EURACHEM / CITAC Guide

Traceability in Chemical Measurement

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Drafting Editors

S L R Ellison (LGC, UK)
B King (NARL, Australia)
M Rösslein (EMPA, Switzerland)
M Salit (NIST, USA)
A Williams (UK)

Composition of the Working Group

EURACHEM members

A Williams *Chairman*	*UK*
S Ellison*Secretary*	*LGC, Teddington, UK*
M Berglund	*Institute for Reference Materials and Measurements, Belgium*
W Haesselbarth	*Bundesanstalt fur Materialforschung und Prufung, Germany*
K Hedegaard	*EUROM II*
R Kaarls	*Netherlands Measurement Institute, The Netherlands*
R Kaus	*EURACHEM Germmany*
M Rösslein	*EMPA St. Gallen, Switzerland*
A van der Veen	*Netherlands Measurement Institute, The Netherlands*
M Walsh	*State Laboratory, Ireland*
W Wegscheider	*University of Mining and Metallurgy, Leoben, Austria*
H van de Wiel	*National Institute of Public Health and the Environment, The Netherlands*
R Wood	*Food Standards Agency, UK*

CITAC Members

B King	*NARL,Australia*
M Salit	*National Institute of Science and Technology USA*
A Squirrell	*NATA, Australia*

AOAC Representative

A Pohland	*AOAC International*

EA Representative

W Richter	*PTB, Germany*

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EURACHEM/CITAC Guide: Traceability in Chemical Measurement

Preface

Measurement underpins a wide range of socio-economic activities, both domestic and international. Thousands of chemical measurements every day support decisions on food safety, health and environmental protection in the present international regulatory environment. 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 and comparable measurement results has never been greater. This need is underscored by the increasing adoption of standards and measurement quality systems, such as laboratory accreditation against ISO 17025:1999, or the pharmaceutical industry's GLP and cGMP requirements. All these standards stress the need for competent staff, validated and tested methods, comprehensive quality systems, and traceability to appropriate measurement references.

Traceability is one of the principal tools required for comparability. While results can be compared directly under repeatability conditions, a more general approach is needed to provide meaningful comparison to results of other determinations made at different times and places. This "comparability over space-and-time" is routinely achieved by linking 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 "traceability."

The *International Vocabulary for Metrology* (VIM)[1] defines traceability as the:

> *"property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties."*

This definition implies a need for effort at national and international level to provide widely accepted reference standards, and at the individual laboratory level to demonstrate the necessary links to those standards.

At the national and 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 Meter 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 systems.

Individual measurement and testing laboratories play their part by careful use of appropriate reference standards 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 reference standards is indeed both appropriate and sufficient.

This is particularly true in analytical chemistry. Chemical measurements 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 operationally defined species, for example "extractable cadmium" (sometimes called “empirical” measurements). 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 adequate traceability.

1. International vocabulary of basic and general terms in metrology. ISO, Geneva (1993)

Contents

1 Scope and Field of Application

1.1 This Guide gives detailed guidance for the establishment of measurement traceability in quantitative chemical analysis, based on the definition in the international vocabulary of basic and general terms in metrology (VIM)[1]. 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 17025.

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 method
- 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.

1.4 It is 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 2 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. 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 SI. With more complex measurement methods, 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 The document is based on the following principles:

- Method development establishes an optimised procedure for obtaining an acceptable estimate 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.

These principles are developed in detail in the section 3, and related to the internationally accepted definition of traceability in section 4.

2.4 The document identifies the key elements in establishing traceability as

i) Specifying the measurand and the acceptable uncertainty

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" 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 reference 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, CITAC guide 1 describes the implementation of quality systems for chemical measurement[2]. The Eurachem Guide[3] "The fitness for purpose of analytical methods" provides detailed guidance on method validation (item iii) above), while the Eurachem/CITAC guide "Quantifying uncertainty in analytical measurement"4 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 traceability

3.1 Methods, Measurands and Results

3.1.1 A *measurand* is a "quantity subjected to measurement', 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 methods used; for example, 'extractable lead' would require specification of the extraction conditions[*]. (Measurands defined in terms of a method are sometimes called 'empirical', in comparison with 'rational' measurands which can be described without reference to a specific method).

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

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

3.2 Measurement scales, standards and units

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, or with any other primary unit. This comparison is therefore most commonly indirect, through reference 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 reference 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.

3.3 What affects measurement results?

3.3.1 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,

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

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, strictly *in vacuo* and in a specified gravitational field; volume is typically taken as 'volume at 20C' 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.

3.3.2 For a given measurement method, if the fixed conditions change, so will the value of the result. For example, if extraction conditions change significantly from those specified in the method, 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 '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.

3.4 Controlling fixed conditions

3.4.1 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 results are *traceable* to the time given by the clock; the clock provides the reference standard of time.

3.4.2 This works well, and (at least for a given method) 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.

3.4.3 This becomes impractical very quickly if close control is needed. 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 reading (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 reference standard – the master clock, in the example - that generates consistent measurement in the different laboratories.*

3.4.4 This leads to one key principle;

- *traceability to common reference 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.

3.4.5 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 method.

3.5 Controlling variables with calibration standards

3.5.1 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.

3.5.2 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 reference 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 value.

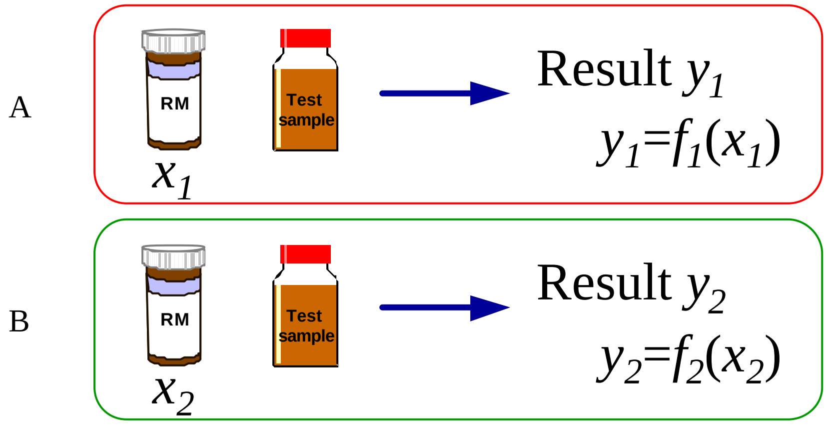
3.5.3 The important question is the relationship between y_1 and y_2. Though the responses are different (usually), is the difference genuine, or just due to different references? Clearly, as things

* 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.

stand 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.

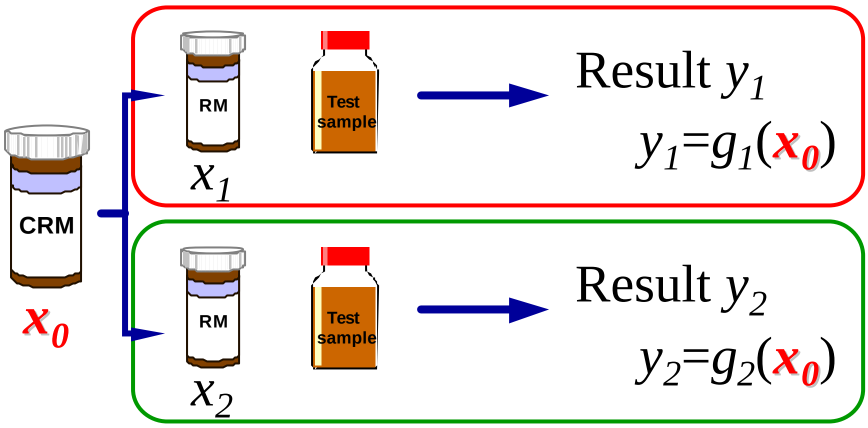
Figure 1



3.5.4 If, however, the two reference 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.

3.5.5 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



3.5.6 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*

3.6 Common references allow arbitrary definition

3.6.1 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. 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.

3.7 Role of method validation

3.7.1 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.

3.7.2 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.

3.7.3 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 making experimental tests of the assumptions, for example by carrying out measurements on appropriate reference materials, or by comparison with the results of independent methods. An overall bias check seeks evidence of significant bias; recovery studies seek evidence of loss of material; linearity checks seek evidence of significant departures from linearity; and ruggedness or similar studies seek evidence for the presence of further effects and so on.

3.7.4 Where an effect is discovered, the method 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 method – that is, another factor requiring traceability.

3.7.5 Where no significant effects are found, the method 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 method 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 method can be expected to produce consistent results.

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

3.8 Traceability and measurement uncertainty

3.8.1 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 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.

3.8.2 Uncertainty of measurement is covered in detail in other publications [Eurachem guide, ISO etc] 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. Where a reference value is uncertain (and all 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.

3.8.3 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 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 reference standards, and the uncertainties associated with these comparisons, are established. These principles lead directly to the definition of traceability in the International Vocabulary of Basic and General Terms in Metrology (VIM):

> Traceability: Property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties
>
> NOTES
>
> 1 The concept is often expressed by the adjective traceable.
>
> 2 The unbroken chain of comparisons is called a traceability chain.

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”.

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 (amp, 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. 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 complete and appropriate traceability, each measurement result should be traceable to a reference for the particular substance.

Table 1 Quantities and units in chemical measurement

Quantity	Units
Concentration of a specified chemical entity	mol/kg; mol/cm^3; g/cm^3; mass or volume ratio
Mole fraction	mol/mol
Purity of a chemical substance	mol/kg; mass ratio
pH	pH (negative logarithm of hydrogen ion activity)
enzyme activity	katal (mol s^{-1}) (SI unit), U (μmol/min)

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 and the acceptable uncertainty

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" 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 reference 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.

6.2 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 20 centigrade, at sea level.
- *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 to be if recovery is significantly different to 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 method*. 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 method 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.

6.2.2 It is often convenient to consider the required performance of the measurement method 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 small 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 method

6.3.1 Once the measurand is known and understood, a method of measurement is selected, or may be developed especially for the purpose. The choice of method involves a range of factors, including, for example, regulatory requirements for particular methods, customer requirements, cost, experience of different methods, availability of equipment, and criticality of decisions. Choice of method 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 method. 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 method is adequate, and once that is decided, this guide can help show that the results are traceable.

6.3.3 The instructions for the method are 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 values is referred to below as the *method specification*, simply for brevity).

6.3.4 The quantities identified in the method specification 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, 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 method specification, 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 and specificity, to ensure that the method responds to the particular species of interest and not to other, similar species.
- A certified reference material check, which demonstrates that the method is not significantly biased by comparison with independently obtained traceable values.
- Reasonable checks on specific, likely effects other than those included in the method specification, which show that no other effects need be included.
- Precision studies over as wide a time interval and set of conditions as reasonable 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.
- A linearity check, to demonstrate that the units given may be calculated and quoted as a simple ratio as implied by the normal use of units in measurement results.

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

6.4.3 The second important consideration in validation studies is that such references as are used to control, calibrate and test the method 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 3.7, above) as playing a key role in establishing traceability. It is not an optional activity. Even when adopting a standard method 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 method specification can be taken to be complete without further detailed checking. But analytical methods are complex and consequently prone to human error. It is invariably necessary to at least check that the laboratory can carry out the method 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 adequate evidence of correct operation of a method.

6.5 Importance of different influence quantities

6.5.1 The relative importance of different influence quantities is important 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 and immediate effect on the results are likely to be important. A second important issue is the likely effect taking into account the uncertainties or possible gross errors involved. Typically, physical measurements 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 associated with a particular effect is small compared to the overall uncertainty, 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 method specification 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 reference 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, 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 methods, is accordingly the key to traceability.

6.6.2 In practice, it is recognised that calibrated and certified reference standards 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 estimation

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 similar information for the result of the measurement. Uncertainty estimation is discussed in detail elsewhere 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 use.
- assessing the overall uncertainty of the result, including the influence of the references used
- confirming that the overall uncertainty meets end-use requirements

6.7.2 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.

7 Choice of the Reference

7.1 Introduction

7.1.1 Sections 4 and 7 make it clear that appropriate references play a vital role in traceability, and hence in achieving consistent results. 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 standards
- Calibrations using pure materials
- Validation studies using certified natural matrix reference materials

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 reference standards for mass, length (including 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, reference 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 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.

[*] 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.

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
- reference data are traceable to appropriate references (for example, wavelength standards)
- the equipment used to generate data for the test items is traceable to the same references.

For most instruments currently available, traceability with adequate uncertainty is easily achieved via routine calibration and quality control.

7.4 Certified reference materials for calibrations

7.4.1 In many cases it is possible to obtain chemical reference standards with certified value and uncertainty and it is convenient and usually cost effective to utilise these. The supplier should be asked to provide information about the traceability of the value of the reference material supplied.

7.4.2 In some cases it may be possible to use a suitable certified matrix reference material for calibration. The points to consider when choosing such a matrix material are the same as those identified in section 7.6.

7.5 Calibration with 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 standards. 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 contaminant. 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.

7.6 Matrix reference materials for Method Development, Validation and Verification.

7.6.1 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 provide not only traceable reference values, but also a valid and useful check of the system with a relevant material.

7.6.2 Factors to be considered assessing the appropriateness of a reference material include the following:

a) 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 (analyte)
   - Measurement range (concentration)
   - Matrix match and potential interferences
   - Sample size
   - Homogeneity and stability
   - Measurement uncertainty
   - Certification procedures (measurement and statistical)

b) The validity of the certification and uncertainty data, including conformance of key procedures with ISO Guide 35.

c) 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.

d) Availability of a certificate and report conforming to ISO Guide 31.

e) Conformance of the production of the reference materials with quality standards such as ISO Guides 34, ISO 17025 or ILAC requirements[5]. Conformance should preferably be demonstrated through third party assessment.

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

7.6.4 In some circumstances it may not be possible to obtain a reference material with a value traceable to the desired level of stated reference. In such cases it should be made clear the limitations on the traceability of the reference material used and the effect of this on the applicability of the result.

7.6.5 More detailed information on the choice and use of reference materials is given in EEE/RM/058.

8 Conclusion

8.1 This guide has presented a discussion of the principles underlying the establishment of traceability for a method 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 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.

8.2 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 method is chosen, if experience and training are inadequate, or if a method 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.

9 Bibliography

1 International vocabulary of basic and general terms in metrology. ISO, Geneva (1993)

2 CITAC Guide 1. [in preparation]

3 The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics. Eurachem (1998). Available from LGC, Queens road, Teddington, England or http://www.eurachem.org/

4 A Williams, S L R Ellison, M Roesslein (eds); EURACHEM/CITAC Guide: Quantifying Uncertainty in Analytical Measurement, 2nd Edition (2000). Available from the Eurachem secretariat (Europe), from LGC, Queens road, Teddington, England (UK) or http://www.eurachem.org/

5 ILAC Guidelines for the Competence of Reference Material Producers, ILAC G12, (2000) (see www.ILAC.org)

Appendix: Examples of Identifying Traceability Chains

The following examples of traceability are based on those in the draft of the revised EURACHEM guide “Quantifying Uncertainty in Analytical Measurement”. This is available from the EURACHEM web-site.

The format of each example follows the list given in section 2.4 and 6.11, which sets out the following activities require to establishing traceability:

i) Specifying the measurand and the acceptable uncertainty

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” 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 reference standards

vi) Estimating the uncertainty

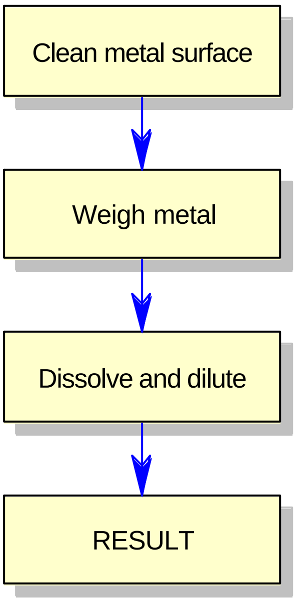
1. Preparation of a calibration standard

Specify the measurand and acceptable uncertainty

A calibration standard is to be prepared from a high purity metal (Cadmium) with a concentration of » 1000 mg l^{-1} with a required combined standard uncertainty of 2 mg l^{-1} or smaller. The concentration is defined at 20°C. Therefore the direct use of a commercial calibration standard solution 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.



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 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

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

Where

c_{Cd}	: concentration of the calibration standard (mg/l)
1000	: conversion factor from (ml) to (l)
m	: weight of the high purity metal (mg)
pur	: purity of the metal given as mass fraction ()
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 traceable. 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 high performance induced coupled plasma optical emission spectrometry (HP 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.

Identify 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 Cd) of different temperature errors were estimated assuming aqueous solution:

Temperature error (°C)	Concentration error (mg/l Cd)
10.0	2.00
5.0	1.00
1.0	0.20
0.1	0.02

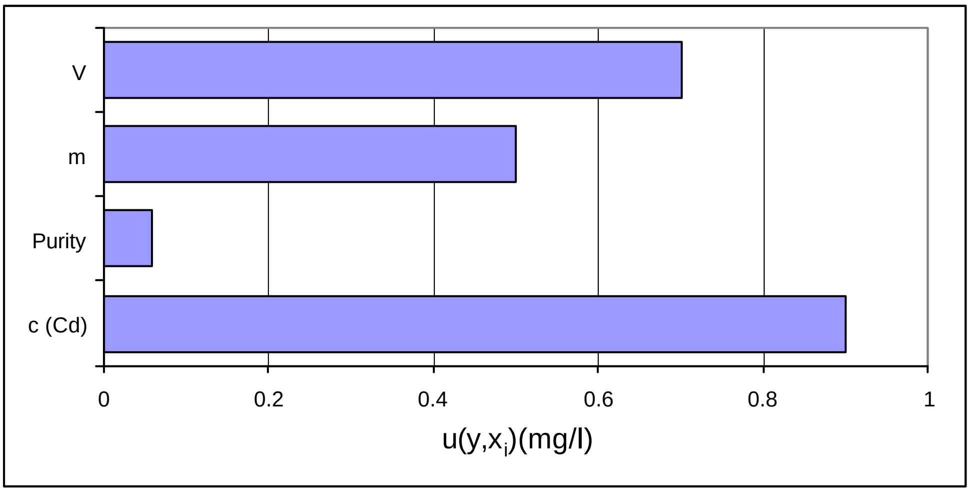
Clearly, the natural temperature range (represented by the 10°C error following the example in section 6.5.3) is likely to be unacceptable. But an error of 5°C leads to an error of only 1 mg/lCd, significantly less than the required uncertainty. This is readily achievable in a routine laboratory with 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 reference 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 a 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 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.

Estimating the uncertainty

The estimation of the combined standard uncertainty is described in the first example in the guide "Quantifying Uncertainty in Analytical Measurement" (second edition). 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, based on an ambient temperature range of 20±4 °C, confirming the acceptability of the ambient temperature control.


V
m
Purity
c (Cd)
0
0.2
0.4
0.6
0.8
1
u(y,x$_i$)(mg/l)

2. Cadmium Release from Ceramic Ware

Specify the measurand and acceptable uncertainty

The amount of released cadmium from ceramic ware is determined using atomic absorption spectrometry. The procedure employed is the empirical method BS 6748. The AAS spectrometer needs at least a detection limit of 0.02 mg/l Cadmium. The acceptable standard uncertainty for this empirical method is 10% (expressed as relative standard deviation).

Establish the procedure to determine the Cadmium release from ceramic ware

The complete procedure is given in British Standard BS 6748:1986 “Limits of metal release from ceramic ware, glass ware, glass ceramic ware and vitreous enamel ware” 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.

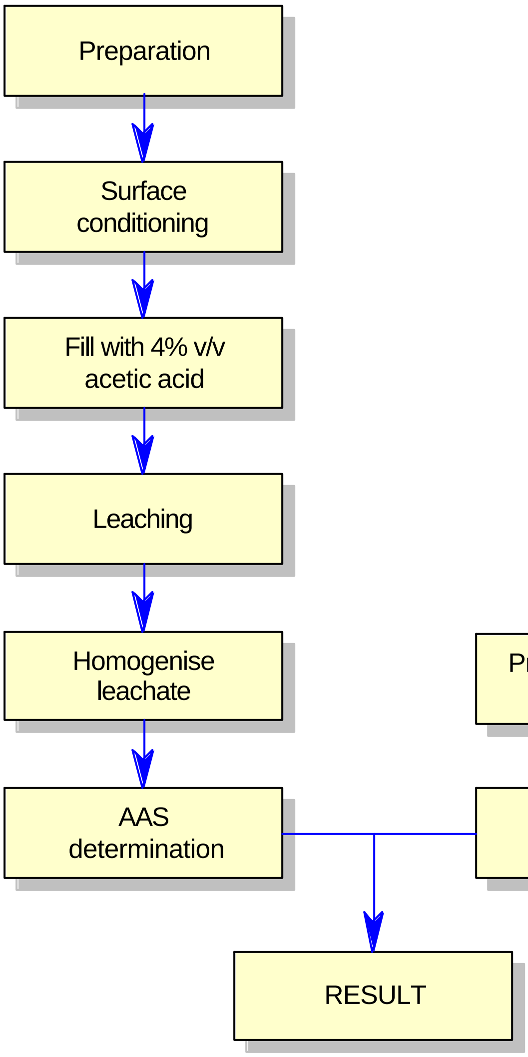
ii. The conditioned sample is filled with 4% *v*/*v* acid solution at (22 ±2) °C to within 1 mm from the overflow point, measured from the upper rim of the sample, or to within 6 mm from the extreme edge of a sample with flat or sloping rim.

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 AA, 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 in the total volume of the extracting solution per milligram of cadmium per square decimetre of surface area, determined using the method specified in British Standard BS 6748:1986 (r), expressed in mg/dm^2, is calculated from*

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

Where

r	:	the 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 method 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.

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 1-2% for

* Note that in reference 4, 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.

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 method 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'.

Validation

This method is an established standard, 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 method with suitable performance. This clearly places the responsibility for choice of AA determination method, and its validation, on the laboratory. The measurement technique is accordingly validated, including a linearity check using serially diluted calibration standards, a precision check, limit of determination (to confirm that the measured value is within the linear range), and a bias check using an independently prepared reference solution. Instrument operating parameters such as pump flow rate 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.

Choosing the references

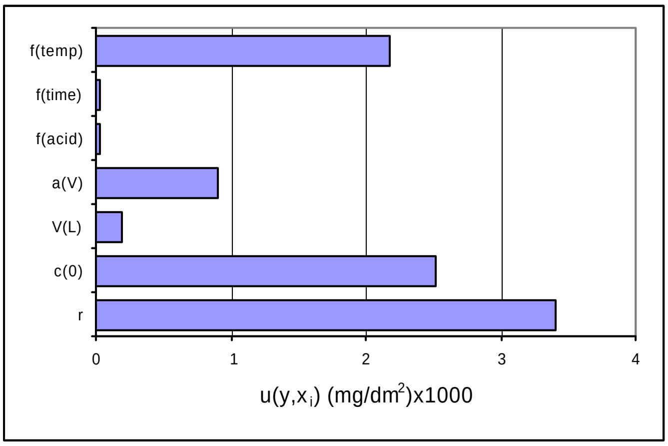
The equation of the measurand has the seven parameters concentration of Cadmium in the extract solution, volume, area, dilution factor, correction factor for acid concentration, for time and for temperature. In order to establish traceability of the result is necessary to establish the traceability of 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 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 reference solution is traceable to 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 ordinarly 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 sufficient 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

The measurement uncertainty evaluation is described in EURACHEM/CITAC Guide "Quantifying uncertainty in analytical measurement" second edition page 70 – 78. 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 estimation[4]).


f(temp)
f(time)
f(acid)
a(V)
V(L)
c(0)
r
0
1
2
3
4
u(y,x_i) (mg/dm^2)x1000