





## What is it that scientist do?

”Scientist simplifies the understanding of a complicated world”

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## Postulate of analytical chemist

”Only when uncertainties are right you can deduce something about the fundamental mechanisms of nature”

”Analytical chemists ought to focus on accuracy - precision is of minor importance to costumers and scientists”

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## The Scientific Method



- **Robert Boyle’s definition of science (Duncan Burns)**  
'Discussions may be closed by performing experiments'
- **Vancouver declaration**
- **ACS ethical guidelines**
- **Bo Karlbergs ethical guidelines**

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## Identification of scientific misconduct



1. **Case of severe fraud in chemistry/analytical chemistry 2008**
2. **Celebrated scientist sentenced to scientific misconduct 2008**
3. **In discussion of QA-science, senior scientist states: "Jens, you'll never get rid of fraud in science" !!?? Who was speaking about fraud??**

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## STDEV's of responses

$$s_y(\text{unknown, repetition}) = s_y(\text{unknown, calibration})?$$



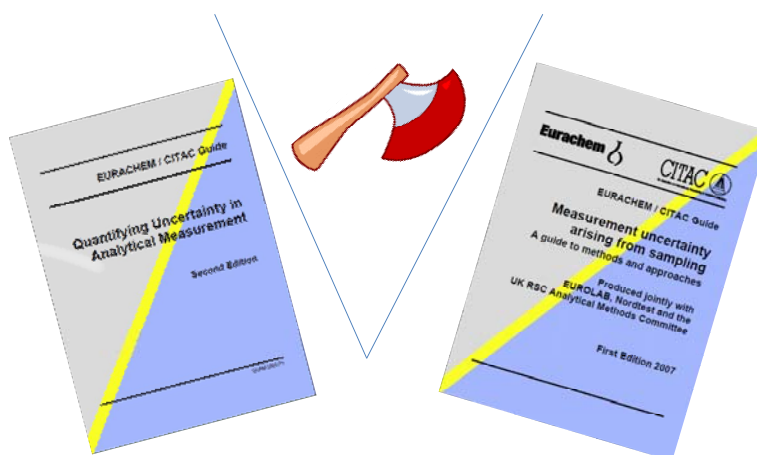
$$s_x(\text{unknown, repetition}) = s_x(\text{unknown, calibration})?$$



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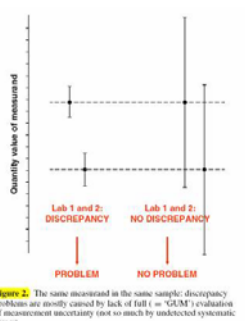


## Method validation



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## BIPM – Paul de Bièvre



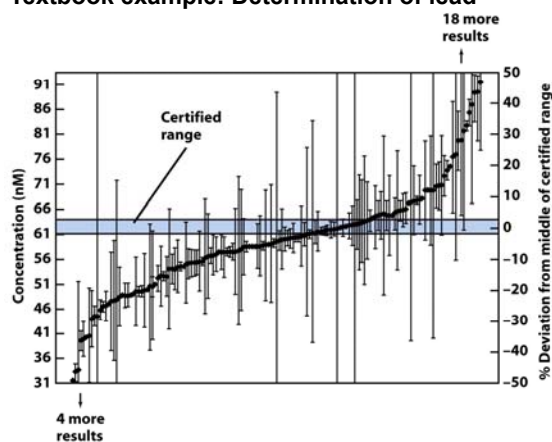
IOP PUBLISHING METROLOGIA  
Metrologia 45 (2008) 335–341 doi:10.1088/0026-1394/45/3/011  
Essential for metrology in chemistry, but not yet achieved: truly internationally understood concepts and associated terms  
Paul De Bièvre  
Independent Consultant on Metrology in Chemistry (MIC), Duineneind 9, B-2460 Kasterlee, Belgium  
E-mail: paul.de.bièvre@skynet.be  
Received 18 June 2007  
Published 16 May 2008  
Online at stacks.iop.org/Met/45/335

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## Proficiency testing IRMM Philip Taylor and Hendrik Emons



Textbook example: Determination of lead



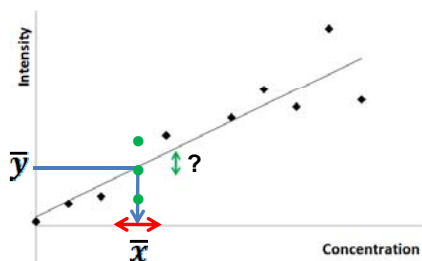
D.C. Harris

Chapter 5 Opener part a  
Quantitative Chemical Analysis, Seventh Edition  
© 2007 W. H. Freeman and Company

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## Calibration



$$s_y^2(\text{calibration}) = \frac{\sum (y_i - \bar{y})^2}{N-1}$$

$$s_x^2(\text{calibration}) = \frac{1}{2 \cdot \alpha^2} \cdot \left[ s_\beta^2 + s_y^2 + (s_\alpha \cdot \bar{x})^2 \right]$$

•  $s_y$  - determine by:

1. Read-off value
2. Perform additional calibrations at same concentration as that of unknown

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## Repetition

$$x = \frac{y - \beta}{\alpha}$$

$$s_x^2(\text{repetition}) = \frac{\sum (x_i - \bar{x})^2}{N-1}$$

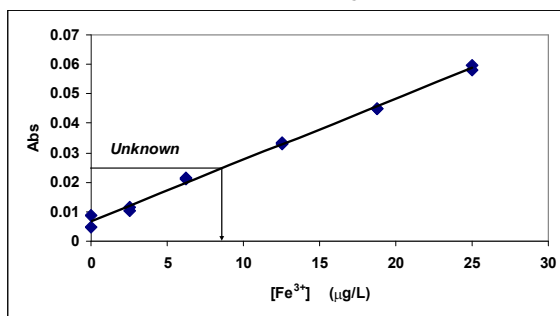
$$s_x^2(\text{calibration}) = s_x^2(\text{repetition})?$$

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## Determination of unknown

Determination of iron by GF-AAS



NIST SRM 1640. Found:  $30.5 \pm 2.7 \mu\text{g/L}$  Certified  $36 \mu\text{g/L}$   
 LOD =  $3.8 \mu\text{g/L}^{-1}$

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## Lower concentrations

$$LOD = \frac{3 \cdot s_y(\text{blanks})}{\alpha}$$

10 blanks and best slope!

$$LLA = \frac{2}{\sqrt{1 - 2 \left( \frac{s_\alpha}{\alpha} \right)^2}} \cdot \frac{s_\beta}{\alpha}$$

RSD > 50%

'N' high – very high!  
 NB! From pooled calibrations

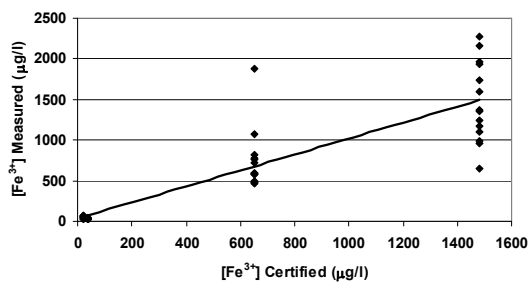
**LOD = LLA?**

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## Repetitions of four CRM's

Determination of iron by GF-AAS



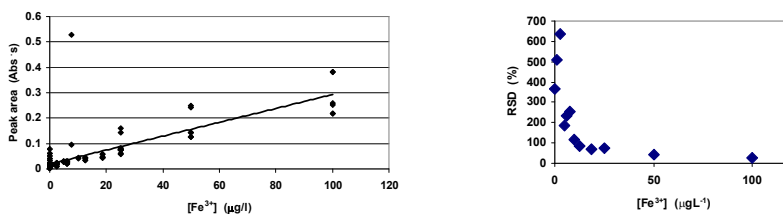
Slope ~ 1!  
RSD~30%, LLA = 140 µgL<sup>-1</sup>

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## Pooled calibrations

Determination of iron by GF-AAS

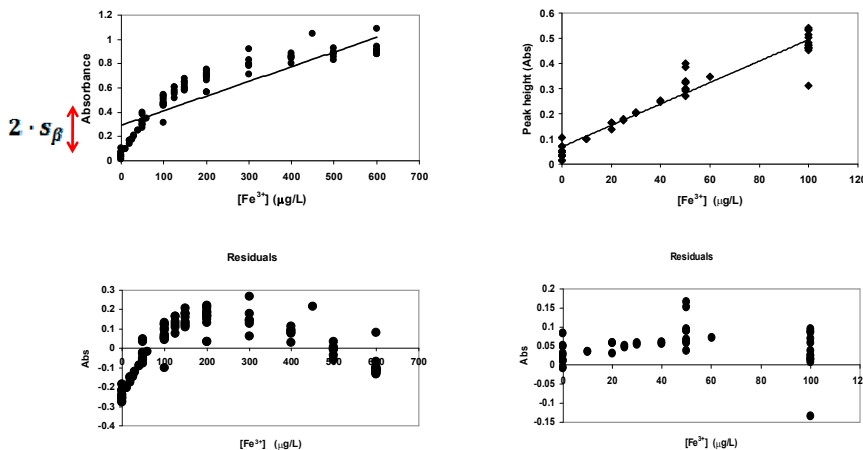


Best RSD of approx. 30% found at high concentrations  
LOD = 16 µgL<sup>-1</sup>

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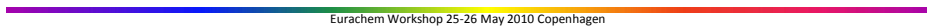
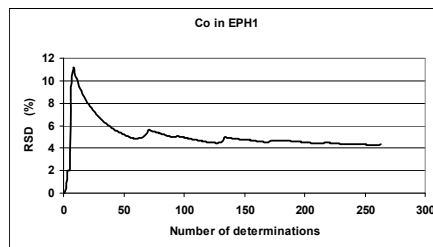
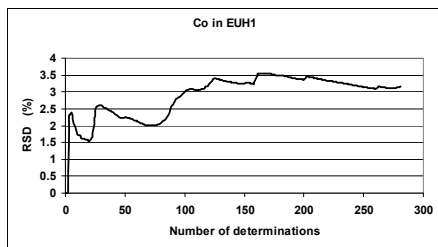


## Straight line?



## Law of great numbers illustrated

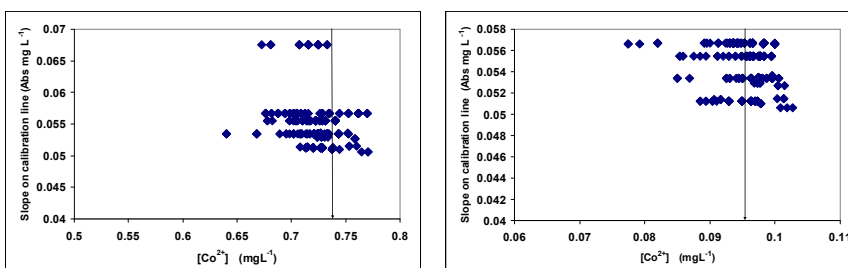
Determination of cobalt by F-AAS in two certified reference materials



## Slope–result correlation



Determination of cobalt by F-AAS in two certified reference materials



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## Reliability



How safe are our conclusions? The reliability may be estimated by the standard deviation of the experimental standard deviation of the mean.

Number of observations N	Reliability = $1 - [2 \cdot (N-1)]^{-1/2}$
2	29
3	50
4	59
5	65
10	76
20	84
30	87
50	90

Determine also reproducibility and robustness

## Conclusions



- **Uncertainties control decision making!**
- **The analytical work is completed when calibration uncertainties correspond to the uncertainty of repetition – new!**
- **The more realistic uncertainty must prevail – not the minimum uncertainty!**
- **Establish database with calibration results of all apparatus!**
- **Never remove any outliers whatsoever!**

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Thank you for your attention!



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