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METROLOGICAL TRACEABILITY OF MEASUREMENT RESULTS IN CHEMISTRY: CONCEPTS AND IMPLEMENTATION (IUPAC RECOMMENDATIONS 2009)

Prepared for publication by

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Metrological Traceability of Measurement Results In Chemistry: Concepts and Implementation
(IUPAC recommendations 2009)

Abstract: This IUPAC study aims at formulating recommendations concerning the metrological traceability of a measurement result in chemistry. It is intended to provide the chemical measurement community with a consistent view of the creation, meaning, and role of metrological traceability and its underpinning concepts. No distinction is made between measurement results obtained in “high metrology” and in the “field”. A description is given of the calibration hierarchies needed in different circumstances to arrive at metrological traceability along a metrological traceability chain. Flow charts of generic calibration hierarchies are presented as well as a variety of examples. The establishment, assessment, and reporting of metrological traceability are discussed, including the needed metrological institutional framework and the role of interlaboratory comparisons. Recommendations are made about the essential steps in planning and performing a measurement, and reporting a measurement result.
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1 INTRODUCTION

In commerce, society, and science metrological comparability of measured quantity values and various published values is essential to determine their spatio-temporal differences, ratios, and drifts. Achieving metrological comparability of measurement results requires definition of calibration hierarchies providing metrological traceability chains which enable the establishment of metrological traceability of measured quantity values to a common and stable metrological reference.

Experience has shown that the definition of the concepts involved, their relation, role, and use is insufficient and varied. Consequently, an attempt is made in this study to use a set of consistent concepts with associated systematic terms for measurement in chemistry, so the reader should not expect in this study to see all the terms used in daily analytical work because their inconsistency would limit the understanding of metrological traceability. The substitution principle is respected as much as possible, i.e. in a definition or text it should be possible to substitute a term by the definition of the corresponding concept without creating circularity.


As this document is concerned with measurement, only properties that possess a magnitude, i.e. quantities, are considered. Nominal properties are therefore not addressed.

1.1 Conventions

The following conventions are followed:

- Following VIM3, single quotation marks ‘...’ refer to any concept when useful, and double quotation marks “...” enclose terms and quotations from other sources.
- Entries from VIM3 are quoted verbatim in the case of terms and definitions and the use of bold type, but might not include all its examples and notes.
- Other entries and the text as such follow the PAC convention of using italic face only the first time a concept appears in a numbered section, be it text, table, figure, or legend.
- Figures, equations, and terms for concepts are numbered according to the section in which they appear and then with a running number. Thus concept 2.4 – 2 is the second concept in section 2.4.

A number of initialisms, acronyms and abbreviations will be used in the text and are listed in Annexe I.

1.2 Stating the challenges

In recent years the concept ‘traceability’ in chemical measurement has received an extraordinary amount of attention, for example:

- It has been the theme of numerous workshops and symposia.
- Demonstration of “measurement traceability” is required in the International Standards on accreditation ISO/IEC 17025, ISO 15195, and ISO 15189 [7-9],
- ‘Traceability’ is the subject of ILAC-G2 [10] and EURACHEM/CITAC Guide [11],
- Two standards for the assignment of quantity values to calibrators used in laboratory medicine stipulate and explain metrological traceability: ISO 17511 and ISO 18153 [12, 13].
- It is mentioned frequently in CIPM-MRA.
It is mentioned in ISO Guides 34 and 35 (REMCO) [14, 15], and in an EU directive [16].

Still the interpretation of “metrological traceability” varies in the literature [17, 18]. Also, many available reference materials often lack information about metrological traceability (and associated measurement uncertainty) for assigned quantity values. The lack of clarity about such an important and widely used concept makes it difficult to reach world-wide agreement on its meaning and application. Furthermore, communication about and use of measurement results is hampered.

Discussions with analytical chemists have revealed that basic concepts in metrology, including ‘traceability’ are generally not an integral part of university or college curricula and are not treated in most textbooks of analytical chemistry.

The concept and term “traceability” present the following challenges.

1. In spite of the definition having traceability as a property of a measurement result (see 1.2-1), it is common to refer to the traceability of a
   a. document such as a measurement procedure (which is a physical object), or
   b. sample (which is a physical object), or
   c. measurement (which is a process).

2. It is often claimed that a measurement result can be traceable to an institution (e.g. a specified NMI).

3. Despite a growing awareness of the need for metrological traceability of measurement results, some field and routine laboratories still assert that metrological traceability is not “applicable” to their measurement results.

4. It is not generally accepted that traceability to a common stated metrological reference is a precondition for metrological comparability of measurement results.

5. The colloquial meaning of the term “comparability” often refers to quantity values of the same magnitude (size).

6. There is the perception that a measurement unit from the International System of Units (SI) is the only possible metrological reference in the metrological traceability of chemical measurement results.

7. There is a belief that the use of a reference material (RM) or a certified reference material (CRM) for quality control purposes automatically establishes metrological traceability.

8. Claims are made that satisfactory participation in an interlaboratory comparison, proficiency testing scheme, or external quality assessment scheme automatically provides metrological traceability of the participants’ measurement results.

9. VIM3 does not define the concept metrological reference.

In response to the group of challenges identified as item (1) above, metrological traceability is only considered to be a characteristic of the concept of a measurement result (and thereby also of a measured quantity value). In cases in which the history of physical objects is to be established, it is suggested to designate other concepts by terms such as “document traceability” or “sample traceability”.

1.2.1. metrological traceability

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

NOTE 1 For this definition, a ‘reference’ can be a definition of a measurement unit through its practical realization, or a measurement procedure including the measurement unit for a non-ordinal quantity, or a measurement standard.

NOTE 2 Metrological traceability requires an established calibration hierarchy.

NOTE 3 Specification of the reference must include the time at which this reference was used in establishing the calibration hierarchy, along with any other relevant metrological information about the reference, such as when the first calibration in the calibration hierarchy was performed.
NOTE 4 For **measurements** with more than one **input quantity to the measurement model** each of the input **quantity values** should itself be metrologically traceable and the calibration hierarchy involved may form a branched structure or a network. The effort involved in establishing metrological traceability for each input quantity value should be commensurate with its relative contribution to the measurement result.

NOTE 5 Metrological traceability of a measurement result does not ensure that the measurement uncertainty is adequate for a given purpose or the absence of mistakes.

NOTE 6 A comparison between two measurement standards may be viewed as a calibration if the comparison is used to check and, if necessary, correct the quantity value and measurement uncertainty attributed to one of the measurement standards.

NOTE 7 The ILAC considers the elements for confirming metrological traceability to be an unbroken **metrological traceability chain** to an **international measurement standard** or a **national measurement standard**, a documented measurement uncertainty, a documented measurement procedure, accredited technical competence, metrological traceability to the SI, and calibration intervals (see ILAC P 10:2002 [18]).

NOTE 8 The abbreviated term ‘traceability’ is sometimes used to mean “metrological traceability” as well as other concepts, such as “sample traceability” or “document traceability”, or “instrument traceability”, where the history (“trace”) of an item is meant. Therefore, the full term of “metrological traceability” is preferred if there is any risk of confusion.

[VIM3-2.41]

EXAMPLES

There are three types of ‘reference’ listed in Note 1. The following examples are taken from the IFCC-IUPAC NPU terminology for laboratory medicine [19]. A question mark stands for a numerical value.

1 Measurement unit
   NPU02319 Blood–Haemoglobin(Fe); amount-of-substance concentration
   = ? millimole per litre.

2 Measurement procedure
   NPU09229 Calculus(Urine)–Carbonate; arbitrary content (measurement procedure)
   = ?, where “arbitrary” indicates that the measurement scale is ordinal (i.e. with no measurement unit) and is defined in the measurement procedure.

3 Measurement standard as a sole metrological reference is hardly possible.

1 Measurement procedure and measurement unit
   NPU19981 Plasma–Alanine transaminase; catalytic activity concentration(IFCC 1998)
   = ? microkatal per litre.

2 Measurement standard and measurement unit
   NPU27287 Plasma–Penicillium species antibody(Immunoglobulin G); mass concentration (WHO International Reference Preparation 67/86); 
   = ? milligram per litre.

3 Measurement unit, measurement procedure, and measurement standard
   NPU04003 Plasma–Choriogonadotropin; arbitrary amount-of-substance concentration (WHO International Standard 61/6; measurement procedure)
   = ? international unit per litre.

1.3 Importance of metrological traceability

Among the many aspects of measurement that affect the reliability of a measurement result, the attainment of metrological traceability is essential. It underpins the ability of the analyst to claim that his or her result “is what it purports to be” [20].
A key requirement in many situations, such as in cross-border trade, in laboratory medicine (clinical laboratory sciences), and in transnational implementation of environmental regulations, is that of *metrological comparability of measurement results*. If a given *quantity* is measured in a given material by both buyer and seller, they should be confident that they will obtain measurement results agreeing within their stated *measurement uncertainties*.

The need for metrological comparability of measurement results also extends in time. In order to understand temporal changes of a monitored system, such as the carbon dioxide concentration in the atmosphere at a particular location, or the cholesterol concentration in a person’s blood plasma, measurement results obtained at one time must be comparable with those obtained at another time, in the same or in another laboratory. This is assured when the results are traceable to the same *metrological reference*, even if calibrators or *measuring systems* or relative measurement uncertainties are different.

### 1.3-1. metrological comparability of measurement results

metrological comparability

comparability of *measurement results*, for *quantities* of a given *kind*, that are metrologically traceable to the same reference

**NOTE 1** See Note 1 to 2.41 *metrological traceability*.

**NOTE 2** Metrological comparability of measurement results does not necessitate that the *measured quantity values* and associated *measurement uncertainties* compared are of the same order of magnitude.

[VIM3-2.46]

The concept of metrological comparability should be distinguished from *metrological compatibility of measurement results* (see Concept ).
2 CONCEPTS RELATED TO METROLOGICAL TRACEABILITY

Before attempting to describe various aspects and relations of metrological traceability, it is necessary to define and comment upon some fundamental concepts used in the description. This is especially true because terminology varies among chemical disciplines. This chapter is based on the concepts and associated terms given in the VIM3 [1], and ISO 17511 [12], interspersed with supplementary proposals.

2.1 General concepts in measurement

2.1-1. measurement
process of experimentally obtaining one or more quantity values that can reasonably be attributed to a quantity

NOTE 1 Measurement does not apply to nominal properties
NOTE 2 Measurement implies comparison of quantities including counting of entities.
NOTE 3 Measurement presupposes a description of the quantity commensurate with the intended use of a measurement result, a measurement procedure, and a calibrated measuring system operating according to the specified measurement procedure, including the measurement conditions.

Nominal properties, such as identity of a chemical compound or a sequence of amino acids in a polypeptide, are important in chemistry; they are not measured but rather examined.

2.1-2. quantity
property of a phenomenon, body, or substance, where the property has a magnitude that can be expressed as a number and a reference

The generically subordinate concepts, here called types of quantity:

- ordinal quantity
- ‘differential quantity’ (also known as “difference quantity” or “interval quantity”)
- ‘differential logarithmic quantity’ (also known as “difference logarithmic quantity”)
- ‘rational quantity’ (also known as “ratio quantity”)

of which the first cannot be associated with a measurement unit whereas the next three all have measurement units. When differential and rational quantities have the quantity dimension one, the coherent measurement unit is one (symbol “1”). Differential logarithmic quantities all have the quantity dimension one, and the coherent measurement unit one.

The division of the concept ‘quantity’ into various types [21] is here preferred as being more fundamental than describing the associated types of measurement scale [22, 23].

The description of a quantity should include information about the system considered, any relevant component(s) and the kind-of-quantity. Each of these three parts may require specifications. The description of the quantity intended to be measured, i.e. the measurand, may be in the format:

System(specification) — Component(specification); kind-of-quantity(specification) [24].

For identification of a particular system (sometimes called instantiation), a stated location and calendar time are required. For a component, it may be necessary to specify information such as oxidation state and speciation of an element in a matrix, or isomeric form of a compound. For a kind-of-quantity, specification can be calibrator or measurement procedure or quantity-value scale.

This format for description of a quantity includes descriptions of “operationally defined quantities” that are measured by so-called “empirical methods” or “standard methods”.

IUPAC and IFCC have published a number of technical reports using this format under the global
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Dedicated kinds-of-quantity [24] for each specific concept under quantity are given in Table 2.1–1.

Table 2.1–1 Dedicated kinds-of-quantity [24] for each specific concept under quantity

<table>
<thead>
<tr>
<th>Type of quantity</th>
<th>System*</th>
<th>Component = Analyte</th>
<th>Kind-of-quantity (symbol)</th>
<th>Measurement unit (symbol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ordinal</td>
<td>petroleum fuel</td>
<td>petroleum fuel</td>
<td>octave number with procedure $\theta$</td>
<td>not applicable</td>
</tr>
<tr>
<td>differential</td>
<td>thermostat</td>
<td>water</td>
<td>Celsius temperature $(^\circ C)$</td>
<td>degree Celsius</td>
</tr>
<tr>
<td>differential</td>
<td>lake</td>
<td>water</td>
<td>pH (pH)</td>
<td>one (1)</td>
</tr>
<tr>
<td>logarithmic</td>
<td>butter</td>
<td>sodium chloride</td>
<td>amount-of-substance content $k$</td>
<td>mole per kilogram (mol/kg)</td>
</tr>
<tr>
<td>rational</td>
<td>ore</td>
<td>iron</td>
<td>mass fraction $w_B$</td>
<td>one kilogram per kilogram (1 kg/kg)</td>
</tr>
<tr>
<td></td>
<td>exhaled air</td>
<td>ethanol</td>
<td>mass concentration $\gamma$</td>
<td>kilogram per cubic metre (kg/m$^3$)</td>
</tr>
</tbody>
</table>

* Location and calendar time are necessary specifications to 'system' for converting a dedicated kind-of-quantity into a singular quantity (corresponding to one instance).

The allowed mathematical treatment of quantity values depends on the specific type of quantity.

The act of measurement requires the following set of interacting elements:

- measurand, defined by kind-of-quantity, any component(s), and instantiated system (i.e. time and place specified) (Table 2.1–1);
- measurement model or measurement function;
- measurement principle(s);
- measurement method;
- validated measurement procedure including a calibration hierarchy;
- measuring system under quality control; and
- operator(s).

2.1.3. measurement result 
result of a measurement

set of quantity values being attributed to a measurand together with any other available relevant information

NOTE 1 A measurement result generally contains “relevant information” about the set of quantity values, such that some may be more representative of the measurand than others. This may be expressed in the form of a probability density function (PDF).

NOTE 2 A measurement result is generally expressed as a single measured quantity value and a measurement uncertainty. If the measurement uncertainty is considered to be negligible for some purpose, the measurement result may be expressed as a single measured quantity value. In many fields this is the common way of expressing a measurement result.
NOTE 3 In the traditional literature and in the previous edition of the VIM, measurement result was defined as a value attributed to a measurand and explained to mean an *indication*, or an uncorrected result, or a corrected result, according to the context.

[VIM3-2.9]

2.1-4. measurand

*quantity* intended to be measured

NOTE 1 The specification of a measurand requires knowledge of the kind of *quantity*, description of the state of the phenomenon, body, or substance carrying the quantity, including any relevant component, and the chemical entities involved.

NOTE 2 In the 2nd edition of the VIM and in IEC 60050-300:2001, the measurand is defined as the 'quantity subject to measurement'.

NOTE 3 The *measurement*, including the *measuring system* and the conditions under which the measurement is carried out, might change the phenomenon, body, or substance such that the quantity being measured may differ from the *measurand* as defined. In this case adequate *correction* is necessary.

EXAMPLE 1 The potential difference between the terminals of a battery may decrease when using a voltmeter with a significant internal conductance to perform the measurement. The open-circuit potential difference can be calculated from the internal resistances of the battery and the voltmeter.

EXAMPLE 2 The length of a steel rod in equilibrium with the ambient Celsius temperature of 23 °C will be different from the length at the specified temperature of 20 °C, which is the measurand. In this case a correction is necessary.

NOTE 4 In chemistry, “analyte”, or the name of a substance or compound, are terms sometimes used for ‘measurand’. This usage is erroneous because these terms do not refer to quantities.

[VIM3-2.3]

Example: The amount-of-substance concentration of sodium ion in blood plasma of a given person at a stated calendar time.

The delineation of a system carrying a measurand will influence the type of sampling plan and thereby the sampling measurement uncertainty.

Example 1: In the measurement of amount-of-substance content of total Cd in a given agricultural piece of land, the measurement results will differ depending on whether the chosen system is the whole field, or a single sample; the sampling plan chosen for the field will also influence the measurement result.

Example 2: The amount-of-substance concentration of glucose in fasting human venous blood plasma will depend on whether the system of plasma comes from a group of healthy persons, a given person, or a given sample of a person.

The definition of a measurand may include a stipulated measurement procedure. Such a measurand is sometimes termed an operationally defined or standardized measurand.

2.1-5. *quantity value*

*value* of a quantity

number and reference together expressing magnitude of a *quantity*

[VIM3-1.19]
2.1-6. **measured quantity value**
measured value of a quantity
measured value

**quantity value** representing a measurement result

NOTE 4 In the GUM, the terms “result of a measurement” and “estimate of the value of the measurand” or just “estimate of the measurand” are used for ‘measured quantity value’.
[VIM3-2.10]

A quantity value can be expressed as a

- product of a number and a measurement unit for a differential or rational quantity, e.g.
  amount-of-substance concentration of Cd\(^{2+}\) in a sample of wine = \(1.2 \times 10^{-6}\) mol/L; or
- number for a differential or rational quantity of metrological dimension one, e.g. pH of a
  blood sample = 7.2, (the SI unit “one” is generally not written out), number fractions of
  lymphocytes among all leukocytes in blood; or
- number and a metrological reference to a measurement procedure for an ordinal quantity, e.g.
  Rockwell C hardness (150 kg load) of a steel sample = 43.4 HRC(150 kg); or
- product of a number, a measurement unit for a differential or rational quantity with kind-of-
  quantity specified by a measurement procedure, e.g. a leaching procedure; or
- number, a non-SI measurement unit for a differential or rational quantity with kind-of-quantity
  specified by convention and carried by a calibrator, and some reference to a measurement
  procedure, e.g. arbitrary concentration(WHO second International Standard 91/666; immunoprocedure) of coagulation factor VIII in a plasma sample = 5 400 International
  Units per litre.

The relation between input and output quantities in a measurement model is described in the most
general way by a

2.1-7. **measurement model**
model of measurement
model

mathematical relation among all quantities known to be involved in a measurement

NOTE 1 A general form of the measurement model is the equation
\[ h(Y, X_1, \ldots, X_n) = 0 \]
where \(Y\), the output quantity in the measurement model, is the
measurand that is to be inferred from information about input quantities in the
measurement model \(X_1, \ldots, X_n\).

NOTE 2 In more complex cases where there are two or more output quantities, the
measurement model consists of more than one equation.
[VIM3-2.48]

A measurement model accommodates algorithms as well as explicit functions and will be used later
for specific examples of metrological traceability chains in Chapter 9.

2.1-8. **measurement function**
function of quantities, the value of which, when calculated using known quantity values
for the input quantities in a measurement model, is a measured quantity value of the
output quantity in the measurement model

NOTE 1 If a measurement model \(h(Y, X_1, \ldots, X_n) = 0\) can explicitly be written as \(Y = f(X_1, \ldots, X_n)\), where \(Y\) is the output quantity in the measurement model, the function \(f\) is
the measurement function. More generally, \(f\) may symbolize an algorithm, yielding for
input quantity values \(x_1, \ldots, x_n\) a corresponding unique output quantity value \(y = f(x_1, \ldots, x_n)\).
The measurement function is used to calculate the measurement uncertainty associated with the measured quantity value of $Y$.

Sometimes, the measurement function may be written as

$$Y = f(X_1, ..., X_j)(X_k, ..., X_n) \quad (2.1-1)$$

where $X_1, \ldots, X_j$ may be

- input quantities in a measurement model, measured in the experiment to establish the quantity value of $Y$, that are given by the defining quantity equation (VIM3-1.22) of the kind-of-quantity for $Y$, such as mass concentration = mass of component (i.e. element or compound) divided by volume of system;
- input quantities in a measurement model, measured in the experiment to establish the quantity value of $Y$, that are different from those given by the definition of the kind-of-quantity for $Y$;
  - quantities, values of which have been taken from literature, such as molar masses or physical constants;
  - corrections (see section 2.10) for quantities that are inherent in the measured system or sample such as a correction for the effect of haemoglobin concentration when measuring bilirubin concentration in plasma by visible light spectrometry; and
  - corrections for external quantities that affect the measured system or the measuring system, such as ambient temperature, pressure, or humidity;
- influence quantities that affect one or more of the input quantities $X_1, \ldots, X_j$ and have given values, such as the specified experimental temperature in measurement of catalytic activity; they can be regarded as specifications to the definition of the measurand.

and $X_k, \ldots, X_n$ may comprise

- influence quantities that affect one or more of the input quantities $X_1, \ldots, X_j$ and have given values, such as the specified experimental temperature in measurement of catalytic activity; they can be regarded as specifications to the definition of the measurand.

All input quantity values $x_1, \ldots, x_n$ must be metrologically traceable. They contribute components of the measurement uncertainty for the measurand $Y$.

The output is a measured quantity value.

The measured quantity value, $y$, calculated by the function $y = f(x_1, \ldots, x_j)$, is an estimate of the location of the distribution of quantity values that is attributed to the measurand, which belongs to, and describes, an investigated system. A measurement function is usually based on the best available theory, which may not be complete. For example, the use of the Bates-Guggenheim equation for the single ion activity for the chloride ion in the measurement function for pH determined using a Harned cell is known to be based on an incomplete theory [27]. Known and presumed deficiencies or intentional omissions in the definition of the measurand and thereby in the measurement function or measurement model contribute components to the measurement uncertainty of the measured quantity value. The combination of such components constitutes a definitional uncertainty component of measurement uncertainty resulting from the finite amount of detail in the definition of a measurand

NOTE 1 Definitional uncertainty is the practical minimum measurement uncertainty achievable in any measurement of a given measurand.

NOTE 2 Any change in the descriptive detail leads to another definitional uncertainty.

NOTE 3 In the ISO/IEC Guide 98-3:2008, D.3.4, and in IEC 60359 the concept ‘definitional uncertainty’ is termed “intrinsic uncertainty”.

Note: Defining the measurand is the first step of any measurement procedure. The ensuing definitional uncertainty can therefore be considered as a part of the measurement uncertainty.
For each measured input quantity in a measurement model, a measurement principle has to be chosen and translated into a measurement method and measurement procedure. A measuring system is then assembled accordingly, including the indicated measuring equipment, calibrators, and any chemical reagents.

2.1-10. measurement principle
principle of measurement
phenomenon serving as the basis of a measurement

[VIM3-2.4]

Examples of measurement principles are:

- absorption of radiation energy in light spectrometry for the measurement of amount-of-substance concentration;
- lowering of the concentration of glucose in blood in a fasting rabbit applied to the measurement of insulin concentration in a preparation; and
- conversion of two different kinds of uncharged particles into ions (“ionization”) in a mass spectrometer for the measurement of their amount-of-substance ratio;
- separation;
- derivatization.

A given measurement method may involve more than one measurement principle.

2.1-11. measurement method
method of measurement
generic description of a logical organization of operations used in a measurement

[VIM3-2.5]

When a measurement requires the sequential or parallel use of several pieces of equipment or reagents or both, the measurement method consists of a short presentation of the procedural structure.

2.1-12. measurement procedure
detailed description of a measurement according to one or more measurement principles and to a given measurement method, based on a measurement model and including any calculation to obtain a measurement result

[VIM3-2.6]

The measurement procedure is usually a document including the measurement model, measurement principle(s), measurement method, description of measuring system, (including equipment, reagents, and utensils), calibrators, metrological traceability of obtainable measurement results, calculation of measurement result, including measurement uncertainty, quality control system, and reporting. Any measurement procedure must be validated.

2.1-13. measuring system
set of one or more measuring instruments and often other devices, including any reagent and supply, assembled and adapted to give information used to generate measured quantity values within specified intervals for quantities of specified kinds

[VIM3-3.2]

2.2 Calibration

Measuring systems in chemistry need to be calibrated in such a way as to ensure metrological traceability of the measurement result. An unknown quantity value embodied in a sample is measured by means of a calibrated measuring system, according to a measurement procedure including a measurement model. The calibrated measuring system provides an indication the value of which is
either, directly, the measured quantity value of the measurand, or is transformed into such a measured quantity value by the measurement model. Measurement uncertainty is obtained via the measurement model. The measurement result then consists of this measured quantity value and its calculated measurement uncertainty.

2.2-1. calibration

operation that, under specified conditions, in a first step establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication.

NOTE 1 A calibration may be expressed by a statement, calibration function, calibration diagram, calibration curve, or calibration table. In some cases it may consist of an additive or multiplicative correction of the indication with associated measurement uncertainty.

NOTE 2 Calibration should not be confused with adjustment of a measuring system, often mistakenly called “self-calibration”, nor with verification of calibration.

NOTE 3 Often, the first step alone in the above definition is perceived as being calibration.

The quantity value, \( y_{\text{cal}} \), of a measurement standard, here chosen to be a calibrator, is the independent variable and the indication, \( I_{\text{cal}} \), is the dependent variable in the first step of the definition corresponding to the calibration model \( h(I_{\text{cal}}, y_{\text{cal}}) = 0 \). The second step produces the inverse measurement model \( h(y_{\text{sample}}, I_{\text{sample}}) = 0 \).

The outcome of the calibration may be documented in a certification report or calibration certificate.

2.3 Measurement standard

Establishing metrological traceability often requires a

2.3-1. measurement standard

etalon

realization of the definition of a given quantity, with stated quantity value and associated measurement uncertainty, used as a reference

[VIM3-5.1]

The “realization of the definition of a given quantity” can be provided by operating a measuring system according to a measurement procedure, or by a material measure, or by a reference material, measurement standard, or calibrator. In the case of chemical measurement standards, the term “embodiment” is here preferred to “realization” as the latter term carries several non-applicable connotations. In many cases in chemistry, measurement standards are embodiments of the definition of a measurement unit. Several quantities of the same or different kinds-of-quantity may be embodied in one measurement standard.

Examples of measurement standards (partly taken from VIM3) are: a 1 kg mass standard; a standard hydrogen electrode; a set of reference solutions of cortisol in human serum having certified concentrations of cortisol; a certified reference material providing certified quantity values for the mass concentration of each of ten different proteins; and an ampoule with WHO International Standard 75/589 containing 650 International Units of chiorionic gonadotropin. In all cases, a quantity value must be accompanied by a measurement uncertainty and stated metrological traceability.

A series of “descending levels” of measurement standards or calibrators, i.e. with increasing relative measurement uncertainties of assigned quantity values in a given calibration hierarchy, is often described by the following concepts.
2.3-2. primary measurement standard

primary standard

measurement standard established using a primary reference measurement procedure

or created as an artifact, chosen by convention

EXAMPLE 1 Primary measurement standard of amount-of-substance concentration
prepared by dissolving a known amount of substance of a chemical component to a known
volume of solution.

[VIM3-5.4]

A primary measurement standard (or a primary calibrator) of a differential or rational quantity
embodies its measurement unit. Ordinal quantities have no measurement units and the established
quantity value and measurement uncertainty rely on the metrological reference and on the means of
embodiment described in Section 1.1.

The first measurement standard (or calibrator) of a calibration hierarchy for a differential or rational
quantity is always a primary measurement standard (or primary calibrator). The assignment of quantity
value with the associated measurement uncertainty to a primary measurement standard is done by
means of a primary reference measurement procedure.

2.3-3. secondary measurement standard

secondary standard

measurement standard established through calibration with respect to a primary
measurement standard for a quantity of the same kind

[VIM3-5.5]

Examples of secondary measurement standards (or secondary calibrators) can be found in the
metrological traceability chains of the figures in chapter 9.

2.3-4. reference measurement standard

reference standard

measurement standard designated for the calibration of other measurement standards
for quantities of a given kind in a given organization or at a given location

[VIM3-5.6]

In a calibration hierarchy the metrologically lowest measurement standard defined by VIM3 is

2.3-5. working measurement standard

working standard

measurement standard that is used routinely to calibrate or verify measuring
instruments or measuring systems

[VIM3-5.7]

Note: A measurement standard used for calibration in a given measurement should not also be used
for trueness control, but can be used for precision control.

The quantity value and measurement uncertainty of a working measurement standard is established
using the measurement procedure located just above the end-user’s measurement procedure in the
calibration hierarchy.

In independent terminological dimensions, modifiers such as “international” [VIM3-5.2], “national”
[VIM3-5.3], “regional”, “travelling” [VIM3-5.8], “intrinsic” [VIM3-5.10] or “reference” [VIM3-5.6]
are sometimes used as prefaces to “measurement standard”.

2.4 Calibrator

When a measurement standard is used specifically for the purposes of calibration rather than for
quality control, it becomes a
2.4-1. calibrator

measurement standard used in calibration

[VIM3-5.12]

Note: The term “calibrant” is also used.

In addition to the assigned quantity value and measurement uncertainty, a calibrator must be accompanied by information about: the origin (material traceability, where such information has a bearing on the use of the material), production, definition of quantity, any matrix, homogeneity, stability, procedure used in the assignment of quantity value and measurement uncertainty, statement of metrological traceability, expiry date, intended use of the calibrator [28, 29], and instructions for use.

In addition to these essential properties, its use in a calibration hierarchy requires that it be commutable.

2.4-2. commutability of a reference material

property of a reference material, demonstrated by the closeness of agreement between the relation among the measurement results for a stated quantity in this material, obtained according to two given measurement procedures, and the relation obtained among the measurement results for other specified materials

NOTE 1 The reference material in question is usually a calibrator and the other specified materials are usually routine samples.

NOTE 2 The measurement procedures referred to in the definition are the one preceding and the one following the reference material (calibrator) in question in a calibration hierarchy (see ISO 17511) [12].

NOTE 3 The stability of commutable reference materials is monitored regularly.

[VIM3-5.15]

Lack of commutability in a reference material leads to measurement bias.

2.4-3. primary calibrator

calibrator established without reference to another calibrator for the same kind-of-quantity

Note 1: The quantity value and the measurement uncertainty of a primary calibrator are obtained by a direct primary reference measurement procedure or by primary preparation procedure.

Note 2: Such a calibrator is usually accompanied by a certification report [28] or a calibration certificate issued by an International or National Metrology Institute, see Figure 3.2-1.

Note 3: A primary calibrator is often assumed to embody a quantity and its quantity value with the smallest achievable measurement uncertainty, but the size of the relative measurement uncertainty is not a criterion for being called “primary”.

2.4-4. secondary calibrator

calibrator established by measurement according to a secondary reference measurement procedure

In case no primary calibrator is available, it is recommended by ISO 17511 [12] to produce an

2.4-5. international conventional calibrator

calibrator established by international agreement

The kind-of-quantity must be specified in the measurement procedure. It is noted that the quantity values of some international conventional calibrators are expressed in SI measurement units or in non-SI measurement units with measurement procedures specified.

The ISO 17511 [12] identifies the following two consecutive levels of material.
2.4.6. manufacturer’s working calibrator

calibrator established by measurement according to the manufacturer’s selected measurement procedure or a higher measurement procedure calibrated by a primary calibrator or secondary calibrator or an international conventional calibrator

[adapted from ISO 17511 [12]]

2.4.7. manufacturer’s product calibrator

calibrator established according to the manufacturer’s standing measurement procedure calibrated by the manufacturer’s working calibrator

[adapted from ISO 17511 [12]]

The manufacturer’s product calibrator may serve as the end-user’s working calibrator. It is the obligation of any producer of such a calibrator to document the metrological traceability of a quantity value and its measurement uncertainty.

2.5 Calibration hierarchy and metrological traceability chain

According to VIM3 metrological traceability requires an established sequence of calibrations and assignments of quantity values between a measurement result and a metrological reference. These operations are performed using calibrators and measuring systems with measurement procedures and constitute a

2.5-1. calibration hierarchy

sequence of calibrations from a reference to the final measuring system, where the outcome of each calibration depends on the outcome of the previous calibration

NOTE 1 Measurement uncertainty necessarily increases along the sequence of calibrations.

NOTE 2 The elements of a calibration hierarchy are one or more measurement standards and measuring systems operated according to measurement procedures.

NOTE 3 For this definition, the ‘reference’ can be a definition of a measurement unit through its practical realization, or a measurement procedure, or a measurement standard.

[VIM3-2.40]

For this definition, a metrological reference for a differential, logarithmic differential, or rational quantity can be a definition of a measurement unit with its embodiment in a primary calibrator (material or device), using a primary reference measurement procedure or a production procedure. For an ordinal quantity, the metrological reference is a definition of an ordinal quantity-value scale with its embodiment in a set of primary calibrators using a production procedure.

The calibration hierarchy extends down from the metrological reference to the end-user’s measuring system, but to describe metrological traceability of the measurement result, the direction is reversed. The sequence between measurement result and metrological reference is termed and defined:

2.5-2. metrological traceability chain

traceability chain

sequence of measurement standards and calibrations that is used to relate a measurement result to a reference

[VIM3-2.42]

A metrological traceability chain requires a pre-established calibration hierarchy that is chosen before the measurements start. As metrological traceability characterizes the concept measurement result, the metrological traceability chain is “attached” to the measurement result and links it to the chosen metrological reference.
In principle, the elements of a single-stranded calibration hierarchy may be coupled as in the generic flow chart shown in Figure 2.5–1, but in many cases additional strands are attached as shown by triangles, circles, squares, and lozenges.

**Figure 2.5–1** Generic flow chart of a calibration hierarchy providing metrological traceability of a measurement result for which the metrological reference can be

a) "definition of kind-of-quantity and measurement unit" which is embodied by preparing a set of one or more primary calibrators, through measurement using a primary reference measurement procedure; or

b) "definition of kind-of-quantity and measurement unit" which is embodied by preparing a set of one or more primary calibrators through a preparation procedure; or

c) "definition of ordinal kind-of-quantity and ordinal quantity-value scale" which is embodied in a set of calibrators through a primary preparation procedure.

unc is an abbreviation signifying a measurement uncertainty that is calculated according to GUM [2] in cases a) and b), but not in c).

runc signifies relative measurement uncertainty.

The symbol $u$ will be used in specific examples of a) and b) and $u_r$ for ‘combined standard uncertainty’.

A rectangle contains a material object, namely a measuring system, calibrator, or sample. A rounded box contains a documentary object, namely a definition, measurement procedure, measured quantity value, or measurement uncertainty.

Down-pointing triangles contain a number labeling a metrological reference for an input quantity in the measurement model shown in up-pointing triangles on the end-user’s or intermediate measurement procedure. Each level in the calibration hierarchy has its own measurement model and set of input quantities in the measurement model, depicted by different shapes attached to the right-hand boxes.

The number in each shape is that of a measurement procedure in the hierarchy, and the type of shape refers to a particular kind-of-quantity.

Note: $Q$ symbolizes a quantity embodied in a calibrator, $I$ an indication.

A given calibrator in a calibration hierarchy serves to calibrate a subsequent measuring system that, by measurement according to a measurement procedure, yields the measured quantity value and measurement uncertainty for the next calibrator or, finally, for the end-user’s sample. The relative measurement uncertainty (runc) associated with the quantity value carried by any calibrator is necessarily greater than that of a preceding calibrator and smaller than that of a following calibrator and the even greater relative measurement uncertainty of the final measurement result. In the figures this is symbolized by a grey triangle to the left, which increases down the page.

In physics, calibration hierarchies have long been an established part of measurement [30, 31]. For complex chemical measurements, the formal establishment of calibration hierarchies is more recent. A particular concern in chemistry is that, when amount-of-substance is reported in the SI unit mole, the embodiment of the definition of the mole would require a primary measurement standard for each of the millions of chemical compounds. CCQM has selected measurement principles and measurement methods which have the potential for the development of primary reference measurement procedures giving component-specific quantity values in mole or its derived units for the quantities carried by primary calibrators. This approach is only possible when the chemical entity or entities, specified in a measurand, can be defined by their atomic or molecular structure, or a suitable part of that. If the elementary entities cannot be thus defined, then amount-of-substance cannot be measured. In this case, and if the component can be otherwise specifically recognized, kinds-of-quantity such as mass, which do not need elementary entities to be specified, can be chosen. Provided that the quantity for measurement is differential or rational, the metrological reference may then be the definition of another measurement unit, such as the kilogram or a WHO International Unit of a given type of biological activity. For an ordinal quantity, no measurement unit is involved and the metrological reference may be a measurement procedure with or without an ensuing calibrator.

As mentioned before, the measurand, for which the measurement result has to be metrologically
traceable, must be carefully defined with regard to system, any component(s), and kind-of-quantity [21]. In a single-stranded calibration hierarchy, the kind-of-quantity is the same throughout.

The term “calibration hierarchy” is used in EAL-G12 [32] and ILAC-G2 [10] in the sense of a plurilevel hierarchy of coordinated and interacting entities responsible for maintaining and disseminating various types and metrological levels of measurement standards. To avoid ambiguity, the present text uses the term “metrological institutional hierarchy” for such a hierarchy. This is further elaborated in Chapter 6.

2.6 Metrological reference

2.6-1. metrological reference

specification of a kind-of-quantity and description of how to obtain one or more conventionally chosen quantity values of that kind-of-quantity

Note 1: The specification is usually in the form of a normative document

Note 2: The types of specification comprise

a) a definition of a measurement unit
b) a measurement procedure
c) a measurement standard
d) a definition of an ordinal quantity-value scale

or combinations of the above.

Note 3: The metrological reference can be local, national, regional or international.

The measurement unit, whether base or derived, coherent or non-coherent, is realized (embodied) in a primary calibrator. The embodiment may be achieved by either

- measurement, using a primary reference measurement procedure and a measuring system, assigning a differential or rational quantity value with measurement uncertainty (see Figure 2.5–1); or

- preparation, using a primary preparation procedure, the execution of which delivers a differential or rational quantity value and its measurement uncertainty [see Figure 2.5–1, legend a) and b]), such as by the preparation of a Josephson junction for the volt, an atomic clock for the second, the international prototype of the kilogram for the kilogram, and a batch of high purity copper for the mole per kilogram.

The ordinal quantity-value scale, unrelated to any measurement unit, is embodied in a set of primary calibrators that are made according to a primary preparation procedure, the execution of which delivers the individual quantity values and their measurement uncertainties [see Figure 2.5–1, legend c]), such as a set of petroleum fuel primary calibrators for measurement of octane number. Measurement uncertainty for an ordinal quantity value cannot be calculated according to GUM, and must be evaluated by another procedure.

2.7 Measurement uncertainty

2.7-1. measurement uncertainty
uncertainty of measurement uncertainty

non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used

[VIM3-2.26]

Components of measurement uncertainty include definitional uncertainty of the measurand, random effects from various sources, components associated with recovery, bias corrections, and the assigned quantity values of measurement standards including calibrators. In the case where many samples of like nature, but having individual recognized systematic effects of unknown magnitude, a component that expresses the dispersion of these effects can be included in the measurement
Components of measurement uncertainty may be evaluated by Type A evaluation of measurement uncertainty, based on the statistical distribution of the quantity values from replicated measurements, and can be described by standard deviations, here termed standard measurement uncertainties [2]. The other components, which may be evaluated by Type B evaluation of measurement uncertainty, can also be described by standard measurement uncertainties, evaluated from assumed probability density functions based on experience, professional judgment, skill, or other information [2].

The measurement uncertainty may be expressed as a standard deviation called standard measurement uncertainty or a given multiple of it, or the half-width of a coverage interval, having a stated coverage probability.

It is understood that the measured quantity value of a measurement result is the best estimate of the quantity value of the measurand.

The quantity value of each calibrator, except the first one, in a calibration hierarchy, has a combined standard measurement uncertainty that incorporates the combined standard measurement uncertainty of the quantity value of the previous calibrator, and must be evaluated and stated. Therefore, in the calibration hierarchy of, for example, Figure 2.5–1, each relative measurement uncertainty $u_i(y_i)/y_i$ is perforce greater than the previous relative measurement uncertainty $u_i(y_i)/y_i$ because $u_i(y_i)/y_i$ combines $u_i(y_i)/y_i$ and the new components of measurement uncertainty incurred at step $i+1$.

How measurement uncertainties are evaluated and combined is beyond the scope of this document. Reference is made to GUM [2] and QUAM [34].

The evaluation of measurement uncertainty requires the establishment of a calibration hierarchy for a measurement result. It is not useful to say that measurement uncertainty demonstrates the “strength” of the metrological traceability chain.

### 2.8 Target measurement uncertainty

The acceptability of a measurement uncertainty is determined by the requirements for the intended use of the measurement result.

#### 2.8.1 Target measurement uncertainty

target uncertainty $U$ specified as an upper limit and decided on the basis of the intended use of measurement results

[VIM3-2.34]

A measurement uncertainty is calculated after a measurement has been performed or is assumed to apply to a measurement result due to validation of the measurement procedure and an accepted outcome of concomitant internal quality control. As the metrological traceability chain of the measurement result to a metrological reference has been decided in the planning stage of the measurement, the types of component of the measurement uncertainty are fixed by that choice. Its actual value can only be calculated after the initial validated measurement or adopted for later measured quantity values obtained by a process under statistical control. The achieved measurement uncertainty can be appropriate for the intended use, or it can be too large, or it can be too small. Thus, the a priori fixing of a target measurement uncertainty requires a study of the intended use of the expected measurement result [35, 36]. Target measurement uncertainty may guide an a priori selection of a calibration hierarchy, using available knowledge and skill, and is influenced by available equipment and measurement procedures. If the minimum measurement uncertainty obtainable in current practice is too large, that may lead to the conclusion that one has either to accept a larger measurement uncertainty than that originally desired, or that better measurement procedures, measuring systems, and measurement standards must be developed to comply with the given target measurement uncertainty.

### 2.9 Multiple metrological traceability chains

The measured quantity value of each quantity in a measurement model must be metrologically traceable. In most chemical measurements there are several input quantities in a measurement model,
each requiring a specified metrological traceability chain. If the specification of the measurand includes quantities with given quantity values they too must have demonstrated metrological traceability chains. For example, the temperature at which a measurement is to be made is often specified.

Where the input quantity in a measurement model is a conversion factor such as molar mass or a fundamental constant, there is no change in the requirement for metrological traceability of its quantity value, but it is likely that its metrological traceability will have been established elsewhere at an earlier time with a sufficiently small relative measurement uncertainty. A short statement to this effect is all that is required when documenting the metrological traceability, for example, quoting, with explicit reference, the use of the latest IUPAC atomic weights (molar masses) [37], and published CODATA fundamental constants [38], with their measurement uncertainties, is sufficient, and no further documentation of metrological traceability of these quantity values is needed.

2.10 Corrections applied for systematic effects

When a quantity value pertaining to a system is estimated by measurement according to a measurement procedure, there are cases in which the ‘initially estimated quantity’, must be adjusted for systematic effects by corrections applied to the indication or to the initially estimated quantity. The effects can be caused inter alia by:

- sampling from an inhomogeneous system;
- inadequate presentation of the system carrying the measurand to the measuring system;
- instrumental bias;
- measurement bias inherent in other elements of a measurement procedure, for example using an indicator in an acid-base titration that changes colour at a value of pH other than at the equivalence point; and
- influence quantities, for example the use of volumetric glassware at a temperature different from that at the time of its calibration.

2.10.1. correction compensation for an estimated systematic effect

[VIM3-2.53]

It is assumed by the GUM [2] that corrections should be applied for all recognized and significant systematic effects, e.g. due to influence quantities. Correction factors or correction addends for systematic effects may be estimated by replicate measurements of an appropriate certified reference material using the measurement procedure, or by comparison between the measurement results obtained with the measurement procedure and those obtained using a reference measurement procedure. When systematic effects are found to be significant, the quantity value of the measurement result is the initially estimated quantity value for the systematic effects adjusted by corrections; the measurement uncertainty in the measurement result is the combination of the measurement uncertainty of the initially estimated quantity value and the measurement uncertainties of the corrections for the systematic effects. Clearly, the metrological traceability of the measurement result requires that both the initially estimated quantity value and the addends or factors correcting for the systematic effects be metrologically traceable. Therefore, in the estimation of addends or factors correcting for systematic effects, the use of measurement procedures that give metrologically traceable measurement results and certified reference materials with metrologically traceable quantity values are necessary.

In some cases the definition of a measurand incorporates the necessity to measure by a specified procedure, sometimes called a “standard method”, in order to avoid a particular systematic effect.

In some types of measurement method, ‘recovery’ is related to a form of systematic effect. The concept ‘recovery’ is currently defined by IUPAC in several ways, and should be re-examined [39].
3 CALIBRATION OF MEASURING SYSTEMS IN A CALIBRATION HIERARCHY

3.1 Function of reference materials in a calibration hierarchy

In any given measurement, a reference material as defined below can function as either a calibrator or a trueness control material, not as both. In a calibration hierarchy, the first is the obvious role. Terminologically, reference material is generically superordinate to the concept certified reference material; yet in a metrological hierarchy, certified reference material has a higher status, as it carries a certified quantity value with associated measurement uncertainty. The definition of reference material in the VIM3 is naturally broad in order to cover a wide variety of meanings, used in practice:

3.1-1. reference material

RM material, sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in measurement or in examination of nominal properties.

NOTE 2 Reference materials with or without assigned quantity values can be used for measurement precision control whereas only reference materials with assigned quantity values can be used for calibration or measurement trueness control.

NOTE 3 ‘Reference material’ comprises materials embodying quantities as well as nominal properties.

EXAMPLE 1 Reference materials embodying quantities:

a) water of stated purity, the dynamic viscosity of which is used to calibrate viscometers;

b) human serum without an assigned quantity value for the amount-of-substance concentration of the inherent cholesterol, used only as a measurement precision control material;

c) fish tissue containing a stated mass fraction of a dioxin¹, used as a calibrator.

EXAMPLE 2 Reference materials embodying nominal properties:

a) colour chart indicating one or more specified colours;

b) DNA compound containing a specified nucleotide sequence;

c) urine containing 19-androstenedione².

NOTE 4 A reference material is sometimes incorporated into a specially fabricated device.

EXAMPLE 1 Substance of known triple-point in a triple-point cell.

EXAMPLE 2 Glass of known optical density in a transmission filter holder.

EXAMPLE 3 Spheres of uniform size mounted on a microscope slide.

NOTE 5 Some reference materials have assigned quantity values that are metrologically traceable to a measurement unit outside a system of units. Such materials include vaccines to which International Units (IU) have been assigned by the World Health Organization.

NOTE 6 In a given measurement, a reference material can only be used for either calibration or quality assurance.

¹ polychlorodibenzodioxin
² 19-norandrost-4-ene-3,17-dione
NOTE 7 The specifications of a reference material should include its material traceability, indicating its origin and processing [40].

NOTE 8 ISO/REMCO has an analogous definition [40] but uses the term “measurement process” to mean ‘examination’ (ISO 15189:2007, 3.4), which covers both measurement of a quantity and examination of a nominal property. [VIM3-5.13]

3.1-2. certified reference material

**CRM**

**reference material**, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures.

**EXAMPLE** Human serum with assigned **quantity value** for the concentration of cholesterol and associated **measurement uncertainty** stated in an accompanying certificate, used as **calibrator** or **measurement trueness** control material.

**NOTE 1** ‘Documentation’ is given in the form of a ‘certificate’ (see ISO Guide 31:2000 [41]).

**NOTE 2** Procedures for the production and certification of certified reference materials are given, e.g. in ISO Guide 34 and ISO Guide 35 [14, 15].

**NOTE 3** In this definition, “uncertainty” covers both ‘measurement uncertainty’ and ‘uncertainty associated with the value of a nominal property’, such as for identity and sequence. “Traceability” covers both ‘metrological traceability of a quantity value’ and ‘traceability of a nominal property value’.

**NOTE 4** Specified quantity values in certified reference materials require metrological traceability with associated measurement uncertainty Accred. Qual. Assur.:2006) [40]. [VIM3-5.14]

### 3.2 Dissemination of calibrators

Typical disseminations of calibrators are shown in Figure 3.2–1, and Figure 3.2–2.

**Figure 3.2–1** A hierarchy of calibrators starting with a “**primary calibrator** with calibration certificate of metrological traceability of a measured quantity value and associated measurement uncertainty to specification of kind-of-quantity and definition of measurement unit”. A vertical arrow between boxes indicates that the **quantity value** and its **measurement uncertainty** of the **quantity** embodied in the material described in the lower box are established by measurement using the calibrator in the upper box as **metrological reference**. A horizontal block arrow indicates that the calibrator in the left hand box is delivered with its calibration certificate to become the calibrator described in the right hand box.

a The **quantity value** and the **measurement uncertainty** of the **quantity** of the calibrator may be assigned by a **reference measurement laboratory** usually designated by an NMI or an international organization.

b The VIM3 definition of **reference measurement standard** covers this hierarchical level of calibrator.

c An end-user may use the purchased calibrator directly for routine measurements or to assign the **quantity value** and **measurement uncertainty** to the **quantity** of the end-user’s working calibrator produced in-house to be used for **calibration** in the measurement of routine samples (not depicted here).

**Figure 3.2–2** A hierarchy of calibrators starting with ‘**international conventional calibrator** with a calibration certificate of metrological traceability of embodied quantity value’.
A vertical arrow between boxes indicates that the quantity value and its measurement uncertainty of the quantity embodied in the material described in the lower box are established by measurement using the calibrator in the upper box as metrological reference. A horizontal block arrow indicates that the calibrator in the left hand box is delivered with its calibration certificate to become the calibrator described in the right hand box.

The quantity value and the measurement uncertainty of the quantity of the calibrator may be assigned by a reference measurement laboratory usually designated by an NMI or an international organization.

The international conventional calibrator is called “International Standard” by WHO. The quantity value and measurement uncertainty of the quantity of such a calibrator may be assigned by one or more reference measurement laboratories under contract with WHO.

The VIM3 definition of reference measurement standard covers this hierarchical level of calibrator.

An end-user may use the purchased calibrator directly for routine measurements or to assign the quantity value and measurement uncertainty to the quantity of the end-user’s working calibrator produced in-house to be used for calibration in the measurement of routine samples (not depicted here).

3.3 Function of reference measurement procedures in a calibration hierarchy

Measurement procedures and calibrators are essential in most calibration hierarchies and in the ensuing metrological traceability chain, which ends in a definition of a measurement unit. The metrological reference may further require stipulating a measurement procedure.

3.3-1. reference measurement procedure

Measurement procedure accepted as providing measurement results fit for their intended use in assessing measurement trueness of measured quantity values obtained from other measurement procedures for quantities of the same kind, in calibration, or in characterizing reference materials.

[VIM3-2.7]

Especially in case an SI measurement unit or another measurement unit is not (yet) available, metrological comparability of measurement results can be claimed if a reference measurement procedure is agreed a priori and preferably internationally, and if this reference measurement procedure is used as the sole metrological reference [26].

The adjective “primary” in relation to measurement procedure is used with different meanings because there is a lack of commonly agreed scientific criteria.

3.3-2. primary reference measurement procedure

Primary reference procedure

Reference measurement procedure used to obtain a measurement result without relation to a measurement standard for a quantity of the same kind

[NOTE 2 Definitions of two subordinate concepts, which could be termed “direct primary reference measurement procedure” and “ratio primary reference measurement procedure”, are given by CCQM (5th Meeting, 1999).

[VIM3-2.8]

The term “method” in the CCQM text is here replaced by the term “procedure”.

3.3-3. secondary reference measurement procedure

Secondary reference procedure

Measurement procedure that has been calibrated by a primary measurement standard
4 ESTABLISHING AND REPORTING METROLOGICAL TRACEABILITY

The following checklist presupposes that the measurement will be made in a laboratory which is operating under an accreditation scheme (e.g. ISO/IEC 17025 [7], ISO 15189 [42], ISO 15195 [43], ISO Guide 31 [41] or GLP [44]) for a specified expertise and scope, or at least has validated measurement procedures as well as appropriate and implemented quality assurance procedures in place. The EURACHEM/CITAC guide to Traceability in chemical measurements [11] gives a procedure for establishing metrological traceability. The following shows the sequence utilizing the concepts previously defined.

- **Definition of measurand, intended use of measurement results, and target measurement uncertainty**
  This will include a clear statement of the specific concept under quantity to be measured, including system, relevant components, and kind-of-quantity with a statement of the measurement model or measurement function and description of the measuring system, measurement procedure including whether any correction is to be made for recovered quantity ratio [39]. The target measurement uncertainty will influence the choice of metrological traceability chain; the end-user’s measurement uncertainty will be larger than that associated with the calibrator(s) used to establish metrological traceability.

- **Selection of metrological reference(s)**
  Establishment of metrological traceability can only be achieved to an existing and documented metrological reference (see 1.1).

- **Selection of calibration hierarchy**
  By making the selection of the end-user’s working calibrator on available documentary evidence, its calibration hierarchy is fixed. Attention should also be paid to the calibration and metrological traceability of measurement results for input quantities in a measurement model and influence quantities, including those measured by accessory equipment such as balances, thermometers, and volumetric ware.

- **Selection of suitably validated measurement procedure**
  The analyst should undertake appropriate verification to discover whether a previously validated ‘standard measurement procedure’ can be implemented in the analyst’s laboratory.

- **Acquisition and verification of end-user’s calibrator** (see Note c to Figure 3.2–1, and Note d to Figure 3.2–2).
  Such a calibrator should be verified for integrity, validated for commutability of a reference material, have documented metrological traceability of its stated quantity value and associated measurement uncertainty.

- **End-user’s measurement on system or sample to obtain measurement result, including measurement uncertainty, based on an uncertainty budget.**

- **Documentation of metrological traceability**
  This requires readily available evidence, e.g. certificates, statements etc, of metrological traceability for all calibrators used, and calibration certificates for equipment.

- **Reporting of metrological traceability.**

The purpose of performing a measurement is to provide information, in the form of a measurement result, on the magnitude of a measurand, embodied in a specified system. The communication of that information can be made orally, in writing, or electronically. The amount of information given directly varies with the intended use of the measurement result. When only the measured quantity value is presented, the associated measurement uncertainty and metrological traceability should be available. The documentation can take the form of a “certificate of analysis”, “test report”, “measurement report” “calibration certificate” or more extensively a “certification report” ([41], [28] – 4.3). A certification report specifies all necessary details to understand the production, properties, and use of the calibrator (measurement standard or certified reference material), its quantity value, measurement uncertainty and their metrological traceability. The documentation of metrological traceability of the measurement result is essential because it

- underpins the authority of the measurement result by demonstrating how the result has been arrived at through the use of calibrators and measurement procedures;
- identifies the metrological reference needed to achieve metrological comparability of
measurement results for quantities of the same kind; and
• shows the elements in the uncertainty budget of the measured quantity value that are necessary for the calculation of the final measurement uncertainty.
5 THE ROLE OF METROLOGICAL TRACEABILITY IN VERIFICATION, VALIDATION, AND ESTABLISHING EQUIVALENCE

An analyst is interested in a “valid” measurement result. A statement of validity of a measurement result for a specified intended use requires metrological traceability and measurement uncertainty against specification fixed a priori, including a target measurement uncertainty.

It is recognized that currently measures of measurement trueness and of measurement precision are often provided instead of measurement uncertainty.

The VIM3 defines verification and validation to make the latter subordinate to the former.

5-1. verification
provision of objective evidence that a given item fulfils specified requirements
[VIM3-2.44]

Note: The concept ‘item’ makes the definition general so that it covers, e.g. measurement procedure, calibrator and measurement results.

5-2. validation
verification, where the specified requirements are adequate for a stated use
[VIM3-2.45]

Note: As ‘validation’ is derived from ‘verification’ applications of the former are given in the Note to the latter.

‘Validation’ is seen to be more demanding than ‘verification’. The former subordinate concept is therefore terminologically derived from the latter superordinate concept.

A validated measurement result can be compared to another validated measurement result for the same measurand in order to establish their

5-3. metrological compatibility of measurement results
metrological compatibility

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

NOTE 1 Metrological compatibility of measurement results replaces the traditional concept of ‘staying within the error’, as it represents the criterion for deciding whether two measurement results refer to the same measurand or not. If in a set of measurements of a measurand, thought to be constant, a measurement result is not compatible with the others, either the measurement was not correct (e.g. its measurement uncertainty was assessed as being too small) or the measured quantity changed between measurements.

NOTE 2 Correlation between the measurements influences metrological compatibility of measurement results. If the measurements are completely uncorrelated, the standard measurement uncertainty of their difference is equal to the root mean square sum of their standard measurement uncertainties, while it is lower for positive covariance or higher for negative covariance.
[VIM3-2.47]

A special case of metrological compatibility of measurement results can be characterized by the property that measurement results can be substituted for each other for a specified intended use.
5.4. metrological equivalence of measurement results

property of two or more measurement results for a given measurand that have metrological compatibility, so that they are each acceptable for the same specified intended use

Note: Measurement results are either metrologically equivalent or they are not.
6 ENTITIES CONCERNED WITH METROLOGICAL TRACEABILITY

To ensure metrological comparability of measurement results across the World, it is necessary to establish and maintain an international framework of entities to provide the elements of metrological traceability. This framework composed of international, regional, national, and local entities, both public and private, is responsible for providing metrological references, the metrological higher elements of calibration hierarchies, and general dissemination of metrological traceability.

The pre- eminent part of this international framework is that responsible for maintaining the International System of Units under the ‘Metre Convention’, an intergovernmental treaty first signed in 1875 (www.bipm.org). The CIPM has the responsibility for the maintenance of the SI under the authority of CGPM. The BIPM is the executive office of the CIPM with laboratories which maintain some primary measurement standards and primary reference measurement procedures.

In principle, the NMIs, operating under the authority of their governments, are members of the various consultative committees of the CIPM, including the ‘Consultative Committee on Amount of Substance: Metrology in Chemistry’ (CCQM). The NMIs produce, acquire, conserve, disseminate, or supervise the required measurement standards and measurement procedures in their respective countries. The CIPM MRAs by way of Key Comparisons lead to the metrological equivalence of the assigned quantity values embodied in international measurement standards (see Section 7.2). They also provide information about and education in the establishment of metrological traceability.

Any measurement laboratory in a given country should have direct or indirect access to calibrators and other tools in order to establish metrological traceability of its measurement results. The NMIs are also collaborating in five regional organizations (Table 6.1). In addition to NMIs there are reference measurement laboratories operating under regional or international authority. A schematic of the links between the BIPM and other entities in the framework described above is given in [45].

Table 6.1 The five regional organizations providing nodes in the international framework supporting metrological traceability

<table>
<thead>
<tr>
<th>Regional organization</th>
<th>URL</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Asia Pacific Metrology Programme (APMP)</td>
<td><a href="http://www.apmpweb.org/">http://www.apmpweb.org/</a></td>
</tr>
<tr>
<td>European Collaboration in Measurement Standards (EURAMET)</td>
<td><a href="http://www.euramet.org/">http://www.euramet.org/</a></td>
</tr>
<tr>
<td>The Inter-American Metrology System (SIM)</td>
<td><a href="http://www.sim-metrologia.org.br/">http://www.sim-metrologia.org.br/</a></td>
</tr>
<tr>
<td>South African Development Community Cooperation in Measurement Traceability (SADCMET)</td>
<td><a href="http://www.sadcmet.org/">http://www.sadcmet.org/</a></td>
</tr>
</tbody>
</table>

An NMI or regional or international body may complement its activities by designating other laboratories to act as Reference Laboratories to provide measurement standards for a variety of types of quantity. Indeed it should be realized that in establishing or operating primary reference measurement procedures and producing primary calibrators can be achieved outside the BIPM, regional metrology organizations, and NMIs provided that the expertise and resources are demonstrably present.
INTERLABORATORY COMPARISON (ILC)

The concept ‘interlaboratory comparison’ includes proficiency testing scheme (PTS), CCQM Key Comparison (KC) and external quality assessment scheme (EQAS).

What is an ILC?

Interlaboratory comparison is a generic concept for an endeavour to obtain and compare measurement results obtained by two or more measurement laboratories for the same measurand embodied in the same material. An ILC usually involves an organization or body responsible for the organizational aspects of the ILC.

Interlaboratory comparison is defined in ISO/IEC Draft International Standard 17043 [46] as

interlaboratory comparison
ILC
organization, performance and evaluation of measurements or tests on the same or similar items by two or more laboratories in accordance with predetermined conditions

In some circumstances, one of the laboratories involved in the intercomparison may be the laboratory that provides the assigned quantity value for the material. The operation enables the determination of the metrological equivalence of measurement results of the participants but does not, by itself, establish metrological traceability.

Purposes of an ILC

Interlaboratory comparisons are organized by many organizations and companies with the aim to evaluate analytical measurement procedures and their results. Harmonization of such studies has benefited from recommendations by the IUPAC/ISO/AOA Interdivisional Working Party on Harmonization of Quality Assurance Schemes for Analytical Laboratories [47-49]. The scope of an interlaboratory comparison evolved from being a measurement procedure validation study to performing proficiency testing and further to assessing the metrological equivalence of measurement results. Infrastructural requirements were described [50] and used in ISO Guide 43 (parts 1 [51] and 2 [52]), currently under revision [46]. A special category of interlaboratory comparisons is a study aimed at assigning quantity values to materials [15]. Categories, names and purposes of ILCs are given in .

Table 7.2–1 Types of interlaboratory comparison and their purposes

<table>
<thead>
<tr>
<th>Category</th>
<th>Usual term</th>
<th>Purpose</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>assessment of participant’s measurement performance</td>
<td>proficiency testing scheme; intercomparison study; intercomparison run; external quality assurance scheme; laboratory measurement evaluation programme</td>
<td>to test the ability of a laboratory to obtain measurement results similar to those of peer laboratories or to document participant’s measurement performance or for education</td>
<td>often required as part of an accreditation (e.g. to ISO/IEC 17025 or ISO 15189) or when taking regulatory or legal action; sometimes external reference measurement procedure quantity values rather than the average of participants’ measurement results are used to assess performance based on a reference quantity value with demonstrated metrological traceability</td>
</tr>
<tr>
<td>interlaboratory measurement bias</td>
<td>to determine measurement bias of</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ISO/IEC DIS 17043 states the term in the plural, but ISO terminology work standards advise to define concepts as singular in general.
<table>
<thead>
<tr>
<th>Category</th>
<th>Usual term</th>
<th>Purpose</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>study; International Measurement Evaluation Programme (IMEP)</td>
<td>measurement results obtained through a measurement procedure, assessment of measurement capability</td>
<td>metrological traceability and associated measurement uncertainty, external to the participants</td>
<td></td>
</tr>
<tr>
<td>cooperative trial, or measurement audit</td>
<td>one-off comparison of participant’s performance</td>
<td>may be for contractual purposes</td>
<td></td>
</tr>
<tr>
<td>assessment of metrological equivalence of measurement results</td>
<td>CIPM Key Comparison, CIPM Pilot Study</td>
<td>assessment of metrological equivalence of any pair of measurement results from participating institutions; assessment of measurement capability</td>
<td>organised in the frame of the CIPM-MRA to support claims of NMIs related to their measurement and calibration capabilities</td>
</tr>
<tr>
<td>measurement procedure validation</td>
<td>method validation study, or collaborative trial</td>
<td>to provide data for the validation of a measurement procedure</td>
<td>determines <em>inter alia</em> the measurement reproducibility of measurement results obtained using a given measurement procedure and, if a CRM is used, the measurement bias of each participant’s measurement result may be calculated</td>
</tr>
<tr>
<td>material characterization</td>
<td>multi-laboratory or multi-measurement method approach to assign quantity values and measurement uncertainties embodied in materials</td>
<td>to provide measurement results to be used in assigning quantity value and measurement uncertainty embodied in an RM or CRM</td>
<td>a <em>measured quantity value</em> from each laboratory must have a stated metrological traceability and associated measurement uncertainty; assignment of the quantity value and measurement uncertainty – and possible certification of the material – is the responsibility of the reference material producer. Note: all participants’ measurement results should be metrologically traceable to the same metrological reference</td>
</tr>
</tbody>
</table>

All of these are tools in quality assurance. Assessment may be based on the evaluation of the participants’ *measurement results* against those assigned to the interlaboratory comparison material before the ILC by a reference measurement laboratory or against an agreed *measured quantity value*. ILCs are announced by the organizers as open or closed, and participation may either be voluntary or compulsory. Participation in ILCs in many cases is an integral part of a laboratory’s quality assurance program, and is complementary to the laboratory internal quality control and on-site assessments by peer experts, but cannot replace them. According to the ISO/IEC 17025 [7] and the ISO 15189 [9] International Standards, regular laboratory participation in ILCs is a requirement for accredited laboratories.

Key Comparisons are organized in a similar fashion in the frame of the CIPM-MRA between National Metrology Institutes or NMI-designated institutions, following established protocols. The main aim of a Key Comparison is a practical support to the MRA in the assessment and confirmation of the metrological equivalence of measurement results obtained by any pair of participating National
Metrology Institutes or laboratories designated by them. A Pilot Study is normally organized to enable the participants to familiarize themselves with any problems arising in the measurement of a particular quantity embodied in a particular material. After a Key Comparison is performed, a Key Comparison Reference Value (KCRV) is established from participants’ measurement results. However, different approaches for calculating the KCRV and associated measurement uncertainty are used and agreed for each Key Comparison. Potential harmonization related to KCRV assignment is still the subject of discussion.

Measurement procedure validation studies (usually called “method validation studies”, or “collaborative trials”) require the use of the same measurement procedure by all laboratories on the same well characterized material or set of such materials.

In material characterization studies aiming at measuring quantity values embodied in candidate reference materials, the organizing body, e.g. a reference material producer, invites participating laboratories on the basis of their demonstrated measurement capability. Material characterization studies are carried out by using prescribed and well established, often different, quality assured measurement procedures [14, 15] yielding quantity values with established metrological traceability and associated measurement uncertainty. The concept ‘measurement capability’ has been used here. It is therefore useful to define it.

7.3 Measurement capability

7.3.1. measurement capability

ability to measure a specified quantity of a given kind, in a specified interval of quantity values, embodied in a specified material, as demonstrated by a measurement uncertainty

Note A comparison of the measurement uncertainty in the measurement result obtained by one participant to that of the measurement result obtained by another laboratory for the same quantity in the same material, compares their respective measurement capabilities.

7.4 Obtaining a reference value of a quantity embodied in an ILC material

A reference quantity value [VIM3-5.18] assigned to a quantity embodied in an ILC material is usually obtained in one of the following ways:

- measurement by a reference measurement laboratory,
- use of materials carrying one or more pre-established quantity values, e.g. an RM or CRM,
- using a reference preparation procedure such as spiking,
- using an agreed quantity value decided by selected or expert laboratories, or
- using an agreed quantity value derived from measurement results reported by the participants.

7.5 ILC and metrological traceability

Each laboratory participating in an ILC establishes its own metrological traceability chain for its measurement results. If the measurement results of all participants are to be comparable, their metrological traceability chains must end in the same metrological reference. With the exception of measurement procedure validation studies, a measurement procedure is usually not prescribed in proficiency testing, intercomparison studies, external quality assurance schemes and laboratory measurement evaluation programs. In some cases the establishment of metrological traceability is arranged as a part of the ILC by provision of a common calibrator and is decided by the organizer prior to the measurements.

7.6 ILC and laboratory performance

An assessment of the ILC participants’ measurement results can be performed by evaluating parameters associated with these results. Which laboratory performance properties might be assessed in a specific ILC depends on a decision taken prior to the execution of an ILC and how the ILC reference quantity value was established. Evaluation of participants’ measurement results will enable the assessment of the metrological compatibility of measurement results, or the metrological equivalence.
of measurement results, independently of whether the results are “correct” or not. Such evaluation may or may not take into account the quantity value and associated measurement uncertainty assigned to the ILC comparison material used.

Use of so-called ‘consensus quantity values’ obtained from a number of selected expert laboratories or as consensus quantity value from all participants in an ILC, is not appropriate. This would constitute a circular approach as the participants’ measurement results, which, on the one side, will influence the ILC quantity value, and, on the other side, will at the same time be evaluated using that same ILC quantity value. In addition, such evaluation might not detect a measurement bias. Also, it is perfectly possible that a laboratory identified as submitting an outlier, may actually be reporting the most correct measurement result, thus demonstrating the importance of an externally metrologically traceable reference value.

Nevertheless, in certain types of ILC, an agreed quantity value is the only quantity value possible to arrive at, e.g. in an ILC assessing laboratory performance of the measurement results obtained for operationally defined measurands. In that case the ILC can only establish metrological equivalence of participants’ measurement results, not metrological traceability.

7.7 ILCs and the assignment of quantity values and measurement uncertainties to reference materials

Currently there are many open questions related to metrological traceability of quantity values assigned to materials using results from participants in ILCs. Although it is clear that combination of results which are metrologically traceable to the same metrological reference leads to a traceable value, a description of the metrological traceability chain becomes a very complex issue. And even more difficult becomes the assessment of measurement uncertainty associated with such a derived result. It is metrologically contradictory that the uncertainties of consensus values are sometimes much smaller than the spread of measurement results used for calculation and also that the final measurement uncertainty of the consensus value is often smaller that the smallest measurement uncertainty of the measurement results reported by individual laboratories.
8 METROLOGICAL TRACEABILITY OF MEASUREMENT RESULTS FROM FIELD LABORATORIES

8.1 Function of metrological traceability in quality assurance

Understanding of, and appropriate dealing with, metrological traceability and measurement uncertainty are important components of any reliable measurement result and its supporting quality system. Consideration of each concept requires a suitable understanding of the analytical problem by the analyst. Before any measurement request is accepted from a customer, the analyst in the receiving laboratory must know how to solve the chemical measurement problem including defining the measurand, choosing a calibration hierarchy, and agreeing on the required target measurement uncertainty.

8.2 Demonstration of metrological traceability by field laboratories

The establishment by the field analyst of the metrological traceability of his measurement results is simple and is illustrated in Figure 8.2–1. The lower levels in any calibration hierarchy are the end user’s calibrator, the end-user’s measuring system calibrated by means of the calibrator, and the sample which carries the measurand. Usually the calibrator is purchased from a producer of reference materials or certified reference materials.

Figure 8.2–1 implies that the calibrator should be sold with an established metrological traceability chain for the assigned quantity value with associated measurement uncertainty that is to be included in the end-user measurement uncertainty budget. Knowing the measurement uncertainty of any quantity value embodied in an RM, also enables the end-user to evaluate, prior to the measurement, whether it will be possible to attain a target measurement uncertainty.

It is recognized that routine measured quantity values are often not delivered with their associated measurement uncertainties, but accreditation according to ISO/IEC 17025 or ISO 15189 requires that the measurement uncertainty be available to the customer, if relevant.

Figure 8.2–1 about here

\[ h(y_{\text{sample}}, Q_{n+1}, I_n, I_{\text{sample}}, X_1, \ldots, X_k) = 0 \]

Figure 8.2–1 Metrological traceability chain available to an end-user.

Note 1: The scheme does not apply in the case of an ordinal quantity.

Note 2: \( Q \) symbolizes a quantity embodied in a calibrator, \( I \) an indication.


9 EXAMPLES OF METROLOGICAL TRACEABILITY CHAINS OF MEASUREMENT RESULTS

In this section examples of metrological traceability chains for measurements are presented. Examples have been chosen to illustrate the application of various measurement principles.

Metrological traceability chains may be longer or shorter than those given, or modified as the circumstances of the end-user require. The details presented for each example are only to be regarded as one possible solution to a particular measurement problem.

A chemist in a field laboratory will probably establish metrological traceability of quantities such as mass, temperature, and volume by purchasing and maintaining suitably calibrated equipment such as balances, thermometers, and volumetric equipment. Metrological traceability chains for quantities may be embedded in other metrological traceability chains as side chains to the one under consideration. Such a ‘graft’ is designated in the figures by a symbol, such as \( \triangle \), attached to the measurement procedure box, and a corresponding down arrow \( \bigtriangledown \) in a box containing the kind of quantity and reference. For further explanation of the conventions used in the flow charts of calibration hierarchies, see the legend of Figure 2.5–1.

9.1 Amount-of-substance concentration of an acid in a material

Titration of an acid with a base, using measurement of pH or the colour change of an added indicator to obtain the end point, is a long established measurement principle for the measurement of amount-of-substance concentration of an acid. In this example the amount-of-substance concentration of a solution of hydrochloric acid (HCl) is measured by titration with a solution of sodium hydroxide (NaOH). The amount-of-substance concentration of NaOH is first measured by titration of a solution of potassium hydrogen phthalate (KHP), which has been prepared from a solid of known, and metrologically traceable amount-of-substance content.

It is noted that the measurement uncertainty for an example of this kind of measurement is presented in Appendix A.3 of the EURACHEM QUAM [34].

9.1.1 The measurement model

The amount-of-substance concentration of HCl can be expressed in terms of a measurement function

\[
c_{\text{HCl}} = c_{\text{NaOH}} \frac{V_{T2}}{V_{\text{HCl}}} \tag{9.1.1-1}
\]

where \( c_{\text{HCl}} \) and \( c_{\text{NaOH}} \) are amount-of-substance concentrations of HCl and NaOH respectively, \( V_{T2} \) is the end point volume of the titration of HCl by NaOH, and \( V_{\text{HCl}} \) the aliquot of HCl taken for the titration.

9.1.2 Primary calibrator, pure potassium hydrogen phthalate

The primary calibrator is solid potassium hydrogen phthalate with an amount-of-substance content measured by coulometric titration. This calibrator is purchased as a certified reference material with calibration certificate stating the purity (mass fraction, or amount-of-substance content) with an expanded measurement uncertainty.

9.1.3 Secondary calibrator, standard solution of sodium hydroxide

The calibrator for the end user’s measurement of the amount-of-substance concentration of the HCl solution is a solution of sodium hydroxide that is freshly standardized against a primary calibrator of dissolved potassium hydrogen phthalate according to the measurement function

---

4 “Standardization” or “calibration” is a term in common use to describe the assignment of a quantity value
\[ c_{\text{NaOH}} = \frac{m_{\text{KHP}} k_{\text{KHP}}}{V_{T1}} \]  

(9.1.3-1)

where \( m_{\text{KHP}} \) is mass of KHP, \( k_{\text{KHP}} \) is amount-of-substance content of KHP [53], and \( V_{T1} \) is the end point volume of the titration of KHP by NaOH.

Note that in the EURACHEM example the equations of the two titrations are combined to give the measurement function, which also expresses the purity of the KHP as a mass fraction. The equivalent measurement function from equations 9.1.1-1 and 9.1.3-1 is

\[ c_{\text{HCl}} = \frac{m_{\text{KHP}} k_{\text{KHP}} V_{T2}}{V_{\text{HCl}} V_{T1}} \]  

(9.1.3-2)

With equations 9.1.3-1 and 9.1.3-2 the measurements are separated to show the role of the secondary calibrator (the NaOH solution).

9.1.4 Measuring systems

The measuring systems for the titrations both include a titration apparatus with a means of obtaining the end point of the titration. For the quantity value assignment of the secondary calibrator, a balance is used to weigh an aliquot of KHP. In the end-user’s measurement, volumetric equipment is required to deliver a known volume of the HCl solution for titration by NaOH.

9.1.5 Metrological traceability of the measured amount-of-substance concentration of HCl

Figure 9.1.5–1 shows the metrological traceability of the measurement result of amount-of-substance concentration of HCl. The amount-of-substance concentration of the secondary calibrator (NaOH solution) is metrologically traceable to the amount-of-substance content of a solution of the primary calibrator, and the volumes of glassware and titrating systems. The amount-of-substance content of the primary calibrator is in turn metrologically traceable to the definition of the SI measurement units mole and kilogram through metrologically traceable measurements of time, electric current, and mass. In addition, the value of the Faraday constant, to relate amount of electricity to amount of substance, is also required.

9.2 pH of a solution

pH is one of the most fundamental and important concepts of chemistry. It is the chemical kind-of-quantity most frequently measured.

The thermodynamic definition of pH is given by the quantity equation [54]

\[ \text{pH} = -\log_{10}(a_{H^+}) = -\log_{10}\left(\frac{b_{H^+} \gamma_{H^+}}{b^+}\right) \]  

(9.2-1)

where \( a_{H^+} \) is the activity, \( b_{H^+} \) is the molality, \( \gamma_{H^+} \) the hydron\(^5\) activity coefficient, and \( b^+ \) is the standard molality in a solution (1 mol/kg). It has long been recognized that this definition cannot be realized because of the impossibility of creating a solution containing a stated activity of hydrons, and the

---

\(^5\) The general name for the cation H\(^+\)
the criteria of a single ion activity without non-thermodynamic assumptions being made [55]. The 1985 IUPAC definition of pH scales [56] left the subject in some confusion, recommending two different approaches that led to different pH values (different by up to 0.02) being assigned to the same buffer solution. The recommendation also did not address the metrological traceability of the measurement results. Measurement results that follow the 1985 IUPAC recommendations appear to be traceable only to the measurement procedure specified (and the SI measurement unit one). There has been no attempt to establish metrological traceability to a higher authority, which leaves the possibility of the assignment of different pH values to the same solution, and therefore the lack of metrological comparability of pH measurement results.

In 2002 IUPAC issued a recommendation for revision of the pH scale based on the concept of a primary reference measurement procedure for pH [27]. The use of the Harned cell fulfils the criteria for a primary reference measurement procedure so that a pH value thus obtained is unequivocally metrologically traceable to the International System of Units, here the SI measurement unit one. A buffer solution, the pH of which is measured by such a cell at the highest metrological level, may be classified as a primary measurement standard. The use of the Harned cell, but not at the highest metrological level, or the use of other procedures that compare the pH of a solution to that of a primary measurement standard, gives buffers that are classed as secondary measurement standards.

9.2.1 Primary reference measurement procedure – the Harned cell

The Harned cell [57] is a cell without transference comprising a hydrogen electrode and a silver, silver chloride electrode:

\[
\text{PtH}_2 \mid \text{solution} \mid \text{Cl}^- \mid \text{AgCl} \mid \text{Ag} \quad \text{(Cell 1)}
\]

the use of which leads to the following quantity equation

\[
\text{pH} = \lim_{b_{Cl} \to 0} \left( \frac{E_i - E_0}{RT \ln 10} + \log_{10} \left( \frac{b_{Cl}}{b} \right) \right) = \frac{A I^{1/2}}{1 + 1.5(I/b^2)^{1/2}} \quad (9.2.1-1)
\]

where \( A \) is the Debye-Hückel constant which is given in tables for the temperature of the experiment, \( I \) is the ionic strength of the solution, \( E_i \) is the cell potential difference, \( E_0 \) is the standard electrode potential of the cell, \( F \) is the Faraday constant, \( b \) is the standard molality (1 mol/kg), and \( b_{Cl} \) is the molality of chloride in the solution. It is suggested that the measurement be made on at least three solutions of different molality of chloride and a linear extrapolation be made.

An uncertainty budget has been prepared [58], and buffer solutions that fulfill requirements for calibration of a pH measuring system have been identified as candidates for primary measurement standards.

9.2.2 Secondary measurements

Operating the Harned cell at the highest metrological level is possible for NMIs but would not be contemplated for routine measurements.

There are a number of cells having liquid junctions, which may be used for comparisons of primary measurement standards (PMS1, PMS2) or the determination of the pH of a secondary measurement standard (SMS) by comparison with a primary measurement standard. These cells are:

- \text{PtH}_2 \mid \text{SMS} \mid \text{PMS}_1 \mid \text{H}_2 \mid \text{Pt} \quad \text{(Cell 2)}
- \text{PtH}_2 \mid \text{PMS}_2 \mid \text{KCl (≥ 3.5 mol L}^{-1}) \mid \text{PMS}_1 \mid \text{H}_2 \mid \text{Pt} \quad \text{(Cell 3)}
- \text{Ag} \mid \text{AgCl} \mid \text{KCl (≥ 3.5 mol L}^{-1}) \mid \text{buffer S} \mid \text{H}_2 \mid \text{Pt} \quad \text{(Cell 4)}
- \text{Ag} \mid \text{AgCl} \mid \text{KCl (≥ 3.5 mol L}^{-1}) \mid \text{buffer S} \mid \text{Glass electrode} \quad \text{(Cell 5)}

Issues concerning the minimization and estimation of residual liquid junction potentials are discussed in detail in reference [27].

9.2.3 Metrological traceability of pH measurement results

It is argued that the measurement procedure using a Harned cell to measure the pH of a solution meets the criteria of a primary reference measurement procedure, because:

(a) the pH value is obtained by a well-defined measurement model in which all the variables can be
determined experimentally in terms of SI measurement units, and

(b) all sources of measurement uncertainty are identified and effects quantified, including that associated with the use of the Bates-Guggenheim convention.

Unfortunately, the measurement uncertainty imparted to the pH value, arising from the use of the Bates-Guggenheim convention to establish \(-\log_{10}(f_{\text{Cl}^-})\) (the value 1.5 in the term \(\frac{A_{1/2}}{1 + 1.5[I/b']^{1/2}}\) in 9.2.1-1), is estimated to be 0.01 (expanded measurement uncertainty, \(k = 2\), corresponding to a level of confidence of approximately 95 %). The experimental expanded measurement uncertainty (\(k = 2\) for a typical primary measurement result is, however, only 0.004. If the measurement uncertainty of the use of the Bates-Guggenheim convention is not included, then the measurement results are still traceable to the SI measurement unit one, but the pH is no longer defined by 9.2.1-1 but by 9.2.1-1. By not including the full measurement uncertainty, if in the future an improved quantity value for the trace activity coefficient of chloride ion were used (\(f_{\text{Cl}^-}\)), then measurement results obtained with the new equation would no longer be metrologically comparable with earlier measurement results.

A metrological traceability chain of a routine laboratory measured quantity value of pH is depicted in Figure 9.2.3–1.

![Figure 9.2.3–1](https://example.com/image.png) about here

measurement model for end-user: \(k(\text{pH}_{\text{sample}}, E, k') = 0\)

**Figure 9.2.3–1** Metrological traceability chain of a pH measurement result using a primary reference measurement procedure (Harned cell). The input quantities in the measurement model, standard electrode potential \(E^0\) and constant \(k'\) are obtained from calibration using the secondary calibrator 2.

Note that cell 2 in Figure 9.2.3–1 could be Cell 2 described in the text above.

There is, therefore, an interesting, but unfortunate dilemma; if we wish to have metrological traceability to the SI without specification, rather than involving a conventional measurement procedure, then we must accept a measurement uncertainty which turns out to be about 2 \(1/2\) times greater, even though the measurement procedure is exactly the same.

### 9.2.4 Metrological traceability of pH values of buffer solutions

The direct assignment of a pH value and associated measurement uncertainty of a particular solution can only be done by the primary reference measurement procedure described above. Aqueous buffer solutions are usually made up from pH reference materials dissolved in a prescribed mass of water. However, in general, the preparation of a buffer solution from compounds according to a recipe cannot be recommended. Not only is the purity of the material but also the stoichiometry very important. The solids for making primary buffer solutions are certified not for purity but only for pH. A detailed instruction is given how to prepare the solution, e.g. for NIST SRM and for commercial solids appropriate for preparation of pH buffers according to DIN 19266. Only these buffer solutions may be termed primary buffer solutions, and can be considered directly metrologically traceable. For example, if the buffer is described as a solution of potassium dihydrogen citrate with a molality of 0.05 mol/kg, and this information is to be used to make up similar solutions that will be assigned the pH value of the primary measurement standard, then the measurement uncertainty of the molality (including the contribution from the imperfect purity of the component used) and its effect on the pH value must be known and quoted. Here lies a problem, as it is usually not known how different impurities will affect the pH of a solution. Indeed citrate is not used to make primary buffer solutions for the reason of lack of source material of sufficient quality [59].

If it is necessary, for any reason, to prepare buffers similar in composition to the primary ones from solids of different kinds it is recommended to use cell 2 for comparison.

If the published pH value of some material has been determined by interlaboratory comparisons between NMIs on many samples of buffer solution made from different sources of solids, then that pH may be deemed to include batch-to-batch variation. If not (i.e. if the pH was established on a single sample) then the batch-to-batch variation must be included separately in the final uncertainty budget. For comparisons, NMIs normally use solutions of compositions different from those of the composition...
of the primary measurement standards.

9.3 Mass concentration of ethanol in breath

Breath analysis, for testing compliance with drink-driving laws, was developed in the USA in the 1950s and is used in many countries. Initially, breath analysis was based on the colour change when ethanol reacts with potassium dichromate. This was replaced in the early 1990s with electronic breath analysis, based on the absorption of infra-red light (at selected wavelengths) by ethanol in a sample of air. The measurement result was expressed as mass of ethanol per volume of blood, multiplied by a factor which represented a conservative estimate (i.e., one which gave the benefit to the tested motorist) of the partition coefficient of ethanol between blood and breath. The use of this conventional factor made metrological traceability of a blood ethanol measurement result by breath analysis impossible because the factor has intra- and inter-personal variation. Thus in some countries there were defined two independent alcohol limits – one for blood alcohol concentration and one for breath alcohol concentration. The limits for breath alcohol concentration are given in grams ethanol per litre breath or in some countries also in grams ethanol per 210 litres breath (here the limits are in numbers equal to the blood ethanol concentration limits). The measuring instruments can now show the result in grams per litre and the conversion factor is no longer necessary.

Evidential breath analyzers are verified and calibrated using aqueous ethanol solutions or dry gas mixtures consisting of ethanol and air. In former times, the solutions have been made by gravimetric dilution of absolute ethanol with water. The hygroscopic nature of ethanol causes an unknown deviation of the solution concentration from the supposed one. It is difficult to obtain a reasonable estimate of the measurement bias that this effect causes, and so to correct the deviation and estimate the measurement uncertainty. It is therefore necessary to measure the ethanol mass fraction in the calibration solution. This is done by several methods, including titration with dichromate, and by gas chromatography. To ensure international metrological comparability of measurement results and to become aware of possible measurement biases, international comparisons have been organised by the CCQM. For ethanol water mixtures a first comparison (CCQM-K27.a) for forensic matrices was made in 2002, a study that included the Australian NMI. It showed that even at the highest level of measurement capabilities measurement biases can arise. As an example it is shown how the metrological traceability chain of a breath alcohol measurement back to a national standard has been realised in Australia. A metrologically traceable quantity value for an ethanol measurement standard has been made in Australia by the measurement of the ethanol mass fraction of a solution by ID-MS. This calibrator (calibrator 3 in Figure 9.3–1) is provided to calibration authorities who prepare working calibrator ethanol solutions that are supplied to the police to calibrate field breath analyzer measuring systems.

Figure 9.3–1 about here

measurement model for end-user: \( h(\rho_{\text{ethanol in breath}}, \rho_{\text{ethanol cal 4}}, \alpha_{\text{breath}}, \alpha_{\text{cal 4}}) = 0 \)

Figure 9.3–1 Metrological traceability chain of measurement result obtained with an evidential breath analyzer calibrated via gas chromatography. Measurement uncertainties are given as relative standard measurement uncertainties. Note that a numerical value of the final measurement uncertainty of a motorist’s breath alcohol is not given. Police authorities assert measurement uncertainties.

9.4 Number ratio of isotopes of an element in a material

Measurements of the quantity ‘number ratio \( R \) between numbers of two isotopic atoms in an element \( E \) of a sample’, are of key importance in the determination of the molar mass \( M(E) \) (or relative atomic mass, atomic weight) of an element \( E \) because, nowadays, all molar mass values are computed from such measured number ratios [60].

---

6 heptaoxidodichromate
9.4.1 The measurement model

Measurements of the measurand ‘number ratio between isotopic atoms E and E in an element E of a sample’

\[ R_{ij} = \frac{N(E_j)}{N(E_i)} \]  

(9.4.1-1)

are carried out by means of a mass spectrometer in which the neutral atoms of the isotopes are converted to singly charged ions forming an ion current which is separated in a magnetic field into as many composing ion currents as there are isotopes. The pairwise ratios of the resulting isotopic ion currents \( I(E_j^+)/I(E_i^+) \) are measured. These electric current ratio measurements must be calibrated in order to yield the corresponding isotope number ratios.

That requires a measurement model which is

\[ h[R_{ij}, K_{ij}, I(E_j^+)/I(E_i^+)] = 0 \]  

(9.4.1-2)

where \( K_{ij} \) is the calibration factor (sometimes called the conversion factor).

From this measurement model, the measurement function can be derived:

\[ R_{ij} = K_{ij} \cdot \frac{I(E_j^+)/I(E_i^+)}{I(E_j^+)/I(E_i^+)} \]  

(9.4.1-3)

But other measurement functions can be derived from this measurement model also, such as

\[ K_{ij} = \frac{(R_{ij})_{cal}}{I(E_j^+)/I(E_i^+)_{cal}} \]  

(9.4.1-4)

where \((R_{ij})_{cal} \) and \([I(E_j^+)/I(E_i^+)]_{cal} \) are the number ratios and their corresponding measured electric current ratios, of the chosen isotopes in the element E in a calibrator, which is an isotope measurement standard, usually called and marketed as a ‘certified isotope reference material’. Such a calibrator enables to determine the calibration factor used in the measurement function described in equation 9.4.1-3.

A description of the related calibration hierarchy is given in the following subsections.

9.4.2 The definition of the measurement unit

Examining the measurement model, the relevant SI measurement unit for number ratio is the coherent derived unit one/one (symbol 1/1) which is equal to one (symbol 1). The embodiment of the measurement unit requires a primary reference measurement procedure or a primary preparation procedure. So far, there is no measurement procedure meeting the VIM3 definition of a primary reference measurement procedure, hence a primary preparation procedure is used to embody the measurement unit.

9.4.3 The primary preparation procedure governing the preparation system 1

A primary preparation procedure can be achieved by using chemically purified and (highly) enriched or pure isotopes which are built into stoichiometrically well-known molecular compounds. These are weighed and mixed to achieve homogeneity of the isotope atoms on the atomic level. The mass ratios of the compounds can be converted to number ratios for the isotopes concerned by measuring the molar mass of the element E in the enriched isotopes E as well as determining the deviation from the theoretical stoichiometry of the compounds used. The closer the degree of isotope enrichment comes to 100 % in each compound, the closer the measurement uncertainties of the molar mass values of the enriched isotopes approach the measurement uncertainties of the atomic mass values of 100 % pure isotopes, typically \( 10^{-7} \) or better.

Figure 9.4.3–1 about here

\[ h[R_{ij}, K_{ij}, I(E_j^+)/I(E_i^+)] = 0 \]

Figure 9.4.3-1: Metrological traceability chain of a measurement result for an isotope number ratio. \( R_{ij} \) defined by equation 9.4.1-3.

9.4.4 The measuring system 2

The measuring system 2, governed by measurement procedure 2, can be used to assign calibrated measured quantity values of a number ratio to a secondary calibrator. See Figure 9.4.3–1.
9.4.5 The end-user’s measuring system

The secondary measurement standard or secondary calibrator 2 can be made available to end-users for measuring unknown isotope number ratios in, e.g., geological, nuclear, or other samples. It is the duty of the seller of calibrator 2 to deliver, together with the calibrator, the higher levels of the metrological traceability chain with associated measurement uncertainty.

In many practical cases, the metrological traceability chain is longer than in the example of Figure 9.4.3–1.

9.4.6 Quantities derived from isotope number ratio(s)

9.4.6.1 Isotope abundance x(E)

In isotope measurements, much use is made of the kind-of-quantity ‘isotope abundance’ x(E) which is the number fraction of atoms of one isotope E in the total number of atoms of the element E. Hence, the sum of abundances Σx(E) is, by definition, always equal to 1 exactly, i.e.

Σx(E) = 1  \hspace{1cm} (9.4.6.1-1)

and

\[ x(E) = \frac{x(E)}{\Sigma x(E)} \] \hspace{1cm} (9.4.6.1-2)

\[ x(E) = \frac{[x(E)/x(E)]/\Sigma x(E)}{x(E)} \] \hspace{1cm} (9.4.6.1-3)

\[ x(E) = \frac{[N(E)/N(E)]/\Sigma N(E)}{N(E)} \] \hspace{1cm} (9.4.6.1-4)

\[ x(E) = \frac{R_{ij}(E)}{\Sigma R_{ij}(E)} \] \hspace{1cm} (9.4.6.1-5)

An isotope number ratio measuring device enables to measure ratios R_ij of an isotope abundance relative to a conveniently chosen abundance of another isotope (E), thus enabling to calculate any isotope abundance x(E).

Measurement uncertainty \( u_x(x(E)) \) is obtained by propagating the measurement uncertainties of \( R_{ij} \).

9.4.6.2 The molar mass \( M(E) \) is calculated from \( x(E) \) by

\[ M(E) = \Sigma x(E) \cdot M(E) \] \hspace{1cm} (9.4.6.2-1)

where \( M(E) \) is the atomic mass of that isotope.

Substitution of \( x(E) \) in Equation 9.4.6.2-1 according to Equation 9.4.6.1-5 leads to

\[ M(E) = \Sigma R_{ij}(E) \cdot M(E) / \Sigma R_{ij}(E) \] \hspace{1cm} (9.4.6.2-2)

Evaluation of combined measurement uncertainty \( u_x[M(E)] \) is performed by propagating the combined measurement uncertainty \( u_x(R_{ij}) \) to \( u_x[M(E)] \).

Note: ‘Atomic weights’ \( A_i(E) \) of the elements are ratios of the molar mass values of that element to \( 1/12 \)th of the molar mass value of \( ^{12}\text{C} \), the latter being set by convention to 12 g/mol exactly.

9.5 Mass fraction of glyphosate in an agricultural chemical

There are different measurement methods to measure the purity of a chemical substance. These include approaches based on the subtraction of the sum of mass fractions of impurities from 1, and those based on chromatography with appropriate detection.

Since its discovery, nuclear magnetic resonance spectroscopy (NMR) has been used as a qualitative technique for the identification and elucidation of structures of an enormous variety of inorganic, organic and biological materials. Quantitative NMR (QNMR) has been reported as the basis of a primary reference measurement procedure for measurement of mass fractions of organic compounds such as agricultural chemicals [61]. The compound of the calibrator need not be the same as the analyte, provided it contains the nucleus of interest. For example, the analysis of the agricultural weedicide, \( N\)-(phosphonomethyl)glycine (‘glyphosate’): HOOCCH_2NHCH_2PO(OH)_2 uses a CRM of dimethyl sulfoxide (CH_2SO(CH_3)_2) as a \(^1\text{H} \) calibrator and a CRM of sodium phosphate (Na_3PO_4) as a \(^31\text{P} \) calibrator. The successful application of these measurement methods relies on the presence of suitable peaks in the NMR spectrum that are uncontaminated with any impurity peaks. Very high field NMR allows discrimination between closely related compounds.
9.5.1 Measurement method
The purity of a compound is determined by the following steps.

- Weigh a mass of sample into an NMR tube by difference (about 5 mg glyphosate).
- Weigh a mass of the calibrator into the NMR tube by difference to give approximately the same amount of substance of the target isotope as of the component.
- Add deuteriated solvent to an appropriate level in the NMR tube.
- Introduce the NMR tube into the instrument. Allow to equilibrate at the set temperature of the probe and measure with instrumental settings for full relaxation (and suppression of the nuclear Overhauser effect as required).
- Record the free induction decay (FID) spectrum.
- Process the FID with window function as required, phase the spectrum manually, and establish the baseline.
- Integrate the peaks to obtain the ratio of the integrated peak for the sample to the integrated peak for the calibrator ($I_{\text{sample}}/I_{\text{cal}}$).

9.5.2 Measurement function
The measurement function for the mass fraction of a sample based on the observation of the NMR signal for $^1$H is

$$w_{\text{sample}} = \frac{I_{\text{sample}} m_{\text{cal}} N_{\text{cal}} M_{\text{sample}}}{I_{\text{cal}} m_{\text{sample}} N_{\text{sample}} M_{\text{cal}}} w_{\text{cal}}$$

(9.5.2 – 1)

where “sample” and “cal” refer to the sample being measured and working calibrator respectively; $I$ is an integrated peak area of the NMR spectrometer for a given chemical shift, $m$ is the mass, $N$ is the number of protons in one molecule, $M$ is the molar mass, and $w$ is the mass fraction. The mass fraction of the primary calibrator can be measured at an NMI by a combination of techniques, including GC-FID, NMR, thermogravimetry, differential scanning calorimetry, Karl Fischer analysis for water, and elemental analysis. In this case the mass fraction can be calculated as one minus the sum of all impurities and reported with a GUM measurement uncertainty. For QNMR measurements in which the isotope of interest is a proton, the mass fraction of a working measurement standard (working calibrator) of sodium acetate can be measured by QNMR calibrated by the dimethylsulfone primary calibrator. The metrological traceability chain is shown in Figure 9.5.2 – 1.

measurement model for end-user

$$h( w_{\text{sample, gly}}, w_{\text{cal, 2}}, I_{\text{cal, 2}}, I_{\text{sample, gly}}, m_{\text{sample, gly}}, N_{\text{sample, gly}}, M_{\text{sample, gly}}, M_{\text{cal, 2}}) = 0$$

Figure 9.5.2 – 1 Metrological traceability chain of the measurement result of the mass fraction, $w$, of a sample of the agricultural chemical glyphosate. $I$ = peak area, $m$ = mass, $M$ = molar mass, $N$ = number of protons contributing to the NMR signal. GC = gas chromatography, DSC = differential scanning calorimetry, TGA = thermogravimetric analysis, KF = Karl Fischer titration procedure.

9.6 Amount-of-substance concentration of creatininium in blood plasma
The amount-of-substance concentration of creatininium in blood plasma is an important inverse indicator of renal function. (“Creatininium” is the IFCC-IUPAC term for the sum of the species ‘Creatinine’$^7$ and ‘Creatininium ion’.)

A current commercial measurement procedure uses a four-stage enzymatic reaction scheme [62, 63]. The reactions involved are

$$\text{creatininium} + H_2O \xrightarrow{\text{creatinase (EC 3.5.2.10)}} \text{creatinine}$$

$$\text{creatinine} + H_2O \xrightarrow{\text{creatinate (EC 3.5.3.3)}} \text{sarcosine} + \text{urea}$$

$^7$ 2-imino-1-methylimidazolidin-4-one
sarcosine + O₂ + H₂O (sarcosine oxidase (EC 1.5.3.1)) → glycine + HCHO + H₂O₂
H₂O₂ + 4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one⁸ + 3-hydroxy-2,4,6-triiodobenzoic acid (peroxidase (EC 1.11.1.7)) → quine imine chromogen + H₂O + HI

where the colour intensity change of the chromogen is directly proportional to the creatinin concentration and is recorded at an endpoint by absorbance at 552 nm corrected for blank at 659 nm [64].

The measurement may be performed on a Roche COBAS INTEGRA 800 and the metrological traceability to an SI unit is claimed [65, 66]. The calibration hierarchy shown in Figure 9.6–1 should reflect this information.

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Figure 9.6–1 about here

Measurement model for end-user: \( h(c_{\text{sample}}, c_{\text{cal 3}}, I_{\text{cal 3}}, I_{\text{sample}}) = 0 \)

where \( I \) symbolizes an indication.

Absorbance, amount-of-substance and volume have their respective measurement models (not shown).

**Figure 9.6–1**: Metrological traceability chain of a measurement result for amount-of-substance concentration of creatinin in human blood plasma using a commercial measuring system.

amsc. = amount-of-substance concentration.

Only data concerning the manufacturer’s product calibrator 3 are available to the end-user.

### 9.6.1 Primary measurement

A primary reference measurement procedure involving an isotope dilution-mass spectrometer (ID-MS) in a reference measurement laboratory is applied to a primary calibrator, called “masterlot calibrator”, and to five serum pools; both primary calibrator and serum pools are produced according to the manufacturer’s standardized protocols. The six quantity values can be assumed to have a good measurement trueness.

### 9.6.2 Secondary measurement

The primary calibrator is used to calibrate the manufacturer’s measuring system operating according to his standing secondary reference measurement procedure. Both equipment, i.e. COBAS INTEGRA 800 with reagents, and secondary reference measurement procedure are essentially identical with those employed by the end-user, except that only the manufacturer has access to the stored primary calibrator whereas the end-user uses the manufacturer’s product calibrator; this, however, is produced in the same way as the primary calibrator.

The manufacturer’s standing secondary reference measurement procedure and COBAS INTEGRA calibrated with the primary calibrator are used to assign a second set of quantity value and measurement uncertainty to each of the five serum pools.

### 9.6.3 Adjustment of quantity value of primary calibrator

For the five serum pools, the ID-MS quantity values on the abscissa and manufacturer’s COBAS quantity values on the ordinate allow the calculation of a regression equation \( y = bx + a \). Then the ID-MS quantity value of the primary calibrator via this regression line corresponds to an ordinate quantity value that may be different from that on the abscissa. In that case, the primary calibrator’s quantity value is adjusted so that the regression line within an appropriate interval around the adjusted quantity value goes through 0.0. The measurement uncertainty of the adjustment depends on the relative magnitudes of the constants \( a \) and \( b \) and must be a part of the combined standard measurement uncertainty of the primary calibrator’s adjusted quantity value.

The rationale of this type of adjustment is that it should reduce the effect of the lack of any analytical specificity of the manufacturer’s standing secondary measurement procedure and measuring

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⁸ 4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one
system as well as any lack of commutability of the primary calibrator. The relative magnitude of the adjustment is not available to the end-user.

Another perhaps more transparent approach would be to apply a correcting algorithm on the actual indications of the manufacturer’s measuring system, involving both constants $a$ and $b$, thus keeping the ID-MS-assigned primary quantity value.

9.6.4 Tertiary measurement

Using the primary calibrator with adjusted quantity value and combined standard measurement uncertainty to recalibrate the manufacturer’s COBAS measuring system operated according to his secondary reference measurement procedure, the manufacturer’s product calibrator obtains its assigned quantity value and combined standard measurement uncertainty, and is delivered to the customer, the end-user.

9.6.5 End-user’s measurement

Using the manufacturer’s product calibrator with associated calibration factors for the end-user’s measuring system operated according to his measurement procedure, routine human samples can now be measured to give directly a measurement result. The quantity value is assumed to be adequately true for the given purpose because the measuring system and measurement procedure used by both manufacturer and end-user are essentially the same.

The uncertainty budget for the end-user’s quantity value first of all relies completely on the adequacy of the measurement uncertainty assigned to the quantity value of the manufacturer’s product calibrator. The uncertainty budget of this calibrator is only available to regulatory authorities, but should include sources of variation such as

- definition of measurand,
- measurement uncertainty of adjusted quantity value for primary calibrator 1 provided by reference measurement laboratory,
- inhomogeneity and instability of primary calibrator,
- inhomogeneity and instability of serum pools,
- measurement uncertainty of manufacturer’s measuring system, twice,
- adjustment procedure,
- lot-to-lot differences for manufacturer’s product calibrator (unless assigned individually), and
- inhomogeneity and instability of the product calibrator.

The end-user further has the following pre-examinational and examinational sources to consider and select according to the purpose:

- inter-individual variation,
- intra-individual variation,
- sampling,
- transport and storage of sample,
- separation and sub-sampling, and
- intermediate precision conditions of measurement (which subsumes some other sources).

The pre-examinational sources may well give the major contributions in this example. The manufacturer lists the following information for his product calibrator with a quantity value of $331 \, \mu\text{mol/L}$:

$$u = 2.12 \, \mu\text{mol/L} \quad [66]$$

CV within run 0.7 % [64] (repeatability)

CV between run 0.9 % [64] (reproducibility, presumably meaning intermediate measurement precision)

With an end-user’s quantity value of, say, $230 \, \mu\text{mol/L}$, which is about twice the upper limit of a central 0.95-interfractile biological reference interval in healthy adults, this quantity value would give the following minimum combined standard measurement uncertainty, based solely on the assigned combined standard measurement uncertainty of the manufacturer’s product calibrator and the standard measurement uncertainty under intermediate precision condition of measurement:
\[
\sqrt{2.12^2 + (0.007 \times 230)^2 + (0.009 \times 230)^2} \text{ mmol/L} \\
= \sqrt{4.49 + 2.59 + 4.28} \text{ mmol/L} = 3.37 \text{ mmol/L} \\
\text{or CV(intermediate) } = \frac{3.37 \text{ mmol/L} \times 100}{230 \text{ mmol/L}} = 1.5 \% 
\]

The quantity values were obtained in the manufacturer's laboratory and the end-user should expect somewhat higher quantity values for measurement uncertainty and increasing with lower measured quantity value.

### 9.6.6 Metrological traceability

A routine measurement result for amount-of-substance concentration of creatinininium in the plasma of a given person at a stated time is metrologically traceable to the SI unit mmol/L. As the calibration hierarchy includes an empirical “holistic” adjustment element, it is necessary to specify the measurement procedure and manufacturer's product calibrator in the metrological reference.

It should be added that various types of adjustment procedure such as the above are not infrequent in commercial measuring systems. It would be an aid to the end-user in evaluating their appropriateness if the data were available on request. In this respect, regulatory rules could help.

### 9.7 Mass fraction of protein in grain

The price of a harvested grain, such as wheat, depends on its protein content. The nitrogen mass fraction is measured in the field by near infra-red (NIR) spectrometry and multiplication by a conventional factor gives a measurement result for the operationally defined measurand 'mass fraction of protein in the sample of grain using the conventional factor to convert mass fraction of nitrogen to mass fraction of protein'. The use of near infra-red spectrometry requires multivariate calibration (i.e. the whole spectrum is used to calibrate the mass fraction of nitrogen) with a whole-grain calibrator. Metrological comparability of measurement results from growers in a particular region is important, and in Australia the industry has commenced work with the NMI to produce grain calibrators that have metrologically traceable quantity values to the SI unit for the kind-of-quantity mass fraction. The primary calibrator selected is a NIST SRM 723d (Tris = 2-amino-2-(hydroxymethyl)propane-1,3-diol) that the NMI, under the powers of the National Measurement Act, has recognized as a legal primary calibrator. The quantity value of this SRM (where SRM is the NIST initialism for CRM) has been established by a primary reference measurement procedure giving metrological traceability to the SI unit.

#### 9.7.1 Description of the calibration hierarchy

Measurement results are metrologically traceable to the nitrogen mass fraction of a NIST standard reference material (Tris). The mass fraction of titratable acid (purity) of the material has been established by coulometric titration, and the material is claimed to be metrologically traceable to the SI unit one for mass fraction. This CRM is used to calibrate measuring systems for analysis of nitrogen by the Dumas method, which involves combustion of the sample followed by gas chromatographic analysis of the nitrogen oxides that are produced. The protein content of a master calibrator grain (usually taken from the previous year’s harvest) is established in an interlaboratory materials-certification campaign that is supervised by the NMI, using the calibrated Dumas systems. The continuity of the metrological traceability chain rests on the assumption of commutability of the reference material i.e. the Tris. The measurement result from each laboratory, and hence the quantity value assigned by the NMI, is metrologically traceable through the Tris CRM. Note that a measured nitrogen mass fraction is converted to a protein mass fraction by multiplication by a conventional factor, \( k \), that has no measurement uncertainty. The master grain is then distributed to all growers who use it to calibrate a near infra-red instrument (NIR) in each of their laboratories, so called master instruments. The calibration is based on a large number of samples and is regularly updated. These master instruments measure the protein mass fraction of working calibrator grain samples that are then used in the field to calibrate NIR instruments that measure the harvested grain.

#### 9.7.2 Metrological traceability chain

A schematic of the metrological traceability chain is shown in Figure 9.7.2–1.
measurement model for end-user: $h(w_{\text{sample}}, w_{\text{call}}, \alpha_{\text{sample}}, \alpha_{\text{call}}) = 0$

Absorbance and wavelength have their respective measurement models, 1 and 2.

* See Figure 9.1.5–1 for side chains associated with a coulometric titration and assignment of mass fraction.

* Tris = 2-amino-2-hydroxymethyl-1,3-propanediol

b Measuring systems are calibrated and then certify grain samples in an interlaboratory comparison.

c The master instruments each measure grain samples to act as grower’s working calibrator for field measurements.

**Figure 9.7.2-1** Metrological traceability chain of measurements of mass fraction of protein in harvested grain. Measurement uncertainties are given as relative standard measurement uncertainties.
10 RECOMMENDATIONS ON PROCEDURES

10.1 Establishing metrological traceability of measurement results in chemistry

- Define the measurand by system (including any matrix), component (sometimes called analyte), and kind-of-quantity with any specification appended to each of the three segments;
- decide on the metrological reference for the final measurement result;
- decide the target measurement uncertainty;
- choose and validate a measurement procedure (for a given measuring system), including a measurement model or measurement function;
- acquire the relevant measuring system including calibrator(s);
- establish the calibration hierarchy providing the metrological traceability chain for the expected measurement result, see Chapter 9;
- decide on the structure of the uncertainty budget;
- estimate an approximate measurement uncertainty;
- check whether the target measurement uncertainty is likely to be met;
- install a quality assessment scheme for the measurement;
- carry out the measurement;
- evaluate or calculate the components of the uncertainty budget, and calculate the actual combined standard measurement uncertainty, e.g., according to the Guide to the Expression of Uncertainty in Measurement (GUM) [2] or the EURACHEM/CITAC Guides [34, 67];
- report the measurement result comprising measured quantity value and measurement uncertainty; and
- specify the metrological traceability chain with its metrological reference.

10.2 Implementation of metrological concepts in chemistry

In support of the recommendations elaborated in Section 1.1, there should be a concerted effort to:
- include basic features metrological concepts in curricula of analytical chemistry; and
- use concepts and associated terms given in the International Vocabulary of Metrology (VIM) [1] for description and communication of measurement.

10.3 Dissemination

The present text may serve as a complement to vocabularies and handbooks on measurement in disciplines other than chemistry by offering new concepts and diagrams of calibration hierarchies with associated metrological traceability chains.
11 CONCLUSIONS

Recommendations are presented for establishing and demonstrating *metrological traceability* of *measurement results* in chemistry.

The basic nomenclature has been identified and should be used in practice to aid common understanding.

*Metrological traceability chains* for various *kinds-of-quantity* are given as diagrams utilizing this nomenclature and show a common structure which should be adopted as appropriate.
12 ACKNOWLEDGEMENTS

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Personal comments were requested and received from M Kuehne (BIPM), L Mackay (NMIA), and F Pavese (INRIM).
13 REFERENCES


Annexe I  Concept diagrams

The concepts presented in the preceding text of this document are related to each other in various ways forming one diagram, which, for convenience, has here been cut up in four diagrams with overlaps.

The three types of relation connecting the concepts are defined by ISO 704 [4] and ISO 1087-1 [3].

- The generic relation (or genus-specific relation) that is hierarchical, connecting a superordinate generic concept to two or more subordinate specific concepts which inherit all characteristics of the former. This relation is shown as a tree, sometimes with a heavy trunk indicating a separate terminological dimension; a short branch with three dots means that other specific concepts exist, but are not presented.

- The partitive relation (or part-whole relation) that is also hierarchical, connecting a superordinate concept to two or more partitive concepts which assembled constitute the former. This relation is shown as a rectangular rake; a continued backline without a tooth means that other, not mentioned partitive concepts exist. Two closed-set teeth show that several partitive concepts of a given type are involved whereas one with broken line indicates two concepts of that type may not be involved.

- The associative relation (or pragmatic relation) that is non-hierarchical, connecting two concepts which are in one of many types of association. This relation is shown as a double-headed arrow. For simplicity, only some of the possible association relations are given.

A hyphenated number without parentheses refers to a concept defined in the text.
A parenthetic number indicates a concept undefined in the text, but defined in VIM3.
A parenthetic concept is either undefined and assumed to be generally understood (a so-called 'primitive') or is not used in the text, but is included in the diagram for better understanding of concept relations.

Figure Annexe I–1 about here

Figure Annexe I–2 about here

Figure Annexe I–3 about here

Figure Annexe I–4 about here
<table>
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KF  Karl Fischer titration procedure (measurement of mass fraction of water in material)

METAS  Bundesanstalt fuer Metrologie und Akkreditierung Schweiz

MiC  Metrology in Chemistry

MLA  Multilateral Recognition Arrangement (under ILAC)

MRA  Mutual Recognition Arrangement (under CIPM)

MU  measurement uncertainty

NARL  National Analytical Reference Laboratory (NMI, Australia)

NATA  National Association of Testing Authorities (Australia)

NIR  near infra-red

NIST  National Institute for Standards and Technology (USA)

NMI  National Metrology Institute, National Measurement Institute

NMR  nuclear magnetic resonance

NPU  Nomenclature for Properties and Units, indicating terms from the IFCC-IUPAC (Sub)Committee on NPU

OIML  Organisation Internationale de Métrologie Légale

PAC  Pure and Applied Chemistry

PCR  polymerase chain reaction

PMS  primary measurement standard

PRMP  primary reference measurement procedure

PTB  Physikalisch-Technische Bundesanstalt (Germany)

PTS  proficiency testing scheme

QNMR  quantitative nuclear magnetic resonance

QUAM  Quantifying uncertainty in analytical measurement [34]

REIMEP  Regular European Interlaboratory Measurement Evaluation Programme at IRMM (for nuclear measurements)

REMCO  Council Committee on Reference Materials (under ISO)

RM  reference material

RMP  reference measurement procedure

runc  relative measurement uncertainty

SI  Le Système International d’Unités

The International System of Units

TGA  thermo-gravimetric analysis

TMU  target measurement uncertainty

unc  measurement uncertainty

UNIDO  United Nations Industrial Development Organization

UTC  Coordinated Universal Time


WHO  World Health Organization
Research Papers


General Papers


Additional Papers of Interest


### Annexe IV   Alphabetical index of terms for concepts defined in text or VIM3

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190x275mm (96 x 96 DPI)
190x275mm (96 x 96 DPI)
fig 9.3.1

275x190mm (96 x 96 DPI)
Fig 0.5.2.1

190x275mm (96 x 96 DPI)
Fig 0.6 - 1

190x275mm (96 x 96 DPI)
Fig 0.7.2 – 1

190x275mm (96 x 96 DPI)
Figure A-1: Concept diagram around ‘quantity’
Figure A1-4: Concept diagram around 'measurement uncertainty'

275x190mm (96 x 96 DPI)