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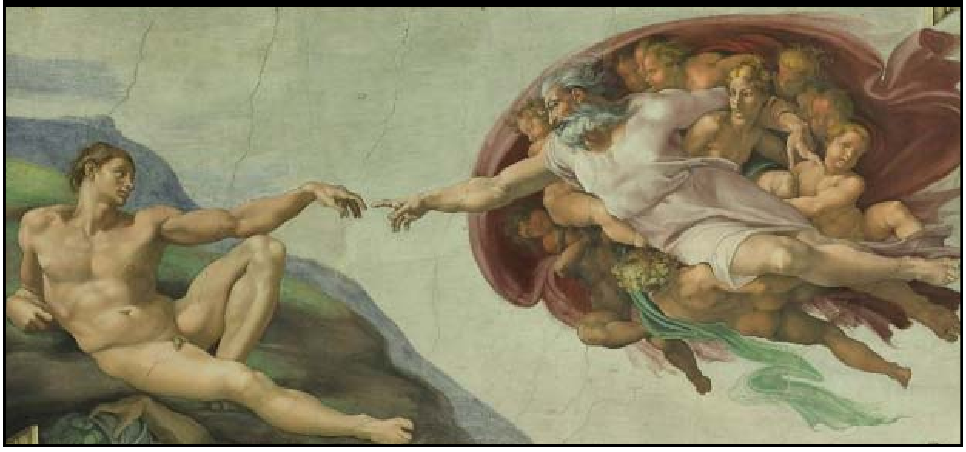
Uncertainty and metrological traceability

Ricardo Bettencourt da Silva



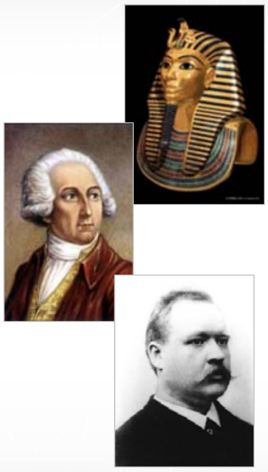
Overview

1. Introduction

- Chemical test are being performed since ancient Egypt (3000 BC) - Determination of gold in gold alloys by gravimetry;

- Modern chemistry was born 200 year ago with Lavoisier;

-Arrhenius proposed that chemical reactions in solution were reactions between ions 100 years ago (…)



Why important developments in metrology in chemistry took place only recently ?

1. Introduction

(…)

Recent technical developments in analytical instrumentation allowed the determination of trace levels of various species in studied items with relevant impact on public health, environment and industrial production.

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1. Introduction

(…)

The globalisation of the market makes it imperative to establish fair and objective rules for trade between multiple competing partners from different continents.

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2. Metrological traceability concept

The metrological traceability concept is intimately related with the uncertainty one since it involves the definition of the reference for the measurement.

Metrological traceability (2.41) [1] - property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty.

1- Joint Committee for Guides in Metrology, International vocabulary of metrology – basic and general concepts and associated terms (VIM), JCGM 200, BIPM, 2008 (www.bipm.org/vim).

2. Metrological traceability concept

The metrological traceability concept is also intimately related with other important concepts (...)

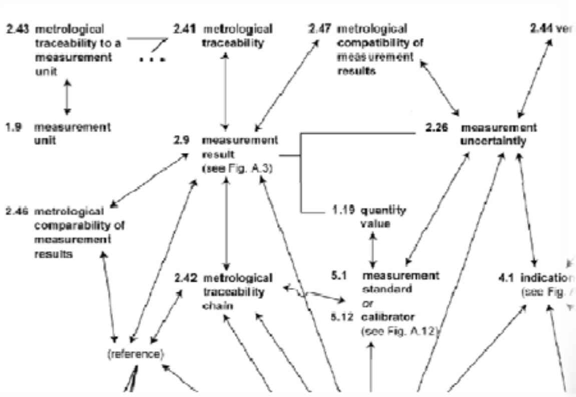

Figure A.7 – Concept diagram [1]

1- Joint Committee for Guides in Metrology, International vocabulary of metrology – basic and general concepts and associated terms (VIM), JCGM 200, BIPM, 2008 (www.bipm.org/vim).

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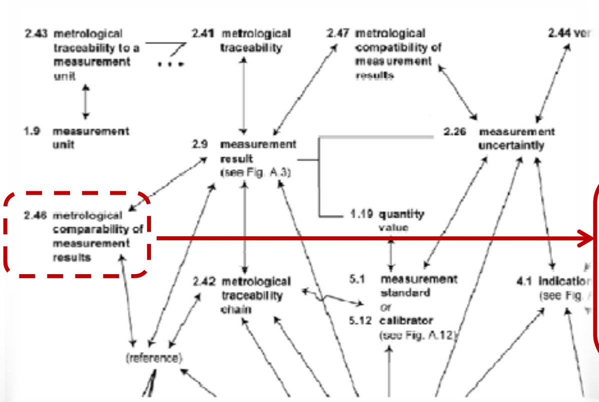

Figure A.7 – Concept diagram [1]

(2.46) comparability of measurement results, for quantities of a given kind, that are metrologically traceable to the same reference.

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Figure A.7 – Concept diagram [1]

(2.47) property of a set of measurement results for a specified measurand, such that the absolute value of the difference of any pair of measured quantity values from two different measurement results is smaller than some chosen multiple of the standard measurement uncertainty of that difference.

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2. Metrological traceability concept

The metrological traceability concept is also intimately related with other important concepts (...)

Measurements from two laboratories (Lab.1=$x_1 \pm U_1$; Lab.2=$x_2 \pm U_2$) are compatible if:

$$|x_1 - x_2| < k\sqrt{\left(\frac{U_1}{k_1}\right)^2 + \left(\frac{U_2}{k_2}\right)^2}$$

Frequently, k, k_1 and k_2 are equal to 2 for a confidence level of approximately 95%.

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The chance of measurement results, obtained by two laboratories, being compatible increases when measurement results are comparable (e.g. traceable to the same reference).

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The chance of measurement results, obtained by two laboratories, being compatible increases when measurement results are comparable (i.e. traceable to the same reference).

In these cases, laboratories most probably would decide equivalently about the compliance with the same legislation or specification, or about the price of the same product.

2. Metrological traceability concept

This concept is also important for fundamental and applied research when results from different systems and obtained in different laboratories are to be compared.

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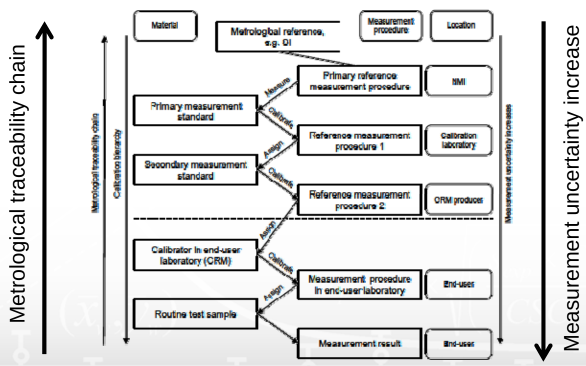
3. Types of measurement references

According to VIM3 [1] measurements can be traced to:

1. A measurement unit (mol L^{-1}; mg kg^{-1}) through its practical realization:



2 - V. J. Barwick and E. Prichard (Ed.) Eurachem Guide: Terminology in Analytical Measurements – Introduction to VIM3 (2011) (www.eurachem.org).

3. Types of measurement references

According to VIM3 [1] measurements can be traced to:

(...)

2. A measurement standard (e.g. Certified reference material, CRM);

   Some analytical field are extensively covered with CRM (...)
   Not available for most analysis of organic compounds in biological samples.

3. Types of measurement references

According to VIM3 [1] measurements can be traced to:

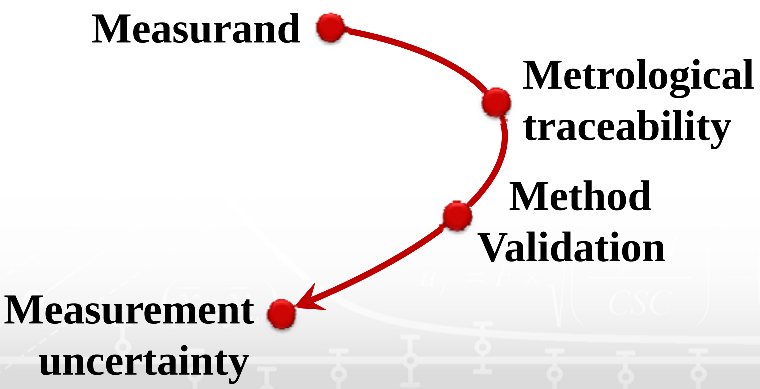
(...)

3. A measurement procedure (operationally defined measurement procedure):

   Some authors prefer to state that measurements: i)are traceable to the value defined by the measurement procedure OR ii) traceability is defined as given by the application of the method.
   Many chemical analysis are performed by operationally defined measurement procedures.

4. When traceability is defined

Metrological traceability is defined when the calibration standard or the operationally defined measurement procedure is selected.



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5. How to demonstrate traceability

The measurement traceability can be demonstrated by:

-listing the traceability statements of all relevant input quantifies;

-describing the traceability of the value of the used standard and proving the adequacy of the measurement procedure to guarantee traceability to this reference (e.g. correction of observed bias in CRM measurements).

The assessment of the metrological traceability aims at checking if it is fit for the intended use.

6. Case studies

Case 1:

Two laboratories analyse the mass fraction of nickel in industrial residue X:

Lab.1: Measurement procedure A – Digestion with aqua regia in defined concentration and temperature conditions: Result 1: 250±30 μg kg^{-1} (k=2);

Lab.2: Measurement procedure B – Digestion with nitric acid in defined concentration and temperature conditions: Result 2: 220±45 μg kg^{-1} (k=2).

6. Case studies

Case 1:

(...) Result 1: 250±30 μg kg^{-1} (k=2);
Result 2: 220±45 μg kg^{-1} (k=2).

- Are measurement results compatible?

$$\left[\left|250-220\right|=30\right] < \left[2\sqrt{\left(\frac{30}{2}\right)^2+\left(\frac{45}{2}\right)^2}=54\right]$$

(...)

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6. Case studies

Case 1:

(...) Result 1: 250±30 μg kg^{-1} (k=2);
Result 2: 220±45 μg kg^{-1} (k=2).

Are measurement results compatible?

$$\left[\left|250-220\right|=30\right] < \left[2\sqrt{\left(\frac{30}{2}\right)^2+\left(\frac{45}{2}\right)^2}=54\right]$$

Measurement results are not compatible since they refer to different measurands:

1 – Mass fraction of nickel in the industrial residue X estimated by measurement procedure A;

2 – Mass fraction of nickel in the industrial residue X estimated by measurement procedure B.

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6. Case studies

Case 1:

(...) Result 1: 250±30 μg kg^{-1} (k=2);
Result 2: 220±45 μg kg^{-1} (k=2).

Are measurement results compatible?

$$\left[\left|250-220\right|=30\right] < \left[2\sqrt{\left(\frac{30}{2}\right)^2+\left(\frac{45}{2}\right)^2}=54\right]$$

These measurement results are also not comparable (measurements procedures 1 and 2 are different operationally defined measurement procedures).

6. Case studies

Case 2:

Laboratory X measured the mass fraction of methamidophos in tomato sample Y and measurement performance is checked through the analysis of a certified reference material of methamidophos in tomato puree. The certified value was estimated by isotope dilution mass spectrometry (IDMS).

Laboratory X is deciding how to deal with the analyte recovery observed from the analysis of the CRM:

(...)

6. Case studies

Case 2:

(...)

Laboratory X is deciding how to deal with the analyte recovery observed from the analysis of the CRM:

Option 1: Do not correct analyte recovery if a mean value between 70-120% is observed;

Option 2: Correct measurements results for observed analyte recovery.

6. Case studies

Case 2:

(...)

Laboratory X is deciding how to deal with the analyte recovery observed from the analysis of the CRM:

Option 1: Do not correct analyte recovery if a mean value between 70-120% is observed:

- Measurement result traceable to the operationally defined measurement procedure;

Option 2: Correct measurements results for observed analyte recovery:

- Measurement result traceable to the quantity value embodied in the CRM [3].

3 - P. De Bièvre, R. Dybkaer, A. Fajgelj, D.B. Hibbert, Metrological traceability of measurement results in chemistry: concepts and implementation (IUPAC Recommendations 2009), IUPAC, 2010

7. Highlights

The metrological traceability concept is the key for justifying differences in evaluations performed in different laboratories in some analytical fields.