Eurachem / **CITAC** **Cooperation on International Traceability in Analytical Chemistry**

Eurachem / CITAC Guide

Metrological Traceability in Chemical Measurement

A guide to achieving comparable results in chemical measurement

2nd Edition in English

2019

INTENTIONALLY BLANK

Eurachem/CITAC Guide:

Metrological Traceability in Chemical Measurement

A guide to achieving comparable results in chemical measurement

2nd Edition in English (2019)

Editors

S L R Ellison (LGC, UK)
A Williams (UK)

Composition of the Working Group*

S Ellison *Chair*	*LGC, Teddington, UK*
B Magnusson *Secretary*	*Trollboken AB, Sweden*
R Bettencourt da Silva	*Univ. Lisboa, Portugal*
W Bremser	*BAM, Germany*
A Brzyski	*Eurachem Poland*
E Christie	*Eurachem Ireland*
R Kaarls	*Netherlands*
R Kaus	*Eurolab DE, Germany*
I Kuselman	*CITAC*
I Leito	*Univ Tartu, Estonia*
O Levbarg	*Ukrmetrteststandart, Ukraine*
R Macarthur	*FERA, UK*
P Pablo Morillas	*EUROLAB-España, Spain*
F Pennecchi	*CITAC*
T Naykki	*SYKE, Finland*
P Yolcu Omeroglu	*Eurachem TR, Turkey*
O Pellegrino	*IPQ/DMET, Portugal*
M Rösslein	*EMPA St. Gallen, Switzerland*
P Robouch	*JRC, EU*
E Sahlin	*RISE, Sweden*
A Van der Veen	*NMi, Netherlands*
M Walsh	*Eurachem Ireland*
W Wegscheider	*Montan Universität Leoben, Austria*
A Williams	*UK*
R Wood	*RSC, UK*

At time of document approval

Acknowledgements

Citation

Eurachem/CITAC Guide: Metrological Traceability in Chemical Measurement

Preface

Measurement underpins a wide range of socio-economic activities, both domestic and international. Every day, thousands of chemical measurements support decisions on food safety, health and environmental protection. The global market, too, needs accurate and reliable measurements so that technical barriers to trade can be minimised. In all these sectors, the concept of "tested once, accepted everywhere" is increasingly important, and the need for reliable measurement results that can be compared across space and time has never been greater. Reliable measurements depend critically on competent staff, validated and tested procedures, comprehensive quality systems, and traceability to appropriate measurement references. Recognition of these requirements is underscored by the increasing adoption of standards and measurement quality systems, such as laboratory accreditation against ISO/IEC 17025:2017 [1], or the pharmaceutical industry's GLP and cGMP requirements.

To achieve comparability of results over space and time, it is essential to link all the individual measurement results to some common, stable reference or measurement standard. Results can be compared through their relationship to that reference. This strategy of linking results to a reference is termed "metrological traceability."

The *International vocabulary of metrology* (VIM) [2] defines metrological traceability as the:

> *"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."*

This definition implies a need for effort at national and international level to provide widely accepted measurement standards, and at the individual laboratory level to demonstrate the necessary links to those standards. Demonstration of appropriate metrological traceability is accordingly a requirement of ISO/IEC 17025:2017 [1].

At the international level, comparability between national measurement systems is being continually improved by intercomparison of measurement standards at the National Metrology Institute (NMI) level. A multilateral mutual recognition arrangement was signed in 1999 by the member nations of the Metre Convention in response to the need for an open, transparent and comprehensive scheme to give users reliable quantitative information on the comparability of national metrology services.

Individual measurement and testing laboratories play their part by careful use of appropriate measurement standards and other references for calibration and control of their measurement processes. In an increasingly regulated environment, however, laboratories are under greater pressure to demonstrate that their use of measurement standards (including certified reference materials and any other references) is indeed both appropriate and sufficient.

This is particularly true in analytical chemistry. Many of the physical quantities used in routine chemical measurement are underpinned by extensive and effective calibration and traceability systems, making the establishment of traceability for these quantities relatively straightforward. However, the values of chemical quantities involved are typically drawn from a wide range of reference materials and data with varying pedigree and provenance, requiring especial care and

judgement in selection of references. Chemical measurements also typically require confirmation of identity as well as measurement of amount. Another challenge is the measurement of a species in complex matrices, which may influence the apparent value of the measured species. Further, it is not uncommon for useful chemical results to arise from the measurement of empirical measurands, for example "extractable cadmium" (sometimes called operationally defined measurands). In such circumstances, it is not always so straightforward to identify the requirements for traceability, or to demonstrate that the traceability in place is adequate.

The purpose of the present document is accordingly to provide guidance on identifying traceability requirements and establishing traceability of measurement and test results. The document describes a consistent set of principles which laboratories can apply in order to establish traceability for their measurement results, and pays particular attention to the use of appropriate references for chemical quantities.

The first edition of this Guide was issued in 2003. This second edition amends the Guide to reflect revised terminology introduced in the third edition of the VIM [2]. Detailed discussion of the revised VIM terminology can be found in the Eurachem Guide "Terminology in Analytical Measurement: Introduction to VIM 3" [3].

Contents

Eurachem/CITAC Guide: Metrological Traceability in Chemical Measurement

1 Scope and field of application

1.1 This Guide gives detailed guidance for the establishment of metrological traceability in quantitative chemical analysis, based on the definition in the International vocabulary of metrology (VIM) [2]. Though it is aimed principally at testing and measurement laboratories carrying out chemical measurement, the principles are expected to apply from routine analysis to basic research. The document is also intended to assist laboratories in meeting the requirements on traceability of results given in ISO/IEC 17025 [1].

1.2 Some common areas in which chemical measurements are needed, and in which the principles of this Guide may be applied, are:

- Quality control and quality assurance in manufacturing industries;

- Measurement and testing for regulatory compliance;

- Measurement and testing utilising an agreed procedure;

- Calibration of standards and equipment;

- Measurements associated with the development and certification of reference materials;

- Research and development.

1.3 Though this Guide discusses measurement uncertainty and method validation in relation to their role in traceability, a detailed description is not attempted in either case. Readers are referred to the Bibliography for additional guidance. Further details of terminology can be found in the Eurachem Guide "Terminology in Analytical Measurement: Introduction to VIM 3" [3] and, for method validation, the Eurachem Guide "Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics" [4]. Additional references can be found in the Eurachem Reading List available at http://www.eurachem.org.

1.4 Traceability is necessary but not sufficient for reliable results; other measures are necessary. It is accordingly assumed throughout this Guide that, whether carrying out measurements or assessing the performance of the measurement procedure, effective quality assurance and control measures are in place to ensure that the measurement process is stable and in control. Such measures normally include, for example, appropriately qualified staff, proper maintenance of equipment and reagents, use of documented measurement procedures and control charts. Reference 6 provides further information on analytical QA procedures.

2 Introduction

2.1 Good analytical results are essential so that reliable decisions can be made. A key property of good results is comparability; the ability to compare results meaningfully wherever they originate. Comparability is provided by, among other things, traceability to a consistent and agreed set of measurement units and scales. For most chemical measurement results, this is best provided by the SI, the internationally accepted system of units [5]. While it is recognised that other units may be required, this Guide will generally assume that measurements will be expressed in, or rely on, SI units.

2.2 Traceability is not a new concept in chemical analysis. Before the advent of automation and instrumental techniques, titrimetry and gravimetry were the workhorses of the chemistry

laboratory and even though the average analyst may not explicitly refer to or recognise the significance of uncertainty or traceability, the core elements for their attainment were in place. For example, great care was, and is, paid to the preparation and calibration of volumetric solutions, including their linkage to the SI. With more complex measurement procedures, it is not always so straightforward to identify the requirements for traceability, or to demonstrate that the traceability in place is adequate. The purpose of the present document is accordingly to provide guidance on identifying traceability requirements and establishing adequate traceability.

2.3 There has been much discussion, both at workshops and in the literature, about the role of traceability in chemical measurement. This document is based on the following principles, which are fully in line with the VIM definition of traceability:

- Method development establishes a measurement procedure for obtaining an acceptable estimate of the value of the measurand. This measurement procedure includes an equation that describes how to calculate a measurement result from other measured quantities, and specifies the conditions under which this equation is expected to hold;

- Validation demonstrates that this equation and set of conditions is sufficiently complete for the purpose in hand.

Establishing traceability ensures that the values of these measured quantities and the values of the specified conditions are related to appropriate standards. This is achieved by calibration using appropriate measurement standards. Calibration is essential for the critical quantities in the measurement (see paragraph 6.5); for less critical values the required control may be less rigorous.

These basic principles are summarised in Box 1. They are discussed in detail in section 3, and related to the internationally accepted definition of traceability in section 4.

2.4 This document identifies the key elements in establishing traceability as:

i)   Specifying the measurand, scope of measurements and the target measurement uncertainty [7];

ii) Choosing a suitable method of estimating the value, that is, a measurement procedure with associated calculation - an equation - and measurement conditions;

iii) Demonstrating, through validation, that the calculation and measurement conditions include all the "influence quantities" (represented by their values x_1 to x_n in Box 1) that significantly affect

---

Box 1. Summary of basic principles

1. We assume that an acceptable estimate y of the measurand value can be obtained from

$$y = f(x_1, x_2, \ldots x_m)\big|_{x_{m+1}, x_{m+2} \ldots x_n} \qquad [1]$$

that is, y is calculated from $x_1 \ldots x_m$ using a relationship f which is valid under measurement conditions specified by $x_{m+1} \ldots x_n$.

2. Validation checks that the equation above is sufficient using suitable tests.

3. y is then considered *traceable* to $x_1 \ldots x_n$

4. Given that Eq 1 is sufficient, all that is necessary for complete traceability to appropriate references is that all the values x_1 to x_n are themselves traceable or defined values.*

In practice, it is sufficient to ensure that values x_1 to x_n are under sufficient control to provide the required uncertainty in y. For critical quantities, this requires traceable calibration against reference values. For less critical quantities, less stringent control may be adequate.

"Defined values": for example, unit conversion factors, mathematical constants, or the values of constants used to relate some SI units to fundamental constants.

---

the result, or the value assigned to a standard;

iv) Identifying the relative importance of each influence quantity;

v) Choosing and applying appropriate measurement standards;

vi) Estimating the uncertainty.

These activities are discussed individually in sections 6 and 7. Other documents in this series do, however, provide substantial additional guidance. In particular, The Eurachem/CITAC "Guide to Quality in Analytical Chemistry" [6] describes the implementation of quality systems for chemical measurement. The Eurachem Guide "The Fitness for Purpose of Analytical Methods" [4] provides detailed guidance on method validation (item iii) above), while the Eurachem/CITAC Guide "Quantifying Uncertainty in Analytical Measurement" [8] describes the evaluation of measurement uncertainty in detail (item vi). In the present Guide, this detail is not repeated, but each of these special topics is discussed briefly to identify their roles in establishing traceability.

3 Principles of metrological traceability

3.1 Measurands, procedures and results

3.1.1 A *measurand* is a "quantity intended to be measured", such as mass, volume or concentration. It is critically important that the quantity to be measured is clearly and unambiguously defined. For example, volume is defined for a specific temperature, and concentration applies to a particular analyte and chemical species. Some measurands are defined in terms of procedures used; for example, 'extractable lead' would require specification of the extraction conditions[*]. (Measurands defined in terms of a procedure are sometimes called 'empirical' or 'operationally defined', in comparison with 'rational' measurands which can be described without reference to a specific procedure.)

3.1.2 Measurement *procedures* are intended to provide *estimates* of the values of measurands. Procedures are developed and documented so that they provide reliable estimates, and for the purpose of this document it will be assumed that the procedure is accepted as providing an adequate estimate for the purpose in hand, and that it incorporates all necessary measurement conditions and corrections.

3.1.3 *Results* are values ascribed to measurands following measurement of test items using an appropriate procedure. Results are accordingly estimates of measurands. Results have properties such as uncertainty and, as will be shown, traceability.

3.2 Measurement units and scales

3.2.1 Meaningful comparisons between measurement results are only possible if the results are expressed in the same *units*. This is actually achieved by quoting measurement results as multiples of a given unit; for example, a mass of 2.1 kilograms has a mass equal to 2.1 times the mass of the international kilogram. The mass of the international kilogram is the 'unit of mass'. Clearly, in order to express one mass as a multiple of another, the two have to be compared. It is impractical to compare all masses with the international kilogram. This comparison is therefore most commonly indirect, through measurement standards, which are in turn calibrated against other standards. This forms a chain of comparisons leading to the relevant primary unit or an accepted 'realisation' of a unit. Providing access to consistent units of measurement by means of measurement standards is the principal function of traceability; without it, there is no meaningful measurement.

3.2.2 A measurement *scale* is simply an agreed method of using units of measurement and defining an origin (a 'zero' point). Mass, length and concentration are expressed using linear measurement scales with zero at the origin (they are 'ratio scales'); pH, for example, is a logarithmic scale with a reference at a hydrogen ion activity of 1. When two results are described as being 'on the same measurement scale' they are both expressed in the same units and using the same origin.

---

[*] Strictly, "extractable lead" is typically an abbreviation for more specific terms such as "*amount concentration ..*" or "*mass fraction...*" of extractable lead.

3.3 Calibration

3.3.1 Section 2.4 stated that calibration is the fundamental process in establishing traceability. It is through calibration that traceability to appropriate measurement standards is actually achieved in practice. The following paragraphs review the internationally accepted definition of calibration, and discuss the calibration of parts of a measurement system and of whole systems.

3.3.2 Calibration is described by the VIM as the process of establishing the relationship between values shown by a measuring instrument or system, and the values provided by measurement standards.

3.3.3 Calibration can be (and usually is) applied to parts of a measurement system. In particular, instruments are normally calibrated in isolation, and then used in a larger measurement system. Items such as balances and thermometers are calibrated less frequently because they are relatively stable in the medium term; instruments such as GC or ICP equipment tend to vary much more and are typically calibrated more frequently, often in the same run as a set of test items. For this purpose, one would generally expect to use a pure chemical as the calibration material, though it may be added to a matrix similar to the samples expected in order to reduce matrix effects. Under these circumstances, the measurement standard values will appear in the calculation of the result (perhaps indirectly) and it is therefore clear that the result is traceable to these reference values.

3.3.4 In some cases, calibration standards are taken through the complete measurement process. For example, a matrix reference material may be analysed at the same time as the test samples and used to correct the results, or a known amount of material (a 'spike') may be used to estimate and correct for the actual analyte recovery, or other effects, during a run. Clearly, if these procedures are employed, either the reference material value or the amount of 'spike' added must appear in the calculation for the result, perhaps via an intermediate 'recovery factor', and the results are accordingly traceable to the value used.

Note: This procedure implicitly assumes that spike recovery is a sufficient correction. See also the note on spiking in section 6.4.1.

3.3.5 One final situation is conceivable. It may be that during method development and validation, it is decided that a fixed correction should be applied to all future measurements, based on observations of a particular reference material which is not used for regular, day to day calibration. This, too, is calibration, and since the value appears in the calculation of each result, it is meaningful to speak of traceability to the value(s) in question.

Note: This should not be confused with a straightforward bias check using, say, a matrix CRM, which does not generate a correction applied to results.

3.3.6 Note that a calibration remains valid only so long as an instrument remains stable. In practice, this is assured through appropriate QC, and recalibration intervals must reflect the rate of drift.

3.4 Effects on measurement results

3.4.1 Any measurement can be thought of as one or more determinations combined to give a result under specified conditions. For example, analysis of a soil sample for, say, contaminants, typically involves the quantitative determination of the mass of soil taken, and the concentration of analyte in a measured volume of solution containing an extract from the sample. All these parameters are qualified to some extent by the conditions of measurement. Mass is determined by

weighing, either in air ("conventional mass") or *in vacuo*; volume is typically taken as 'volume at 20 °C' and extraction conditions – whether for complete extraction or for a defined partial extraction - are typically defined in terms of time, solvent, and temperature. The mass, concentration and perhaps volume will of course vary from one measurement to the next, as different sized samples are taken – they are the measured values of the 'variables' in the calculation of the final result. The extraction and other conditions are usually held close to their nominal values and are not expected to change; they are fixed conditions, and are not generally included in the calculation.

3.4.2 For a given measurement procedure, if the fixed conditions change, so will the value of the result. For example, if extraction conditions change significantly from those specified in the procedure, the result will be wrong, just as it would if the mass or concentration values are in error. It follows that both the fixed conditions required for the measurement, and the other measured values obtained and put into the calculation of the result, affect the analytical result. If either fixed conditions or variable measured quantities are incorrect, then so will be the result. These measured values, whether included in the calculation or among specified conditions, are the values of all the 'influence quantities' for the measurement – all have an influence on the result and all must be controlled. It is simplest to look first at how the fixed measurement conditions are controlled; the control of the variable parameters will be considered later.

3.5 Controlling fixed conditions

3.5.1 If two scientists want to get the same reading for a measurement, the simplest method is to use the same measuring instrument. To continue the soil analysis example with one simple physical aspect of the measurement, if a consistent extraction time is important, then two analysts could simply use the same clock to determine the extraction time. If this is done, it is possible to say that all the extraction times, and consequently the analytical results, are *traceable* to the time given by the clock; the clock provides the measurement standard of time.

3.5.2 This works well, and (at least for a given procedure) is not even reliant on the clock being correct. As long as the clock is consistent, if everybody involved uses the same clock and times the same interval (i.e. every result is traceable to the clock's extraction time interval), everybody involved will share a consistent set of conditions, and extraction timing will not cause a spread in the results.

3.5.3 This becomes unworkable very quickly if tight control is needed; it is clearly impractical for the same clock to be used by many different scientists at different times and places. What is needed is a collection of clocks which all show the same time. In practice, the simplest way of achieving this is to ensure that all the clocks are themselves compared with a master clock and shown to be indicating the same interval, or corrected so that the correct interval can be deduced from each clock's readings (this is 'calibration' against the master clock). Each analyst using their own clock then generates the same extraction time. Now, it is possible to say not only that each analyst's results are traceable to their own clock's interval, but also that they are all

traceable to the master clock. It is this traceability to a single measurement standard – the master clock, in the example – that generates consistent measurement in the different laboratories.[*]

3.5.4 This leads to one key principle:

- *traceability to common measurement standards allows laboratories to obtain the same set of fixed conditions required for measurements.*

This in turn minimises variation due to changes in fixed conditions of measurement.

3.5.5 The issues raised here also apply when measurement conditions are required to vary in a prescribed way. For example when a chromatography column temperature is 'ramped', the times, temperatures and ramp rates all fall into the category of 'conditions of measurement' specified by the chosen procedure.

3.6 Controlling variables with calibration standards

3.6.1 Very similar principles apply when looking at the measured variables included in the calculation of the result, but the picture is more complex since the values are not supposed to be fixed, but 'consistent' in some way. In particular, each needs to use a consistent measurement scale. This 'consistency' is achieved by using the same calibration standards for successive measurements. The following short discussion develops this concept. For simplicity, only one reference is shown, though of course most measurements rely on several.

3.6.2 Consider two laboratories, A and B, carrying out measurements on samples of broadly the same type (see Figure 1). Each calibrates their equipment using a measurement standard with a known nominal concentration (x_1 and x_2 respectively). They calculate their respective results y_1 and y_2 from a calibration equation including the respective values of x. In each case, the result y is a function of the reference value x (usually a simple multiple, assuming a linear response). The reference value x, of course, provides the units of measurement. Where there is such a relationship – one value is calculated from another, reference, value – the calculated value can always be claimed to be traceable to the reference value[+]. Here, y_1 is traceable to x_1, and y_2 to x_2, though so far that has very limited consequence.

3.6.3 The important question is the relationship between y_1 and y_2. Though the values of y_1 and y_2 are (usually) different, is the difference genuine, or just due to different references? Clearly, as presented in Figure 1, there is no basis for comparing the two results; certainly we cannot write a mathematical equation that would show, for example, y_1 in terms of y_2.

---

[*] Clearly, in practice, fully calibrated clocks are rarely necessary; simple checks against a time signal are generally adequate for typical time intervals. But the principle is the same; all the clocks are compared with a single reference.

[+] To support a claim of traceability according to the VIM definition, and to be practically useful, the uncertainty associated with y also needs to be known.

Figure 1
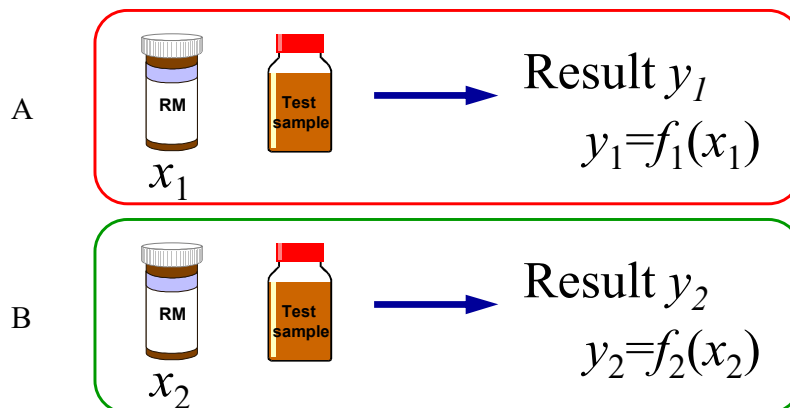
3.6.4 If, however, the two measurement standards are both calibrated against some common reference, a comparison becomes meaningful (Figure 2). Now, both results are derived from the same value (x_0). Both will now have the same units of measurement, (the same scale and units as x_0), and direct comparison of the values y_1 and y_2 is now not only possible but also meaningful. By analogy, of course, x_0 could also be derived from a yet higher reference to allow global comparisons.

3.6.5 In this instance, therefore, traceability does not make the results identical; after all, for different samples, they would generally be different. But traceability through calibration permits meaningful comparison by ensuring 'consistency' of measurement units.

Figure 2
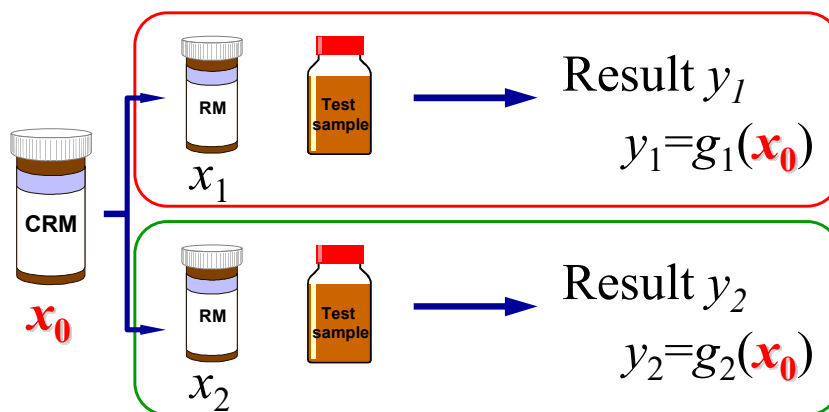
3.6.6 This discussion illustrates two further principles:

- *When a result is calculated from a reference value, it is traceable to that value;*
- *Traceability to common references allows meaningful comparisons between results.*

3.7 Common references allow arbitrary definition

3.7.1 Though the point is abstruse, there is another implication of traceability to a common reference, which is important in metrology. Looking again at figure 2, in principle, it now becomes possible to derive a direct mathematical relationship between y_1 and y_2 in which the value of x_0 is eliminated (at least to first order). For example, in the simple case of linear responses, the ratio y_1/y_2 does not contain x_0 (though in the situation of Figure 1, it would simply include both x_1 and x_2). It follows that if traceability to a common reference is assured, the value of the common reference can, in principle, be defined arbitrarily without affecting the relationship between end results. This is a very useful result; the international kilogram is just such an arbitrary reference, and without traceability to this single artefact, there would be no basis for comparing mass determinations around the globe.

3.8 Role of method development

3.8.1 Method development typically produces a standard operating procedure, incorporating a set of instructions for carrying out a measurement, a set of measurement conditions defining the values of parameters that must be held stable, and an equation from which the result is calculated using the values of the measured parameters. It accordingly provides an equation, which is expected to generate consistent results provided that the specified conditions are correctly set and stable. The implication is that if the values of all these parameters are traceable to stable references, the results will be consistent.

3.8.2 However, this expectation is invariably based on some assumptions; specifically, linearity of response, freedom from overall bias, and absence of other significant effects. If those assumptions are incorrect, for example due to the presence of unsuspected effects, results will be unreliable and often incorrect. Practical experience indicates only too clearly that unknown effects are frequent and often large; such assumptions should therefore not go unchallenged.

3.9 Role of method validation

3.9.1 Method validation, among other important functions concerned with adequacy of performance, is the mechanism used to test these crucial assumptions. It answers the question "are these assumptions valid?" by reviewing the measurement model and making experimental tests of the assumptions, for example by carrying out measurements on appropriate reference materials, or by comparison with the results of independent procedures. An overall bias check seeks evidence of significant bias; recovery studies seek evidence of loss of material (and can provide information on other biases); linearity checks seek evidence of significant departures from linearity; ruggedness or similar studies seek evidence for the presence of further effects and so on.

3.9.2 Where an effect is discovered, the procedure needs to be modified and subjected to further development and validation. Such a modification can take three basic forms:

- elimination of the effect (for example, changing digestion conditions to eliminate precipitation in elemental analysis);

- reducing variation caused by the effect by adding or reducing a control range. For example, it may become necessary to specify a particular operating temperature or range of temperatures to reduce variation;

- correcting for the effect by including it in the calculation of the result.

Notice that the last two actually have the effect of introducing another measurement into the procedure – that is, another factor requiring traceability.

3.9.3 Where no significant effects are found, the procedure is considered validated and may be used without modification; the equation, and the specification of measurement conditions, can now be accepted as a sufficient basis for measurement. By implication, of course, the procedure now explicitly includes all the factors known to require traceability – there are no other known significant effects. If all the identified factors are indeed made traceable to suitable references, the procedure can be expected to produce consistent results.

3.9.4 The role of validation in establishing traceability is accordingly to test whether the procedure is sufficiently well defined and incorporates all necessary traceability requirements.

3.10 Traceability and measurement uncertainty

3.10.1 In Figure 2, the two analysts have reached the point where a comparison between their results is at least meaningful. But if they are to decide with any confidence that one sample has a significantly higher level of analyte than another (and not just different results), one more piece of information is essential. The uncertainty of the results is needed.

3.10.2 Uncertainty of measurement is covered in detail in other publications [8, 9] and will not be described in detail here. For the current discussion, the most important points are:

i)   Uncertainty arises, at least in part and sometimes entirely, from inputs to the calculation of the result. Since reference values are uncertain, the uncertainty in the reference value contributes to the uncertainty in the result;

ii)   Uncertainty in results therefore arises from the combination of all the uncertainties in reference values and those arising from the measurement procedure, both from random variation and from other causes.

3.10.3 To estimate the uncertainty on a particular result, then, the analyst needs not only the contributions to uncertainty arising from the measurement procedure itself (from precision, operator limitations etc.), but also the uncertainty associated with their reference values. It follows that useful measurements with uncertainties can only be provided if all the necessary parameters are traceable to appropriate references *and* the uncertainty on each of those references is known.

4 Metrological traceability: The international definition

4.1 The previous section has shown that, for consistent and useful measurement results, it is important both that a chain of comparisons to agreed references, and the uncertainties associated with these comparisons, are established. These principles lead directly to the definition of traceability in the International vocabulary of metrology (VIM):

> 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

4.2 The definition establishes traceability as a property of measurement results, that is, of values obtained by measurement. Strictly, therefore, the phrase "traceable to a given laboratory" is shorthand for "traceable to a reference value maintained by that laboratory". Similarly, "traceable to the SI" is shorthand for "traceable to reference values obtained by agreed realisations of the SI units" (for example, a result cited in units of mg l^{-1} and claimed as "traceable to the SI" would need to be traceable to realisations of the kilogram and metre).

4.3 The VIM definition is accompanied by several informative Notes. These are discussed in the Eurachem Guide to Terminology in Analytical Measurement [3].

5 International system of quantities and units (SI)

5.1 Section 3.2.1 shows that measurements need to be expressed in agreed measurement units. The appropriate system of units for most chemical measurement is the "Systeme Internationale" (SI). The SI units form a coherent system which is used almost universally in science and very widely in trade.

5.2 The SI defines base units for mass (kilogram, kg), length (metre, m), time (second, s), thermodynamic temperature (kelvin, K), electric current (ampere, A), luminous intensity (candela, cd) and amount of substance (mole, mol). It also defines many derived units in terms of the base units, and a selection of important derived units for chemical measurement is provided in Table 1 (references 10 and 11 provide more comprehensive examples). Note that the mole is the only base unit that requires further qualification; it is essential to specify the *entity* concerned, that is, the specific substance referred to.

5.3 The nature of the substance analysed is, of course, important in all chemical measurements, whether or not they are expressed in moles. In particular, quantities such as mass fraction in chemical measurement are not 'dimensionless' in that they invariably refer to the fraction of one substance as a portion of a mixture of other substances. The implication is that for appropriate traceability, each measurement result should be traceable to a reference for the particular substance.

Table 1. Common quantities and units in chemical measurement

Quantity	Units
molar fraction	mol/mol, %
mass fraction	kg/kg, %
volume fraction	m^3/m^3, %
molar concentration	mol/m^3
mass concentration	kg/m^3
volume concentration	m^3/m^3
molality	mol/kg
pH	1 (negative logarithm of hydrogen ion activity)
enzyme activity	katal (mol s^{-1}) (SI unit), U (μmol/min)
Purity, an important characteristic for many reference materials and other substances, is generally expressed in terms of one of the fractions or concentrations above	

6 Establishing traceability

6.1 Essential activities in establishing traceability

6.1.1 The introduction stated a set of activities which are necessary to establish traceability in a working laboratory:

i)   Specifying the measurand, scope of measurements and the target measurement uncertainty [7];

ii)   Choosing a suitable method of estimating the value, that is, a measurement procedure with associated calculation - an equation - and measurement conditions;

iii) Demonstrating, through validation, that the calculation and measurement conditions include all the "influence quantities" (represented by their values x_1 to x_n in Box 1) that significantly affect the result, or the value assigned to a standard;

iv)   Identifying the relative importance of each influence quantity;

v)   Choosing and applying appropriate measurement standards;

vi)   Estimating the uncertainty.

This list does not necessarily imply an order or priority among the activities; they are all important. Some interdependencies will also occasionally result in revisiting prior decisions. The important issue is that they are all carried out adequately for the purpose in hand. For consistency, however, the following paragraphs consider each in turn in the order above.

6.1.2 Note that these steps are sufficient for claiming traceability of results on the assumption that other QA measures, including staff training, measurement quality control etc. are in place.

6.2 Specifying the measurand and required uncertainty

6.2.1 A meaningful measurement requires unambiguous specification of the measurand, or quantity to be measured. For the purposes of this Guide, a measurand is usually described adequately in words, but close attention needs to be paid to some specific issues. These are:

- *Identity of the analyte*. Chemical measurement most commonly quantifies particular molecular or elemental species. It will clearly be necessary to take extra care if different forms of a material occur and if the difference is important. For example, different isotopes, isotope mixtures, isotopomers, enantiomers, or crystalline forms may need to be distinguished.

- *Implied measurement conditions*. Most analytical results are expected to be obtained under conditions close to normal ambient temperature, pressure and humidity, and it is common practice to omit these conditions from the stated description of the measurand. In considering traceability, however, it is important to understand exactly what conditions apply, as these form part of the formal definition of the measurand. Where the conditions are not specified, it is normally sufficient to assume that the measurand is defined at NTP (Normal Temperature and Pressure: 20 °C, 1 atmosphere).

- *Recovery correction*. It is most important to state clearly whether the quantity of interest is an amount of material recovered from a substrate, or whether it is the total amount believed to be present. The former is not normally corrected for analytical recovery. The

latter may need a recovery correction if recovery is significantly different from 100%. This is important because recovery correction requires an additional measurement to calculate the correction, and will generally add to the traceability requirements.

- *Specification in terms of a procedure*. The guidance in this document is unchanged whether a measurand is defined in terms of a procedure or not; definition in terms of a procedure simply leads to a longer list of fixed parameters. Note, however, that defining a measurand in terms of a procedure does not restrict the procedure used. Though unusual, it is possible in principle to use an entirely different procedure to make the measurements. For example, a purely spectroscopic technique may be used to estimate 'fat content', though 'fat' is most commonly defined in terms of a mass of material extracted under specified conditions. However, it will always be necessary to demonstrate that alternative procedures provide equivalent results for test items within the scope of the procedure.

6.2.2 It is often convenient to consider the required performance of the measurement procedure at this stage. In considering traceability, the most important concern is the measurement uncertainty required. This is important because:

a) The uncertainty in a result cannot be better than the uncertainty arising from the measurement standards in use; uncertainty requirements accordingly influence the choice of measurement standards.

b) For a given measurement technique, achieving a smaller overall uncertainty is likely to require greater control. This will normally increase the number of variables which need to be controlled.

6.3 Choosing a suitable procedure

6.3.1 Once the measurand is known and understood, a measurement procedure is selected, or may be developed especially for the purpose. The choice of procedure involves a range of factors, including, for example, regulatory requirements for particular procedures, customer requirements, cost, experience of different procedures, availability of equipment, and criticality of decisions. Choice of procedure is accordingly a matter of judgement informed by customer needs.

6.3.2 This Guide is concerned only with the establishment of traceability for a chosen procedure. It *assumes* that the choice is the best available in the circumstances. It is for the measurement scientist to decide and, if necessary, demonstrate, whether the procedure is adequate, and once that is decided, this Guide can help show that the results are traceable to appropriate references.

6.3.3 The documented procedure is expected to include the necessary calculations and to specify any controls required, including but not limited to those required by the definition of the measurand. Typically this will take the form of an equation or set of equations for calculating the measurement result, together with a list of conditions such as times, temperatures, reagent concentrations etc. which must be adhered to. (This equation and set of conditions is referred to below as the *measurement equation*.)

6.3.4 The quantities identified in the measurement equation are all the relevant *influence quantities* for the purpose of establishing traceability, subject to validation as described below.

6.4 Validation

6.4.1 Validation is covered in detail in other sources [4], and a full discussion is not required here. However, the main requirements relating to traceability need to be considered. First, to fulfil its role in confirming the adequacy of the measurement equation, method validation should provide a reasonable test of the measurement equation and conditions. It must be recognised that this cannot be exhaustive, and practical considerations may limit the testing possible. But in an ideal case, validation within a single laboratory will include the following activities for the reasons given:

▪ Assessment of selectivity, to ensure that the measuring system responds to the particular species of interest and not to other, similar species.

▪ A certified reference material check, which demonstrates that the procedure is not significantly biased by comparison with independently obtained traceable values.

▪ Reasonable checks on specific, likely effects other than those included in the measurement equation, which show that no other effects need be included.

▪ Precision studies over as wide a time interval and set of conditions as reasonably possible, which provide another test for presence of significant unsuspected effects.

▪ Additional studies on specific and likely sources of bias, including spiking and recovery studies, likely interferences and cross-reactivity studies, which demonstrate, again, that no additional effects are important.
Note: The behaviour of added ("spiked") analyte may not be equivalent to that of native or "incurred" analyte; spiking may therefore fail to give a true indication of native analyte recovery.

▪ A linearity check, to demonstrate that the measurement system response is proportional to the value of the measurand.

Other performance characteristics, such as detection capability, will often be assessed in addition to the above in order to assess fitness for purpose.

6.4.2 Intercomparisons between analysts and different laboratories, or with other procedures, can also demonstrate possible deficiencies in the procedure. If duly treated as tests for additional effects, these, too, will add evidence of the sufficiency of the measurement equation.

6.4.3 The second important consideration in validation studies is that such references as are used to control, calibrate and test the procedure during validation are themselves traceable. This is important to ensure that the validation studies are directly relevant to results obtained in routine use.

6.4.4 Validation has been identified (section 3.9, above) as playing a key role in establishing traceability. It is not an optional activity. Even when adopting a standardised procedure which has been validated and thoroughly tested, some level of validation remains necessary. It is not normally necessary to repeat the complete study of all possible or likely effects; the measurement equation can be taken to be complete without further detailed checking. But analytical procedures are complex and consequently prone to human error. It is invariably necessary to at least check that the laboratory can carry out the procedure correctly (this is often called verification). This is best done with an appropriate certified reference material. Evidence from proficiency tests and other studies may, dependent on the nature of the exercise, also provide evidence of correct operation of a procedure.

6.5 Importance of different influence quantities

6.5.1 Establishing the relative importance of different influence quantities is crucial in deciding the appropriate degree of control or calibration. It is not always necessary to establish a specific calibration for every quantity.

6.5.2 In general, the importance of different influence quantities is dictated by their quantitative effect on measurement results. Quantities with large effects on the results are likely to be important. A second important issue is the likely effect on the result given the uncertainties involved. Typically, effects from physical quantities such as time, mass and volume are well controlled and easily measured compared to many chemical effects, particularly at trace levels. Though this situation arises only because a great deal of care has already been paid to physical measurements, it is very likely in practice that that an analyst will need to pay far more attention to chemical effects than to intermediate physical measurements.

6.5.3 To decide whether an effect needs to be measured and included in provisions for traceability, it is normally sufficient to consider whether the worst case that might reasonably arise would lead to a significant error in the measurement. If it would not, there is clearly no strong case for additional calibration. For example, ambient temperature in a working laboratory in the UK is extremely unlikely to be outside the range 10-30 centigrade and if such a range is not significant for any measurement within the laboratory, there is no strong case for calibration and control of the room temperature.

6.5.4 A formal uncertainty assessment covering all possible effects (and not just those known to be significant) is clearly an exceptionally powerful tool in deciding the relative importance of different effects. If the uncertainty (expressed as a contribution to the combined uncertainty) associated with a particular effect is small compared to the combined uncertainty in the measurement result, further control is unnecessary.

6.5.5 It should be clear that despite the foregoing discussion, environmental and other conditions which are not explicitly stated in the measurement equation may nonetheless exert some influence on the results. Further, most method development is carried out under relatively restricted environmental conditions and it is rarely possible to test extremes; instead, it is generally assumed that laboratories generally operate in approximately the same conditions as applied in method development. This amounts to an unstated requirement to control environmental or other conditions, and a laboratory will normally be expected to take due care in controlling measurement conditions. In the context of this Guide, the most important question is whether such care necessarily extends to traceable measurement and control of conditions. Evaluation of the possible impact should normally follow the principles outlined in paragraph 6.5.3. However, it is common to find that environmental conditions do need some level of control for at least some measurements, and it is accordingly good practice to at least monitor conditions with appropriately checked equipment.

6.6 Choosing and applying appropriate measurement standards

6.6.1 To make sure that all the values used in the measurement equation, and all other fixed values used in the measurement are traceable to appropriate references, all that is necessary in practice is to establish procedures for calibration of the equipment measuring or controlling fixed values, and for ensuring the calibration, certification or control of all the references used in the

measurement. Calibration, together with validated procedures, is accordingly the key to traceability.

6.6.2 In practice, it is recognised that calibrated measurement standards or certified reference materials are not always available, but it is always necessary to establish sufficient control by appropriate choice of measurement standards. There are, however, many different types of measurement standard, particularly for chemical measurement, and there are different circumstances for their use. These issues are accordingly discussed in detail in section 7.

6.7 Uncertainty evaluation

6.7.1 The requirement for uncertainty information follows from the need to ensure first, that the references used are sufficiently accurate for the purpose, and second, to provide complete information for the result of the measurement. Uncertainty evaluation is discussed in detail elsewhere [8] and will not be discussed here. But the minimum required for useful measurements is:

- *either* assessing the contribution of each reference value uncertainty to the uncertainty of the measurement result (which may rely on validation to show that changes within the uncertainty make negligible differences to the result)
  or if appropriate, complying with the equipment, calibration and control requirements of the standard method ("norme", in French) in use.

- assessing the overall uncertainty of the result, including the influence of the references used

- confirming that the overall uncertainty meets end-use requirements.

7 Choice of the reference

7.1 Introduction

7.1.1 Sections 4 and 6 make it clear that appropriate references play a vital role in traceability. The choice of reference is therefore crucial. The following paragraphs consider the choice of reference for:

- Physical measurements made during analytical work

- Confirmation of identity

- Calibrations with certified reference materials

- Calibrations using other materials

- Calibration using reference data

- Method development, validation and verification.

7.1.2 In some circumstances it may not be possible to obtain a suitable certified measurement standard. In such cases the limitations on the traceability of the results should be made clear and any adverse effect of this on the applicability of the results should be conveyed to the customer.

7.2 Physical measurements

7.2.1 A large range of physical measurements is common in analytical work. Fortunately, suitable calibration of physical measurement equipment and availability of standards is rarely a major problem in analytical measurement. Equipment and measurement standards for mass, length, volume, temperature, time and for electrical measurement normally provide calibration uncertainties well below any level of significance compared to the uncertainties found in analytical measurement. This is, however, entirely dependent upon a long-established and carefully maintained infrastructure, reliant on traceability to national and global references. For all practical analytical work, therefore, measurement standards must be chosen to be appropriate to the equipment being calibrated, of sufficiently small uncertainty for the purpose in hand, and their values must be traceable to relevant references. In most cases, this will require a certificate of calibration provided by a competent authority.

7.2.2 Where equipment is calibrated by a third party, and the laboratory does not maintain a calibration standard, the calibration provider must be able to provide a certificate of calibration including uncertainty values. In addition, the laboratory should monitor the continuing performance of the equipment between calibrations, using local, stable check standards to confirm continued operation within calibration uncertainties.

7.3 Confirmation of identity

7.3.1 In most analytical measurements, the identity of the material needs to be confirmed by reference to an authentic sample or reference data[*]. Identity confirmation by comparison is not generally considered to constitute traceability in the sense defined by the VIM. Nonetheless, due

---

[*] Some techniques, such as NMR spectroscopy, may provide sufficiently predictable responses from theory and/or model systems that identity can be confirmed without an authentic sample, but this is not common in general analysis.

care will always need to be taken in selecting appropriate references for this comparison. Certified pure materials will often serve for identity confirmation where available in sufficient quantity. Authentic samples from a reputable source are usually adequate substitutes provided that the purity is sufficient to generate an essentially pure response for the analyte of interest.

7.3.2 Comparison with reference data, for example in the form of spectroscopic data, is normally acceptable evidence of identity. In this case, however, it is important to ensure that:

- the reference data are obtained under closely similar conditions to those used in the laboratory. For example, infrared spectra of solids should be compared with reference data for solids and not for solutions unless the effects of the change of state are taken into account;

- the reference data and the data on the test items are traceable to appropriate references (for example, wavelength standards) so that direct comparison is possible.

For the purpose of confirming identity, traceability with adequate uncertainty is usually achievable for most instruments currently available via routine calibration and quality control.

7.3.3 Identity can also be established by, for example:

- Knowledge of the synthetic route. For example, if acetic acid is reacted with ethanol then ethyl acetate can be expected;

- Measurement of basic characteristics that allow the identity to be deduced. For example, elemental composition, molecular weight, or presence of specific functional groups, may be established;

- Direct comparison with authentic materials.

7.4 Calibration with certified reference materials

7.4.1 The VIM [2] defines a "certified reference material" as a "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". The key features which distinguish these materials from other calibration standards are therefore:

- Demonstrable traceability to national or international standards;

- A statement of uncertainty.

7.4.2 In many cases it is possible to purchase certified reference materials or calibration solutions and it is convenient and usually cost effective to utilise these. Because the values are traceable to national or international standards and are consequently very reliable, their use is recommended where practicable. The supplier should be asked to provide information about the traceability of the value of the reference material supplied.

7.4.3 In some cases, e.g. XRF analyses of alloys, it may be possible to use a suitable certified matrix reference material for calibration. In these cases the result is clearly traceable to the value of the reference material. The points to consider when choosing such a matrix material are the same as those identified in section 7.7. Note, however, that certified matrix reference materials are not generally recommended for calibration; the cost is typically prohibitive, sufficiently close matrix matching is rare in practice, and the uncertainties associated with the values for certified natural matrix materials are often too large for calibration purposes.

7.5 Calibration with other materials

a) Pure materials

7.5.1 In many cases, the measurand is an amount of a chemically distinct substance; an element or single molecular species. Chemists have a long history of isolating and purifying such substances, and it is common to find relevant materials of purity sufficient to serve as reference materials. This follows from an almost unique feature of chemical measurement; 100% purity forms a natural reference value, which cannot be exceeded. Coupled with widely available and excellent reference data for atomic and molecular weight, and often with additional data on physical parameters such as density, a high purity material represents a local, practical realisation of concentration units, through conversion of mass to molar quantity. Calibration with materials of well-established purity is accordingly a valid means of establishing traceability.

7.5.2 Establishing purity relies primarily on appropriate techniques for preparing and purifying a material (which provides a strong expectation of high purity), followed by reasonable efforts to detect significant *im*purity, usually by application of a battery of techniques capable of detecting a wide variety of likely contaminants. The reliability of these processes cannot readily be verified except by long experience and sound professional judgement based on a good understanding of the chemistry involved. Without clear evidence of traceable values of known uncertainty, the adequacy of such a material can only be a matter of care and judgement. Laboratories will, in general, need to be particularly careful to ensure reliable supply, to check materials as required, and to use all reasonable checks to confirm reliability of uncertified pure materials.

7.5.3 Preparation of pure reference materials is sufficiently costly that most working analytical laboratories will not undertake it. Nonetheless, there will be many cases where in-house preparation is the only option, the most common, perhaps, being the need to test for a proprietary material synthesised in house. Such a material should be checked by all available means, typically including (but not limited to) melting point and other thermal properties, spectroscopic evidence of several independent types, moisture determination, non-metal contamination, checks for inorganics (in organic materials), elemental microanalysis, chromatographic examination, and specific checks for any likely impurities.

7.5.4 Finally, even when materials of good purity are available, the continuing need for trace analysis leads to a requirement for low-level solutions of material, and at low concentrations, the analyte content and purity of the material are frequently affected by secondary effects such as container adsorption, contamination, oxidation etc. Considerable care in supplier selection will be necessary, as will care in use and storage, and it is wise to check successive batches of material against one another.

b) Other reference materials

7.5.5 A wide range of other materials and formulations is available for calibration, including, for example, mixed element calibration solutions, alloys, and carefully characterised novel pharmaceutical reference materials. Without formal evidence of traceability and associated uncertainty information, it must be the laboratory's responsibility to demonstrate that the materials are fit for their intended purpose. As in 7.5.4, considerable care in selection is necessary.

7.6 Calibration using reference data

7.6.1 In some situations, reference data are used either to support calibration using a well characterised material, or as calibration factors. Examples might be the use of reference spectroscopic data to calibrate wavelength scales (as in infrared spectroscopy), or the use of reference absorbance data to establish concentrations directly from absorbance measurements. In such cases, the values of the measurement results are traceable to the reference data.

7.6.2 As in section 7.3, it is important to ensure that:

- the reference data apply under the conditions used in the measurement (which may involve appropriate conversion methods);
- the reference data are traceable to appropriate references (for example, traceability to wavelength standards is important in using spectroscopic absorbance data).

7.7 Reference materials for method development, validation and verification

7.7.1 As is pointed out in sections 4 and 7, reference materials, particularly matrix reference materials, play an important role in method development, validation and verification, and their use for this purpose is strongly recommended. It is, however, important that the material should not only provide traceable reference values, but should also be relevant to the application.

7.7.2 Matrix effects and other factors such as concentration range can be more important than the uncertainty of the certified value. The factors to consider include:

- Measurand (for example, analyte concentration);
- Measurement range (for example, concentration range);
- Matrix match and potential interferences;
- Sample size;
- Homogeneity and stability;
- Measurement uncertainty;
- Characterisation and certification procedures (measurement and statistical).

7.7.3 More detailed information on the choice and use of reference materials is given in EEE/RM/062 "The Selection and use of reference materials" [13] and in ISO Guide 33 [12].

7.8 Assessing the traceability of commercial reference materials

When choosing a supplier of reference materials the following factors should be taken into account:

a) Conformance of the production of the reference materials with quality standards such as ISO 17034 [14] or ISO/IEC 17025 [1]. Conformance should preferably be demonstrated through third party assessment.

b) Track record of both the producer and the material. For example, whether the RM in use has been subjected to an interlaboratory comparison, cross-checked by use of different methods, or there is experience of use in a number of laboratories over a period of years.

c) Availability of a certificate and report conforming to ISO Guide 31 [15].

d) The validity of the certification and uncertainty data, including conformance of key procedures with ISO Guide 35 [16].

7.8.1 Some or all of these requirements may be specified in the customer and analytical specification, but often it will be necessary for the analyst to use professional judgement. Note that quality does not necessarily equate to small uncertainty and fitness for purpose criteria need to be used.

8 Reporting traceability

8.1 Evidence of traceability is reported in calibration certificates (for which it is mandatory under ISO/IEC 17025) or where required by a customer. Such a report should identify (by reference to other available data if necessary):

- All the chemical calibration standards used;
- Where significant, the identity of measurement standards used to control the conditions of measurement.

8.2 It is not normal practice to give details of traceability on test reports. However, where it is necessary to report evidence of traceability of results, the report will typically include:

- The identity of calibration standards used;
- Where significant, the identity of references used to control the conditions of measurement.

9 Conclusion

9.1 This Guide has presented a discussion of the principles underlying the establishment of traceability for results obtained by a procedure in use by a calibration, measurement or testing laboratory. The document takes the view, summarised in the Introduction, that:

- Method development establishes an optimised procedure for obtaining an acceptable estimate of the value of the measurand, including the calculation and a set of measurement conditions;

- Validation demonstrates that this calculation and set of conditions is sufficiently complete for the purpose in hand;

- Once these conditions are met, the laboratory need only establish traceability or control for each value in the equation and for each of the specified conditions;

- Traceability, established by calibration using an appropriate measurement standard, is essential for the critical values in the measurement; for less critical values, it is recognised that the required control may be less rigorous.

The detailed discussion of traceability principles, and the activities that are necessary, are developed from this viewpoint to provide a self-consistent and practical approach to establishing and demonstrating the traceability of results.

9.2 It is important, in closing, to note that these simple principles apply well only in the context of a sound quality control and assurance system, and that is an important assumption made in this Guide. No amount of attention to traceability, as discussed in this Guide, will provide a useful result if the wrong procedure is chosen, if experience and training are inadequate, or if a procedure is used well outside its scope. But given good attention to all the other factors necessary for laboratory competence, adherence to this Guide will allow a laboratory to declare that its results are fully traceable to appropriate references.

Appendix: Examples of establishing traceability

The following examples of traceability are based on those in the Eurachem/CITAC Guide "Quantifying Uncertainty in Analytical Measurement". This is available from the Eurachem and CITAC websites.

The format of each example follows the list given in section 2.4 and 6.1.1, which sets out the following activities required to establish traceability:

i)   Specifying the measurand, scope of measurements and the target measurement uncertainty [7];

ii)   Choosing a suitable method of estimating the value, that is, a measurement procedure with associated calculation - an equation - and measurement conditions;

iii)   Demonstrating, through validation, that the calculation and measurement conditions include all the "influence quantities" (represented by their values x_1 to x_n in Box 1) that significantly affect the result, or the value assigned to a standard;

iv)   Identifying the relative importance of each influence quantity;

v)   Choosing and applying appropriate measurement standards;

vi)   Estimating the uncertainty.

A1. Preparation of a calibration standard

Specify the measurand and the target measurement uncertainty

A calibration standard is to be prepared, for use within the laboratory, from a high purity metal (cadmium) with a concentration of $\approx$1000 mg l^{-1} with a required combined standard uncertainty of 2 mg l^{-1} or smaller. The concentration is defined at 20 °C. Because of the small uncertainty required, the use of commercial calibration solutions is not feasible.

Establish the procedure to prepare the calibration standard

The surface of the high purity metal is cleaned to remove any metal-oxide contamination. Afterwards the metal is weighed and then dissolved in nitric acid in a volumetric flask.

```
┌─────────────────────┐
│  Clean metal surface │
└─────────────────────┘
           │
           ▼
┌─────────────────────┐
│     Weigh metal     │
└─────────────────────┘
           │
           ▼
┌─────────────────────┐
│  Dissolve and dilute│
└─────────────────────┘
           │
           ▼
┌─────────────────────┐
│       RESULT        │
└─────────────────────┘
```
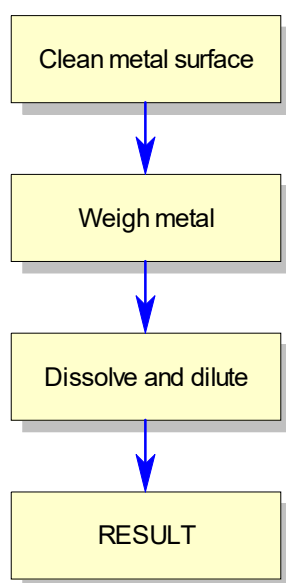
The separate stages are:

   i.   The surface of the high purity metal is treated with an acid mixture to remove any metal-oxide contamination. The cleaning method is provided by the manufacturer of the metal and needs to be carried out to obtain the purity quoted on the certificate.

   ii.   The volumetric flask (100 ml) is weighed without and with the purified metal inside. The balance used has a resolution of 0.01 mg.

   iii. 1 ml of nitric acid (65% m/m) and 3 ml of ion-free water are added to the flask to dissolve the cadmium (approximately 100 mg, weighed accurately). Afterwards the flask is cooled and filled with ion-free water up to the mark and mixed by inverting the flask at least thirty times.

   iv.   The concentration is calculated from

$$c_{\text{Cd}} = \frac{1000 \cdot m \cdot p}{V} \qquad (\text{mg} / \text{l})$$

Where

c_{Cd} : concentration of the calibration standard (mg l^{-1})

1000   : conversion factor from (ml) to (l)

m : mass of the high purity metal (mg)

p : purity of the metal given as mass fraction (kg/kg)

V : volume of the liquid of the calibration standard (ml)

Mass, purity and volume are all part of the equation, and are consequently influence quantities and expected to be appropriately controlled. Noting that the specification of the measurand implicitly includes the temperature as a fixed value, it follows that the four values which need to be considered for traceability are mass, purity, volume and temperature.

Validation

Validation is a prerequisite in establishing traceability. For this simple and well-understood procedure, the principal influences are well known. However, an important assumption is the implicit assumption of complete dissolution of the material. To check this in practice, a simple cross-check against an independent preparation is normally sufficient. The validation therefore consists of two major parts. First a calibration solution with a similar combined standard uncertainty has to be obtained. This solution could be either the calibration solution used before in the same laboratory, a solution which has been prepared according to a different procedure, or a solution provided by a national standard program, like an SRM solution from NIST. Second, the concentration of the two solutions has to be compared using an analytical technique with measurement capabilities sufficient to detect the kind of gross effect which might arise from incomplete dissolution or reprecipitation. On performing this check, using inductively coupled plasma optical emission spectrometry (ICP-OES), good agreement is found between observed and expected values. In the light of long experience of dissolution, this is sufficient to confirm the sufficiency of the simple specification.

Identifying the relative importance of each influence quantity

Mass, purity and volume are all clearly critical, since they form part of the calculation for the result. The relevant references will accordingly need to be chosen with close attention to their uncertainty. Temperature, however, is not part of the equation, and following sections 6.5.2-3 it is useful to consider whether special attention is required. Section 6.5.3 suggests a 'worst case' check. The following effects (in mg l^{-1} Cd) of different temperature errors were estimated assuming aqueous solution:

Temperature error (°C)	Concentration error (mg l^{-1} Cd)
10.0	2.00
5.0	1.00
1.0	0.20
0.1	0.02

Clearly, the natural temperature range (represented by the 10 °C error following the example in section 6.5.3) is likely to be unacceptable. But an error of 5 °C leads to an error of only 1 mg l^{-1} Cd, significantly less than the required uncertainty. This is readily achievable in a routine laboratory with ordinary temperature control. It is likely that no additional measurement or calibration will be required, though as indicated in section 6.5.5, temperature monitoring would be sensible.

Choosing and applying appropriate references

▪ The mass m needs to be traceable to measurement standards with sufficiently small uncertainty. This is provided routinely by normal calibration procedures for the balance, and confirmed by the associated calibration certificate. Since calibration intervals are relatively long for analytical balances, the linearity is checked on a regular basis with the internal check weights of the balance to stay within the limits given in the manufacturer certificate. Its validity is further reviewed with daily check weights, which are traceable to national standards and capable of showing significant deviation from nominal values.

▪ The purity is the certified property of a reference material, as certified by the supplier, and the uncertainty is demonstrably small enough for the purpose (see the uncertainty figures below). Provided that the metal surface is cleaned according to the instructions given by the supplier, purity can be considered traceable with adequate uncertainty.

▪ The volume is measured using a flask chosen from a manufacturer who provides information about the traceability of the flask volume to a national standard, through a calibration certificate. The resulting uncertainty is a substantial contribution, but acceptable. Because glassware can deform slightly over time, and the glassware calibration is a dominant uncertainty source, the volume of the flask is checked regularly by weighing the given volume of water.

▪ The flask has been calibrated with water at a temperature of 20 °C. A check on the laboratory temperature shows effective control within 20±4 °C, which is within acceptable limits as expected (see above), so equilibration of solutions at room temperature is sufficient. The laboratory temperature must clearly be monitored using a thermometer with a smaller uncertainty; in practice this can be readily achieved with an ordinary mercury-in-glass thermometer checked against a calibrated thermometer.

Evaluating the uncertainty

Evaluation of the combined standard uncertainty is described in the first example in the Eurachem Guide "Quantifying Uncertainty in Analytical Measurement" [8]. The overall

uncertainty and major contributions are shown in the figure below. Note that the volume uncertainty includes a temperature uncertainty contribution equivalent to approximately 0.4 mg l^{-1}, based on an ambient temperature range of 20±4 °C, confirming the acceptability of the ambient temperature control.
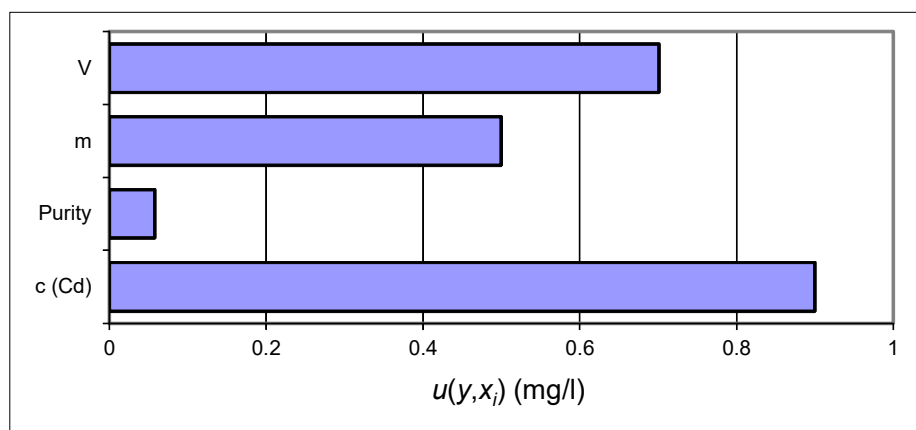
A2. Cadmium release from ceramic ware

**Specify the measurand and the target measurement uncertainty**

The amount of released cadmium from ceramic ware is determined using atomic absorption spectrometry. The procedure employed is the empirical (or 'operationally defined') procedure specified in the standard method BS 6748 (below). The AAS spectrometer needs a detection limit below 0.02 mg l^{-1} cadmium. The target measurement uncertainty for this empirical procedure is 10% (expressed as relative standard uncertainty).

Establish the procedure to determine the cadmium release from ceramic ware

The complete procedure is given in British Standard BS 6748:1986 "Specification for limits of metal release from ceramic ware, glassware, glass ceramic ware and vitreous enamel ware" [17] and this forms the specification for the measurand. Only a general description is given here.

The general procedure is given in the following steps and illustrated schematically:

  i.   The sample is conditioned to (22 ±2) °C. Where appropriate ('category 1' articles), the surface area of the article is determined. For the example, a surface of 2.37 dm^2 was obtained.

  ii.   The conditioned sample is filled with 4% *v/v* acid solution at (22 ±2) °C to within 1 mm from the overflow point, measured from the upper rim of the sample, or to within 6 mm from the extreme edge of a sample with flat or sloping rim.

  iii. The quantity of 4% *v/v* acetic acid required or used is recorded to an accuracy of ±2% (in this example, 332 ml acetic acid was used).

  iv.   The sample is allowed to stand at 22 ±2 °C for 24 hours in darkness with due precaution to prevent evaporation loss.

  v.   After standing, the solution is stirred sufficiently for homogenisation, and a test portion removed, diluted by a factor *d* if necessary, and analysed by atomic absorption spectrometry (AAS), using appropriate wavelengths and in this example, a least squares calibration curve.

  vi.   The result is calculated and reported as the amount of cadmium in the total volume of the extracting solution, expressed in milligrams of cadmium per square decimetre of surface area for category 1 articles, or milligrams of cadmium per litre of the volume for category 2 and 3 articles.
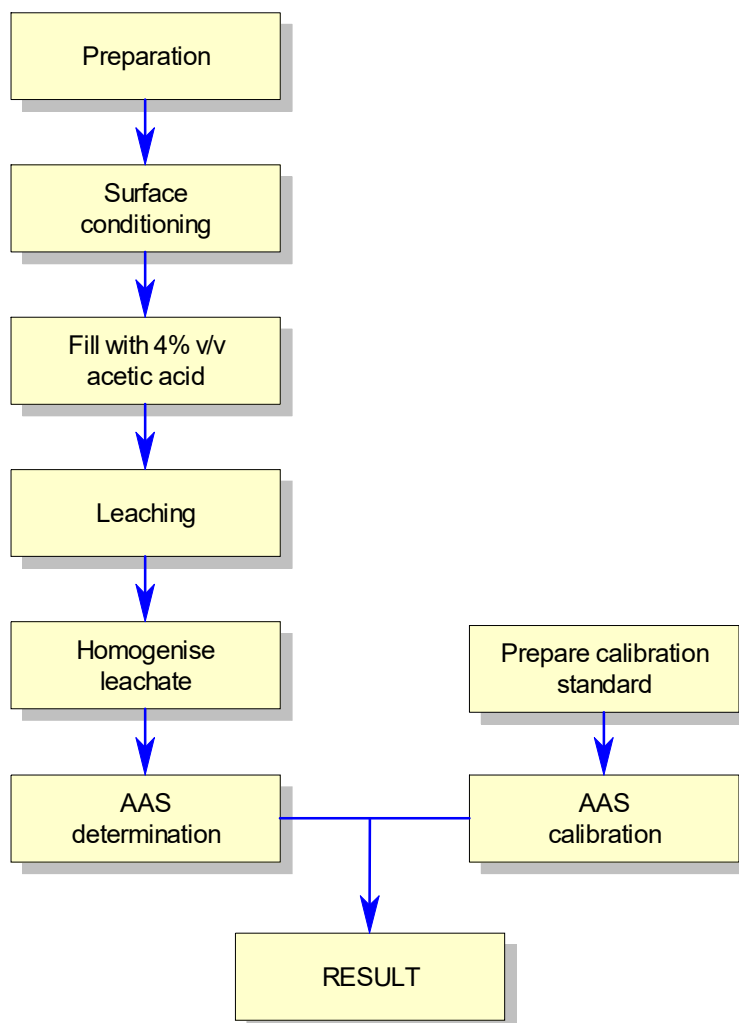
The apparatus and reagent specifications affecting the uncertainty are:

- A freshly prepared solution of 4% v/v glacial acetic acid in water, made up by dilution of 40 ml glacial acetic to 1 l;

- A (500 ± 1) mg l^{-1} standard cadmium solution in 4% v/v acetic acid;

- Laboratory glassware is required to be of at least class B that will not release detectable levels of cadmium in 4% acetic acid during the test procedure;

- The atomic absorption spectrophotometer is required to have detection limits of not greater than 0.02 mg l^{-1} for cadmium.

The amount of cadmium r in the total volume of the extracting solution per milligram of cadmium per square decimetre of surface area, determined using the procedure specified in British Standard BS 6748:1986, expressed in mg dm^{-2}, is calculated from[*]

$$r = \frac{c_0 \cdot V_L}{a_V} \cdot d \qquad (\text{mg dm}^{-2})$$

Where

r : the measurement result; mass of Cd leached per unit area (mg dm^{-2})

V_L : the volume of the leachate (l)

a_V : the surface area of the vessel (dm^2)

d : factor by which the sample was diluted

c_0 : concentration of cadmium in the extraction solution (mg l^{-1})

With

$$c_0 = \frac{(A_0 - B_0)}{B_1}$$

A_0 : absorption of the metal in the sample extract

B_0 : intercept of the calibration curve

B_1 : slope of the calibration curve

There are four parameters in the equation for the result, and three additional parameters specified in the procedure to control the leaching process. This gives seven important influence quantities: concentration of cadmium in the extract solution, volume, area, dilution factor, acid concentration, time, and leaching temperature.

Validation

This local procedure is based on an established standard procedure, previously validated, and the list of parameters is accordingly taken as complete. There is, in addition, substantial literature on the process, which confirms that the time, temperature and acid concentration are the sole important parameters in leaching into an unstirred solution.

The standard method does not specify the exact form of the calculation of c_0, permitting any procedure with suitable performance. This clearly places the responsibility for choice of AAS determination procedure, and its validation, on the laboratory. The measurement technique is accordingly validated, including a linearity check using diluted calibration standards, a precision check, limit of quantification (to confirm that the measured value is within the linear range), and a bias check using an independently prepared reference solution. Instrument operating parameters

---

[*] Note that in reference [8], this equation is expanded to include factors for reagent concentration, time and temperature, simply to make uncertainty estimation explicit. Here, only the calculation used for the result is presented, in accordance with section 6.

such as gas flow rates were varied to check for significant effects. These measures confirm that, provided the calibration is performed in the same analytical run as the test solutions are measured and the instrument parameters are not changed during the run, there are no additional significant factors. The equation can accordingly be accepted as sufficiently complete, and no additional parameters need be considered.

Identifying the relative importance of each influence quantity

This standard method gives explicit directions for the control of all the influence quantities, including tolerances on measuring equipment and calibration standards. There are only two noteworthy issues; length-related measurements, and the particular calibration method used for the spectrometer.

Length measurements underpin both the area determination and the volume of leachant used, as the latter is specified by reference to a measurement between the surface of the liquid and the edge of the vessel to be tested. Specifically, British Standard BS 6748:1986 requires the vessel to be filled to within 1 mm from the overflow point, measured from the upper rim of the sample, or to within 6 mm from the extreme edge of a vessel with flat or sloping rim. The requirements themselves are not especially stringent, but still reduce the possible errors in filling to under 2% for most practical purposes. It is consequently clear that the measurement of the tolerances (1 mm or 6 mm respectively) will have little effect on the test results as long as the requirement is met.

Area measurement will be harder to achieve with sufficient uncertainty, principally because of simple practical difficulties in measuring interior dimensions for even simple shapes. However, while care will be needed in the measurements, control of the ruler or caliper used is a relatively minor problem. Typical requirements will be to measure of the order of 10 cm, and most technical rulers can easily measure this with uncertainties well below 1% (as rsd). While the area measurement is important, therefore, the actual measuring device is unlikely to require close attention.

Though the procedure specifies the uncertainty for the calibration solution, the exact application of this measurement standard is at the laboratory's discretion. This is considered further under 'validation'.

Choosing and applying appropriate references

There are seven influence quantities: Concentration of cadmium in the extract solution, volume, area, and dilution factor in the measurement equation, and the acid concentration, time and temperature specified as conditions. In order to establish traceability of the result, it is necessary to establish the traceability of these parameters with adequate uncertainty.

- *Concentration c_0 A_0, B_0 and B_1* relate the concentration of the extraction solution, which has the largest contribution to the overall uncertainty, to the concentration of the calibration solutions, establishing traceability to the values of the calibration solutions. These calibration solutions were obtained by diluting the reference solution of (500 ± 1) mg l^{-1} cadmium in 4% *v/v* acetic acid. The concentration of the reference solution is traceable to a NIST SRM solution according to the certificate of the manufacturer. NIST has shown its measurement capabilities for determining the concentration of cadmium in solution in a key comparison at CIPM. The dilution steps were done using volumetric glassware, whose manufacturer specifies the value of the volume and its tolerance. Details were also available about the procedure used to establish

traceability to the SI. The calibration solutions were measured using atomic absorption spectrometry and then the absorption values and the concentration of the calibration solution were employed to calculate the intercept (B_0) and slope (B_1) of the calibration curve by least square linear regression. These activities achieve traceability for c_0.

- V_L is the volume of the leachate. It is measured using a measuring cylinder. The volume determined by the measuring cylinder is adequately controlled by manufacturing tolerances according to the glassware standards referenced, so purchase from a reputable source according to specification is sufficient. As usual, however, a brief check on laboratory glassware on receipt, if only against similar equipment, is prudent to guard against the occasional, if rare, manufacturing error.

- The length measurement is done by placing a mark on the vessel employing a ruler to check the distance of 1 or 6 mm. This is not a critical measurement, so specific calibration of the ruler is unnecessary. As a matter of ordinary prudence, however, the ruler was checked on initial receipt in the laboratory using a calibrated vernier caliper (available for other measurements).

- a_V is the surface area of the vessel. It is measured using a ruler checked as above.

- d is a factor by which the sample was diluted. It is not used in this determination, therefore no traceability statement is needed.

- *Acid concentration.* The British Standard BS 6748:1986 specifies the values for the acid concentration, based on glacial acetic acid of stated purity. Because the influence of changes in acid concentration is small (the uncertainty estimate is based on the manufacturer's purity range), no further measures are required for traceability to the SI.

- *Time.* The duration of the leaching process is specified in the BS and has to be controlled. Because the time has such a minor influence on the combined standard uncertainty, it is sufficient to control the duration with a normal laboratory clock, which need only be checked occasionally against an appropriate time signal.

- *Temperature.* BS 6748:1986 quotes a temperature range of (22 ± 2) °C. Because the temperature influence is the second largest contribution to the overall uncertainty, it is necessary to control and measure it with a thermometer, which is checked and calibrated by the manufacturer every two years. The manufacturer has accreditation to perform this calibration service. In this way traceability to the SI is established.

Measurement uncertainty evaluation

Measurement uncertainty evaluation is described in the Eurachem/CITAC Guide "Quantifying Uncertainty in Analytical Measurement" page 72 – 80 [8]. The uncertainties arising from the different influence quantities are given in the following figure (the time, temperature and acid concentration uncertainty contributions are associated with nominal correction factors, introduced solely to support uncertainty evaluation [8]).

$u(y, x_i)$ (mg/dm^2)x1000
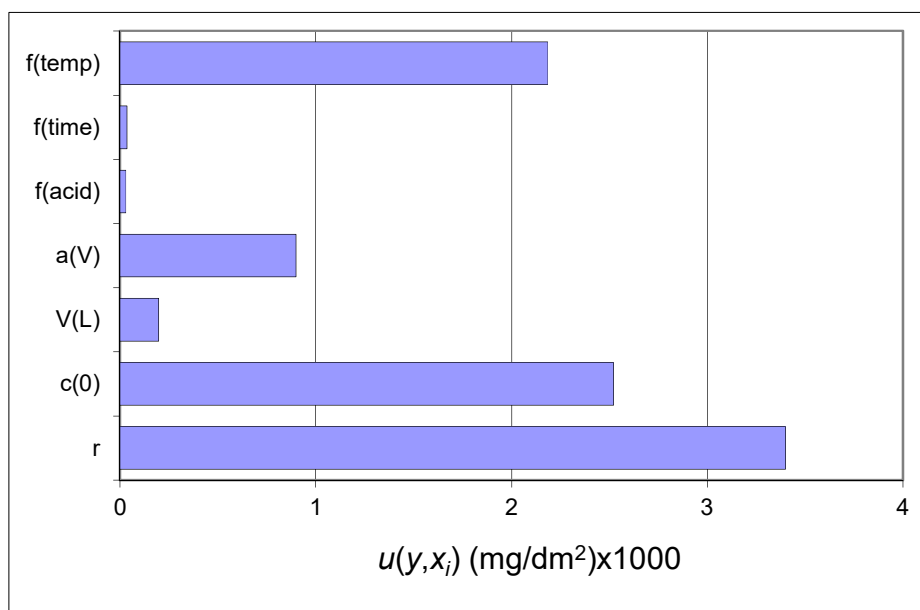
Bibliography

1. ISO/IEC 17025:2017, General requirements for the competence of testing and calibration laboratories ISO, Geneva, (2017).

2. ISO/IEC Guide 99:2007, International vocabulary of metrology - Basic and general concepts and associated terms (VIM) ISO, Geneva, (2007). Also published (with minor corrections) as JCGM 200:2012, available from http://www.bipm.org/en/publications/guides/vim.html.

3. V J Barwick and E Prichard (Eds), Eurachem Guide: Terminology in Analytical Measurement – Introduction to VIM 3 (2011). ISBN 978-0-948926-29-7. Available from http://www.eurachem.org.

4. B Magnusson and U Örnemark (Eds.) Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics, (2nd ed. 2014). ISBN 978-91-87461-59-0. Available from http://www.eurachem.org.

5. The International System of Units (SI), 8th Edition, 2006 (updated in 2014) (http://www.bipm.org).

6. V Barwick (Ed), Eurachem/CITAC Guide: Guide to Quality in Analytical Chemistry: An Aid to Accreditation (3rd ed. 2016). ISBN 978-0-948926-32-7. Available from http://www.eurachem.org and http://www.citac.cc.

7. R. Bettencourt da Silva and A. Williams (Eds), Eurachem/CITAC Guide: Setting and Using Target Uncertainty in Chemical Measurement, (1st ed. 2015). Available from http://www.eurachem.org.

8. S L R Ellison and A Williams (Eds). Eurachem/CITAC Guide: Quantifying Uncertainty in Analytical Measurement, (3rd ed. 2012) ISBN 978-0-948926-30-3. Available from http://www.eurachem.org.

9. ISO/IEC Guide 98-3:2008, Uncertainty of measurement - Part 3: Guide to the expression of uncertainty in measurement (GUM:1995), ISO, Geneva, (2008). Also available as JGCM 100:2008 at http://www.bipm.org/en/publications/guides/gum.html.

10. B Taylor. NIST Special Publication 811: Guide for the Use of the International System of Units (SI). (U.S. Government Printing Office, Washington, DC, October 1995).

11. ISO 80000-9:2009, Quantities and units - Part 9: Physical chemistry and molecular physics, ISO, Geneva, (2009).

12. ISO Guide 33:2015. Reference materials - Good practice in using reference materials, ISO, Geneva, (2015).

13. EEE/RM/062, The selection and use of reference materials; A basic guide for laboratories and accreditation bodies (2002). Available from http://www.eurachem.org.

14. ISO 17034:2016, General requirements for the competence of reference material producers. ISO, Geneva, (2016).

15. ISO Guide 31:2015, Reference materials – Contents of certificates, labels and accompanying documentation. ISO, Geneva (2015)

16. ISO Guide 35:2017, Reference materials – Guidance for characterization and assessment of homogeneity and stability. ISO, Geneva (2017)

17. BS 6748:1986, Specification for limits of metal release from ceramic ware, glassware, glass ceramic ware and vitreous enamel ware. British Standards Institution, London (1986)

Note: Additional reading material, together with current references for most of the cited sources above, can be found in the Eurachem Reading List at http://www.eurachem.org.

INTENTIONALLY BLANK