring the **validity of tests**…

5.9.2. Quality control data shall be analyzed and, where they are found to be **outside pre-defined criteria**…

ISO/IEC 17025 Lab System



5.9 @ 17025

Measure the measurer!

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What does HorEq show?

- It’s an empirical number
- It is a CV
- Comes from on analytical laboratories
- Reproducibility of analytical processes
- CV Horwitz = σ
  - N > 1000 items
  - Data distribution were as standard

How is it expressed?

$$CV\ \% = 2C^{-0.15}$$

Where C, is the concentration of the **analyte** expressed as a **mass fraction**

How does it look?

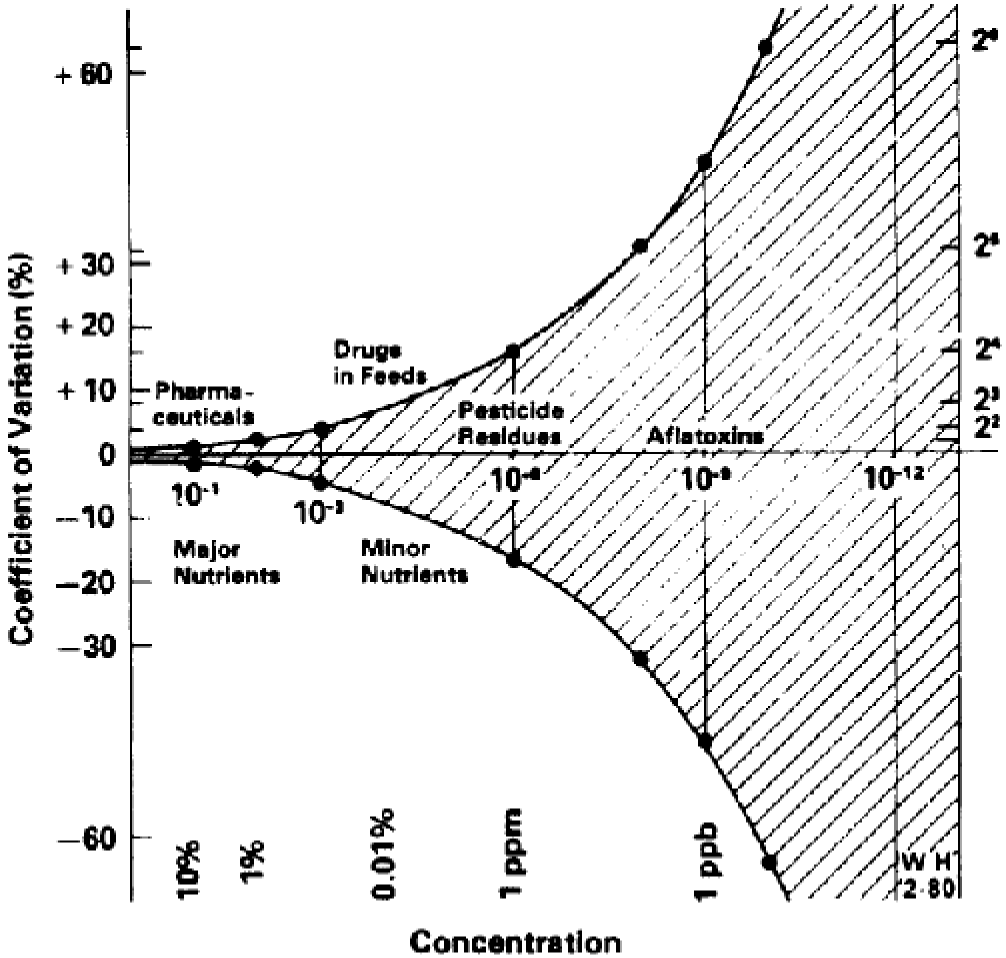


Figure 1. Interlaboratory coefficient of variation as a function of concentration.

HORWITZ ET.AL. Assoc. of Anal. Chem. (Vol. 63, No. 4, 1980); p. 1345

When can it be used?

CANNOT

- Calibrations
- Physical measurement
- Empirical analyte

When can it be used?

NOT FOR…

Humidity; ash; fiber; **analyte** defined by method where its **concentration depends** on procedure.

Neither for **undefined analytes** such as enzymes, polymers and bimolecules.

Which is its working range?

$$1.2 \times 10^{-7} \leq C \leq 0.138$$

This **range** was **validated** for mycotoxin in milk, **but**…

Which is its working range?

- … "Without further experimental **confirmation**, similar **conclusions** have been **incorporated** into several recent **EU Directives** dealing with **other analytes**."

HORWITZ & ALBERT Journal of AOAC International (Vol. 89, No. 4, 2006); p. 1103

Which is its working range?

- "… as the **concentration** decreases as the **detection limit** is approached (at about 10 ppb), the number of **false negatives** increases."

HORWITZ & ALBERT, (Ibid.) page 1103

Which is its working range?

$1.2 \times 10^{-7} \leq C \leq 0.138$

- **Limited** scope of validation
- **Accepted** by EU regulations

$100\ ppb \leq C$

- **Experimental** finding by Horwitz et.al.

What applications have been tried?

•**Oil Reclaiming accredited lab (ema),** that tested **Horwitz Equation** as **QC benchmark** to:

–**Monitor performance** of gas chromatography

  –**Bias**

  –**Reproducibility** of process

–**Estimate uncertainty** of measurement

Performance of Gas Chromatography

- **ASTM D3612 – 02** Analysis of **Gases** Dissolved in Electrical Insulating Oil

- **ASTM D4059 – 00** Analysis of Polychlorinated **Biphenyls** in Insulating Liquids

Precision values at standards

- **ASTM D3612 – 02**

$$I_n\,(R)_{95\%} = K_n\,(R)_{95\%} \text{ X } C_n$$

- **ASTM D4059 – 00**

$$I(r)_{0,95} = k(r) \text{ x } (X_{media})^{0,75}$$

Comparision

ASTM	Range	Conc.	(1) CV_R $\%_{(95\%)}$	(2) CV_H $\%_{(95\%)}$	Ratio (1)/(2)
D3612	H_2 @ 90-710	90	38	16	2
D3613	CO @ 110 - 930	110	79	16	5
D3614	CH_4 @ 35 - 620	35	72	19	4
D3615	C_2H_5 @ 40 - 400	40	75	18	4
D3616	C_2H_4 @ 30 - 800	30	82	19	4
D3617	C_2H_2 @ 25 - 335	25	64	20	3
D3618	CO_2 @ 25 - 335	25	76	20	4
D4059	Megabore	5	30	25	1
D4059	Megabore	50	30	18	2
D4059	Megabore	500	17	13	1

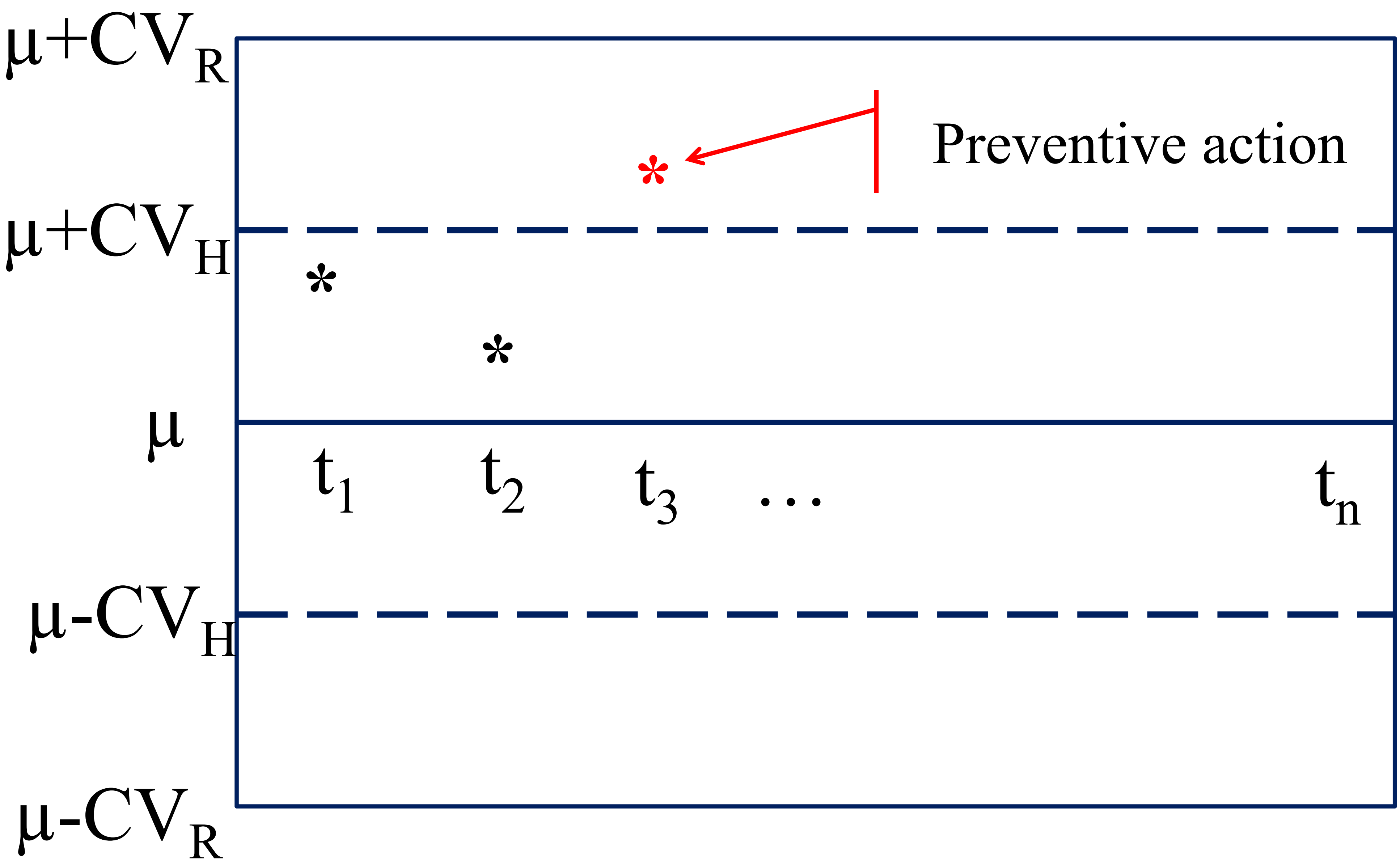
CV_H vs CV_R

- **CV_R** control limits, **too open** to allow effective preventive actions.

- **Closing CV_R** limits is a good practice but;

- **CV_H closes** limits of reproducibility to a **benchmarked** value

Control Chart



APPLICATIONS

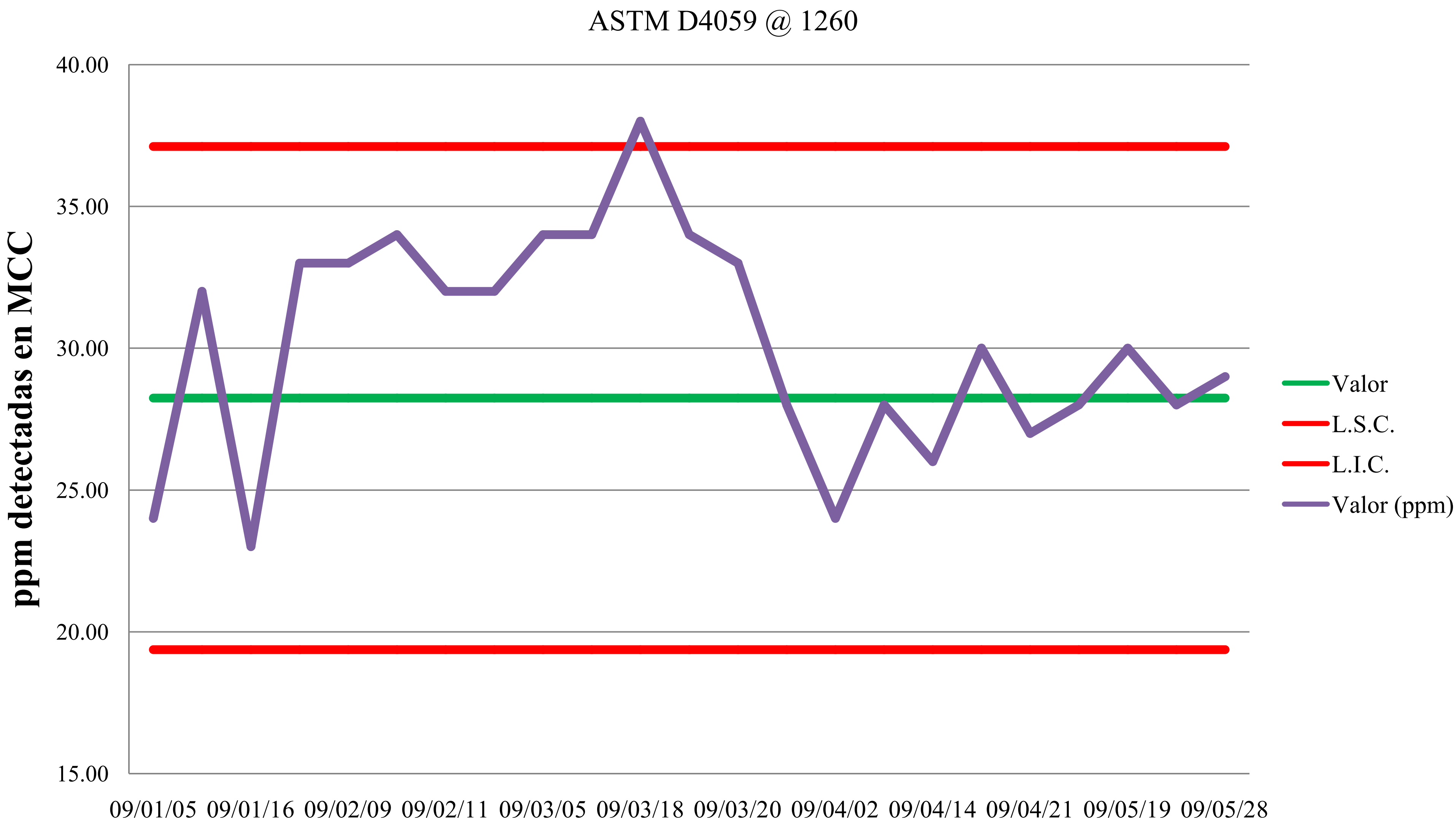
Control chart of BIAS with reproducibility limits

Evaluates BIAS of measurement process using a **characterized** sample essayed; in different days.

Fixed limits on the **Hor Eq** value calculated; **expanded 95%** under standard probability curve.

Presents **variance** among results; on controls.

Control chart of BIAS with reproducibility limits



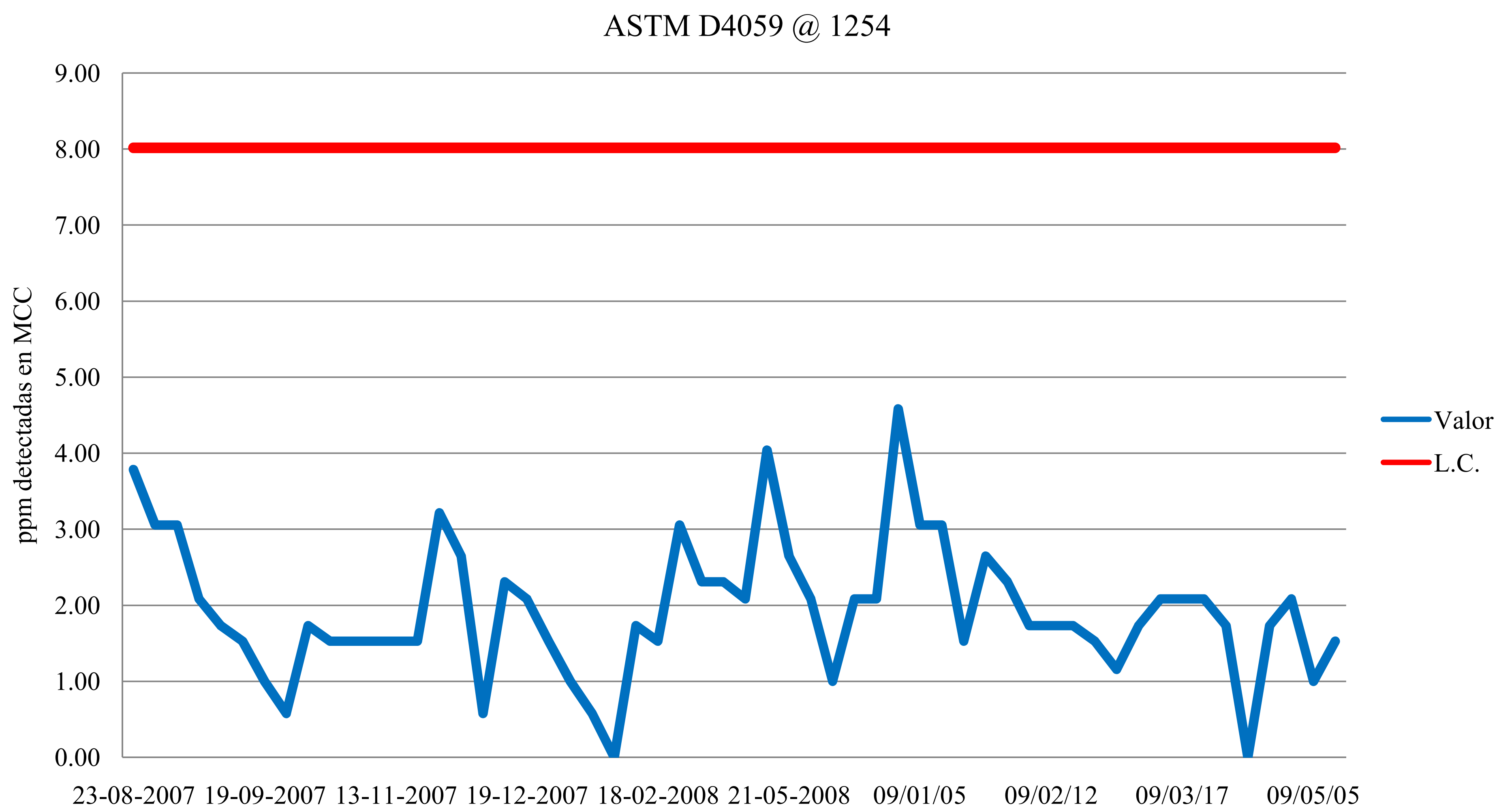
Control chart of variance with reproducibility limits

Evaluates CV of measurement process using a characterized sample; essayed in different days.

Values come from **standard deviation** of the **last three values** at characterized sample.

Limits were fixed on the value **calculated** from **Horwitz** Equation expanded 95% under standard probability curve.

Sample of control chart of reproducibility



Uncertainty of Measurement

- Laboratory **controls** shows **stability.**
- Performance on **variance below Horwitz** limits and **ASTM** known **reproducibility.**
- Laboratory analyzing **Horwitz Equation** as the equation **of uncertainty.**

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Policies for uncertainty in accreditation

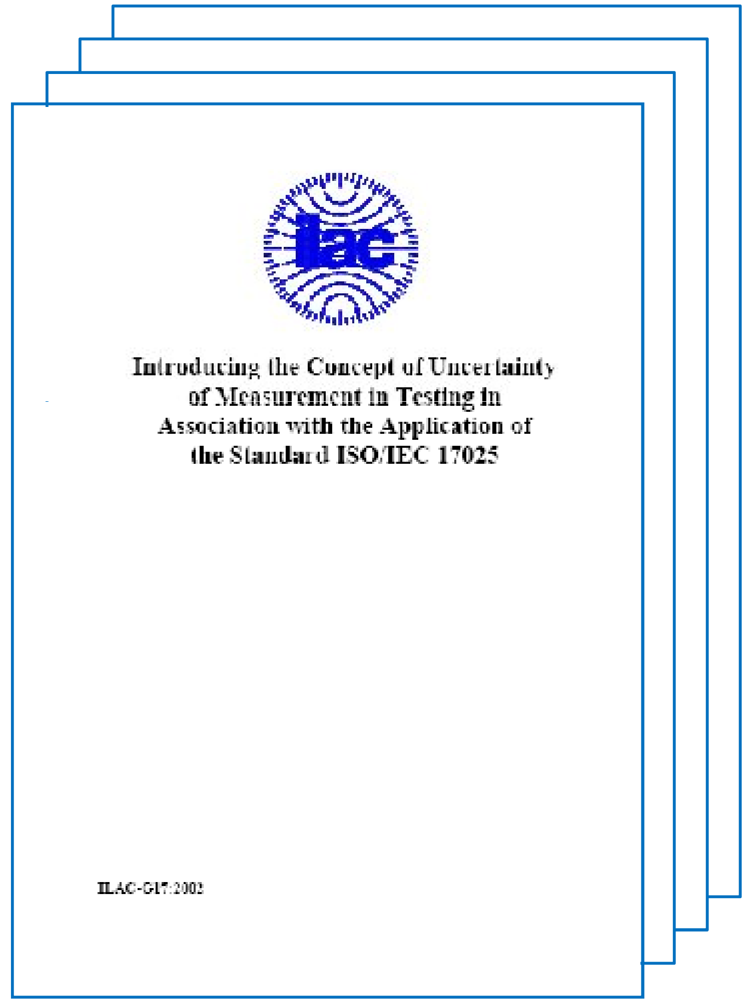
- International Laboratory Accreditation Cooperation.

- International cooperation among various accreditation schemes throughout the world.

www.ilac.org

Accreditation Bodies

- Mutual Recognition Arrangement
- Similar procedures
- Policies on uncertainty aligned to ILAC's guidelines



ILAC G 17

The level of **uncertainty** that is **acceptable:**

Decided on the basis of fitness for purpose.

Occasionally **large uncertainty** may be **acceptable**; sometimes a **small uncertainty** is **required**.

G 17 about standardized methods

- **Well-recognized methods** specifying limits of the major sources of uncertainty require no special action.

- Laboratories are allowed to **quote the typical uncertainty of measurement** if they can demonstrate full compliance with the test method.

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CONCLUSIONS

Conclusions

Benchmarking with **Horwitz allows** scoped laboratories to track the performance of their processes;

Appropriate to express **CV** at framed essay methods;

Reporting uncertainty of measurement through Horwitz Equation **acceptable** under **ILAC** guidelines.

Thank you!

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