Metrological traceability: A cornerstone of valid analytical measurement, Divisional Plenary (Analytical & Cereal)

Author:
Hibbert, D. Brynn

Publication details:
Book of Abstracts, CONNECT2005
pp. 43

Event details:
CONNECT2005
Sydney, Australia

Publication Date:
2005

DOI:
https://doi.org/10.26190/unsworks/426

METROLOGICAL TRACEABILITY: I make it 42; you make it 42; but is it the same 42?

D Brynn Hibbert,
School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia
Tel: +61 2 9385 4713
Fax: +61 2 9385 6141
e-mail: b.hibbert@unsw.edu.au

Abstract

The paper reproduces a talk given at a two day symposium on quality assurance in chemistry held in Brisbane, Australia in 2005. Intended for an audience of analysts in the field the theme of the symposium drew inspiration from the series of books by Douglas Adams "The Hitchhiker's Guide to the Galaxy". An introduction to basic concepts of metrological traceability is followed by a discussion of practical steps to ensure metrological traceability of field measurement results. The relationship between metrological traceability and comparability of measurement results is discussed. To achieve metrological traceability in the field the use of appropriate certified reference materials for calibration is recommended. Examples of atmospheric carbon dioxide and roadside breathalyser measurements are given.

Keywords : Metrological traceability, Measurement uncertainty, CRM, Reference materials

Introduction

Why do we care about metrological traceability? Why did the International System of Units come into existence with the Treaty of the Metre in 1875? Why was the unit and definition of amount-of-substance finally agreed in the late 20th century, the culmination of a movement that can be said to have started with medieval trade fairs in Europe? It is because we wish to compare measurements in time and space. My ten ells of cloth taken from Paris in 1200 suddenly became shorter when they arrive in Brussels. The 12.3 % protein mass fraction of my wheat shipped from Australia to the Middle East in 2006 might find itself only 11.9 % (and therefore worth less) when it arrives. How can we decide that the atmospheric carbon dioxide content has been steadily increasing since the 1950s in Hawaii unless we have confidence that the carbon dioxide is being measured in strictly the same units during that time? Is a 1950's ppm the same as a 2005 ppm?

Unfortunately traceability remains one of the least well understood aspects of the requirements of a metrologically-sound measurement result. Making a measurement and expressing the result in a unit always implies traceability of that result to the definition (or some realisation of) the unit. Calibration with proper standards is the key to metrological traceability, and the calibrators that are used must be themselves demonstrably traceable.

This paper will show that the combination of metrological traceability and proper measurement uncertainty is the only way measurement results can be legitimately compared.[1]

Traceability and ISO 17025

If your laboratory is to be accredited to ISO/IEC 17025, then you have two sections that must be addressed with particular care: 5.4.6 Uncertainty of Measurement and 5.6 Measurement Traceability. The standard covers both calibration and testing laboratories and the references to traceability appear directed towards the

[1] Note: The author is a task group member of an ongoing IUPAC project 2001-010-3-500 titled 'Metrological traceability of measurement results in chemistry' http://www.iupac.org/projects/2001/2001-010-3-500.html. The author has drawn heavily on the work of the project, but takes full responsibility for the contents of this paper.

former. Some interpretation for chemical laboratories is needed to turn the requirements of 17025 into practical reality.

Metrological traceability – defined

The second edition of the International Vocabulary of Basic and General Terms in Metrology, (the "VIM") [1], defines traceability as:

> 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 sequence of comparisons all having stated uncertainties
>
> [VIM2-6.10]

The 'stated reference' includes a definition of a measurement unit through its practical realisation, or a measurement standard. For a working laboratory a CRM used as a calibrator with documented traceability fulfils the definition by filling in the chain all the way up to the definition of the unit. It should be noted that the term calibrator used in this paper refers to a measurement standard used for calibration.

The answer – real life traceability

The answer to "life the universe and everything"[2] (42) is simple, and for metrological traceability it is that each analytical method must be calibrated with standards that are themselves traceable. In real life this means buying a certified reference material (CRM) and using it to make working standards in the laboratory that are then used only for calibration.

[2] An explanation of the significance of 42 and the "Hitchhiker's Guide to the Galaxy" is given in the report of the symposium elsewhere in this issue.

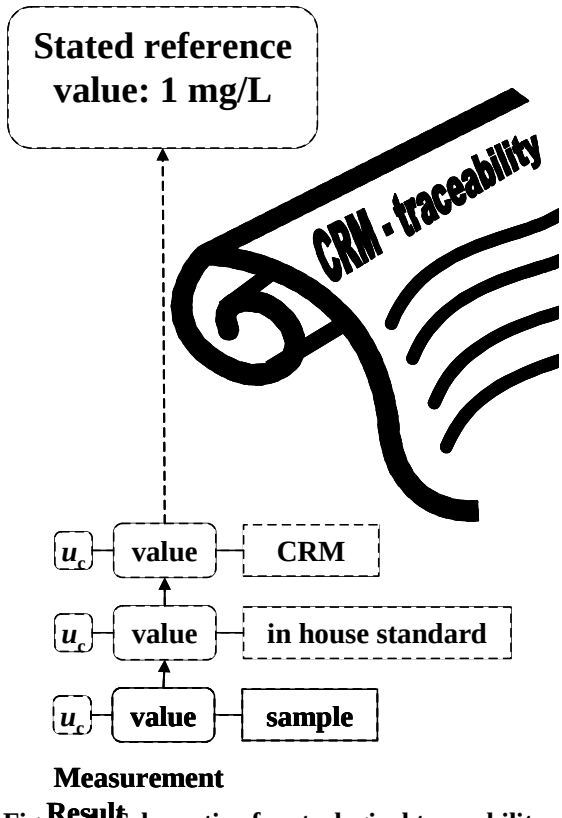

Figure 1. Schematic of metrological traceability established for a field measurement result via a purchased CRM.

A certified reference material is so-called because the certificate that accompanies the material defines the quantity that is being certified, and gives its value and uncertainty. CRMs are expensive because to establish the value of a quantity in a properly traceable way, complete with appropriate uncertainty is not a simple matter. Having a CRM from an accredited and reliable source should take away a laboratory's concern about the traceability chain. A proper CRM should have a metrologically traceable quantity value, and therefore when a laboratory makes a measurement that itself is traceable to the quantity value embodied in the CRM, then the rest of the chain to the ultimate stated reference of the CRM (perhaps, but not necessarily an SI unit) is also established as evidenced by the certificate. Within a laboratory the CRM may be used to calibrate an in-house working standard, thus preserving the expensive CRM. As long as this is done properly, and with the increased uncertainty calculated for the in-house standard, then the traceability chain is maintained. In general, if the quantity value of the in-house standard is the mean of n independent measurements calibrated using the CRM, and the standard uncertainty of a single measurement has been established as u_{meas} then

$$u_{\text{in-house}} = \sqrt{\frac{u_{\text{meas}}^2}{n} + u_{\text{CRM}}^2} \qquad (1).$$

The standard uncertainty of the value of the quantity carried by the CRM is u_{CRM} and is stated on the certificate. The standard uncertainty $u_{\text{in-house}}$ of this working calibrator can now be used to calculate the uncertainty of a measurement that uses the calibrator. The in-house standard must also satisfy other requirements of a calibrator such as to be stable over time, and to be commutable (meaning that the material used for measurement must give the same result with different measurement procedures). The certificate of a CRM is only worth more than the paper it is written on if there is confidence in the truth of the claims that are contained in it. Producers of CRMs can establish their credentials through demonstration of their expertise, perhaps by accreditation. ISO Guide 34 establishes requirements for reference material producers and many bodies, such as NATA in Australia, now accredit producers to this Guide.

More on the definition of traceability

In the revision of the VIM, due sometime in 2006, the term ‘traceability’ used in earlier definitions will be expanded to ‘metrological traceability’. This is to make sure that the concept of which we speak is distinguished from a number of other traceabilities, such as the material traceability of a piece of evidence, documentary traceability or the traceability in an audit trail. As ever, metrological traceability is a property of a measurement result. As ever, we point out that metrological traceability tells us about a measurement result, not a method, not an institute, nor a laboratory. At the moment an analyst makes a measurement and writes that result in a report, metrological traceability must be assured, demonstrable and as a result of the quality assurance process of the laboratory. Incorrect thinking about the ‘traceability of a method’ leads to the implication that the analytical system will somehow always be traceable. Unfortunately this is not correct – every measurement that is made must be shown to be traceable. The concept that there should be an unbroken chain of calibrations or comparisons meshes with the understanding that a measurement may be understood in terms of the comparison of a known with an unknown quantity value (Figure 2).

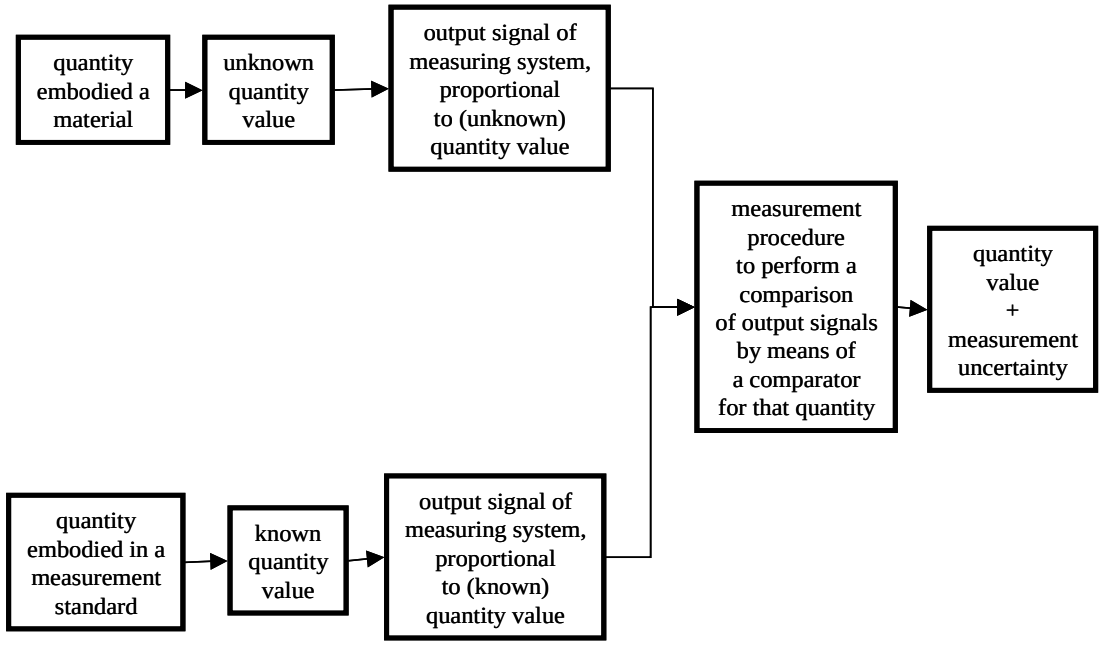

Figure 2: Schematic showing the nature of a (wet) chemical measurement as a comparison. (With thanks to P De Bièvre for permission to use this figure)

Traceability to an SI unit

It is often asked whether “traceability to the SI” is the only option. The definition of metrological traceability has never included reference to the SI, and indeed asking the question implies less than a full understanding of the subject. In a cyclic and not very useful truism, results are traceable to what they are traceable to. At worst, this may be only to the value of a quantity in whatever material was used to effect the calibration of the instrumental response, but at best metrological traceability might be assured to a definition of an SI unit. The point about metrological traceability to the definition of an SI unit is that it does provide an ultimate reference that, should measurements be made in proper SI units around the world, and at different times, they will all be mutually comparable through that traceability. It also goes without saying that should a measurement be made of a quantity that precludes traceability to the SI, for example a hardness measurement on the Rockwell scale, then there is no question that the result will not, and cannot, be traceable to the SI. On the other hand, if a measurement is made that could be in SI units, i.e. a mass or amount-of-substance or length or volume, then it would not be sensible or advisable to trace to some arbitrary standard.

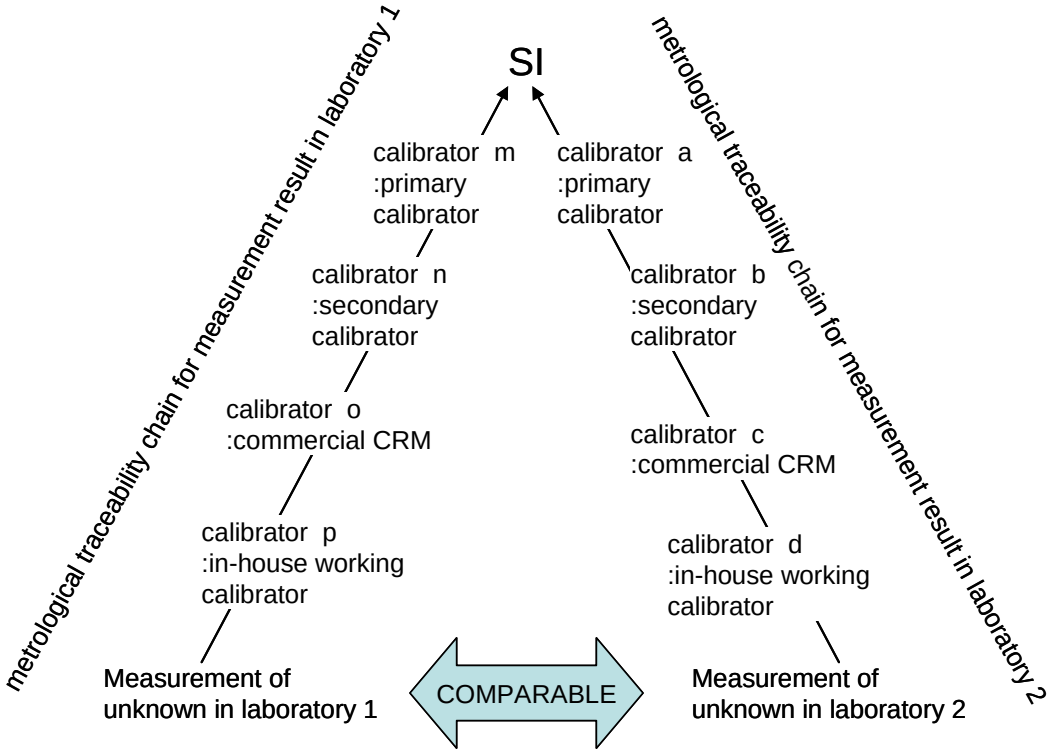

Figure 3: Results are comparable if traceable to the same unit.

Traceability and comparison of results

What does comparability mean? The ability to compare two measurement results, not that these two results are of similar magnitude. We may compare results only when they are expressed in the same units, otherwise we are comparing ‘apples with oranges’.

A second aspect of comparability is the requirement for the uncertainty of the values to be known.

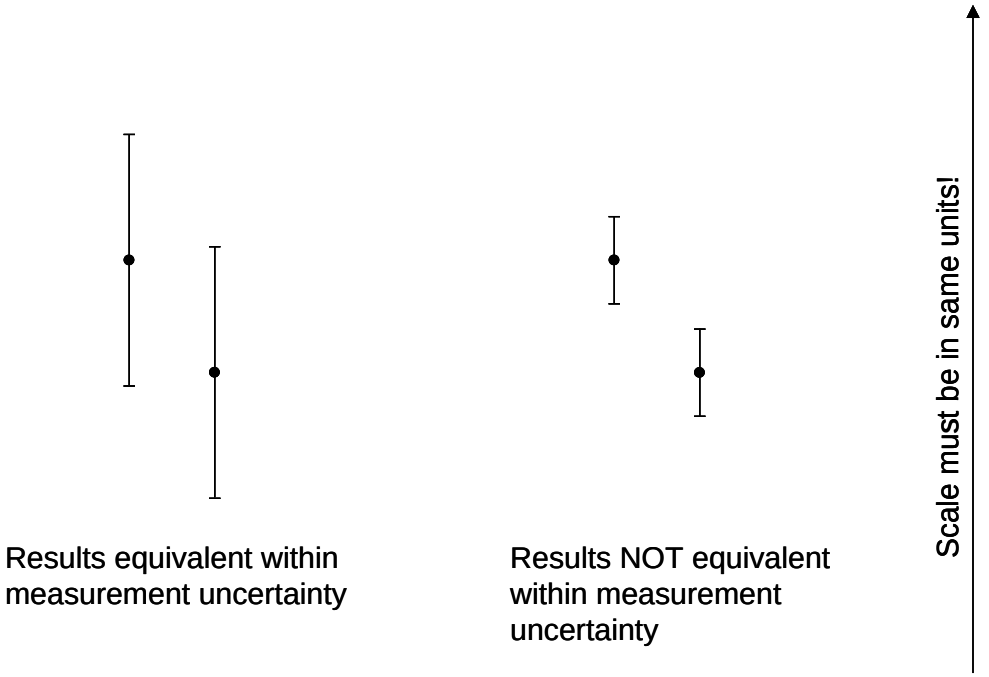

Figure 4: Results, to be comparable, must be metrologically traceable to the same metrological reference, which implies that they have the same units. Comparison also requires measurement uncertainty.

In Figure 4, comparing the two results on the left leads to a conclusion that, within measurement uncertainty the values are equivalent. The results on the right, however, having much smaller measurement uncertainty, may be concluded by the user not to be equivalent at a certain level of probability. Often unremarked is the notion that before any consideration of measurement uncertainty, the two results being compared must be measured on the same scale.

Comparability is necessary in space, between laboratories making measurements on a material, perhaps for trade between countries, but also in time. The most important debate on the apparently inexorable rise in the levels of atmospheric carbon dioxide rests on our confidence in the comparability, through metrological traceability, of the results in time. Figure 5 shows measured carbon dioxide at Mauna Loa, Hawaii from 1955 (re-plotted from data, See [2]). The Scripps Institute, which makes atmospheric carbon dioxide measurements, is very concerned about the accuracy of its measurements and has gone to considerable trouble to create appropriate standards over the years. In December 1983, CO_2-in-N_2 calibration gases were replaced with the currently used CO_2-in-air calibration gases [2]. This does not appear to have caused a discernable hiatus in the graph, but other changes (for example 1973, 1989 and 1995) may warrant scrutiny.

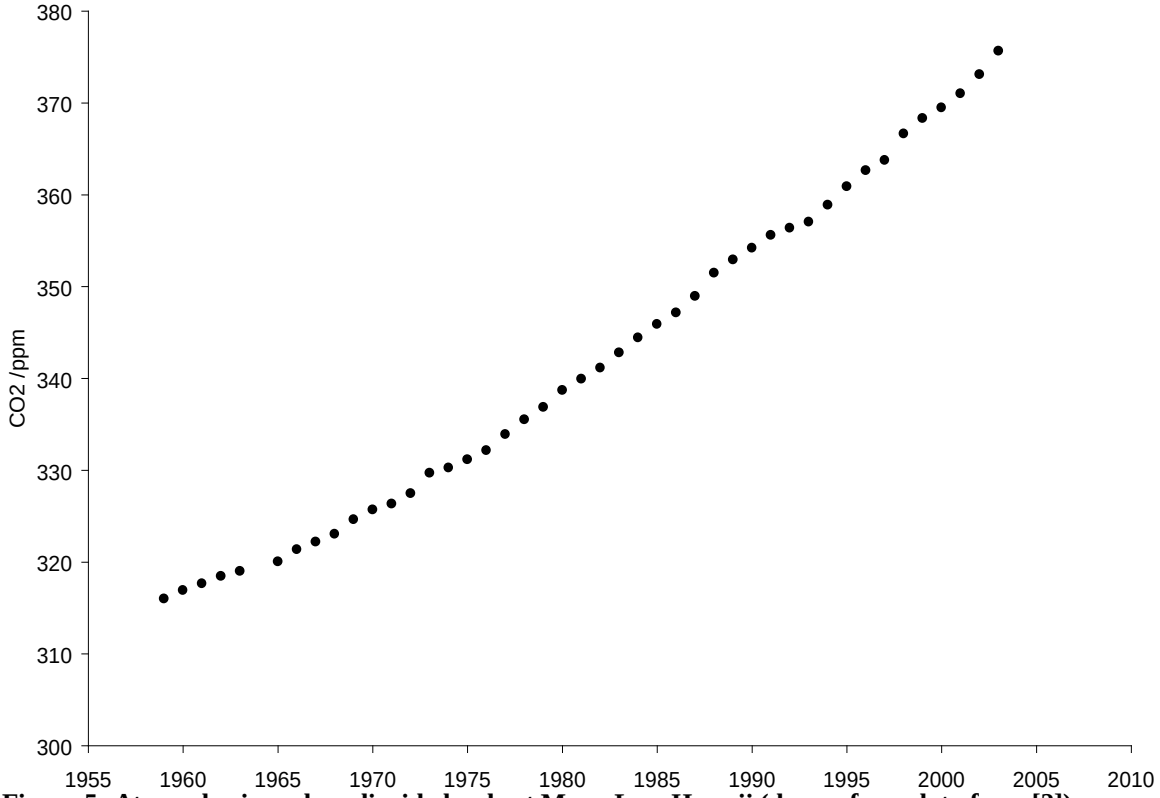

Figure 5: Atmospheric carbon dioxide levels at Mona Loa, Hawaii (drawn from data from [2])

So what makes a result traceable?

Metrological traceability is established via an identified calibration hierarchy from the stated reference to the calibrator of the final measurement. Each calibrator in the chain has its quantity value established by comparison to the preceding calibrator. An example from recent Australian practice is the establishment of a traceable breath alcohol measurement (Figure 6). In this figure the boxes on the right represent measuring instruments and the procedures for their use, and on the left, artefacts with their quantity values and uncertainties.

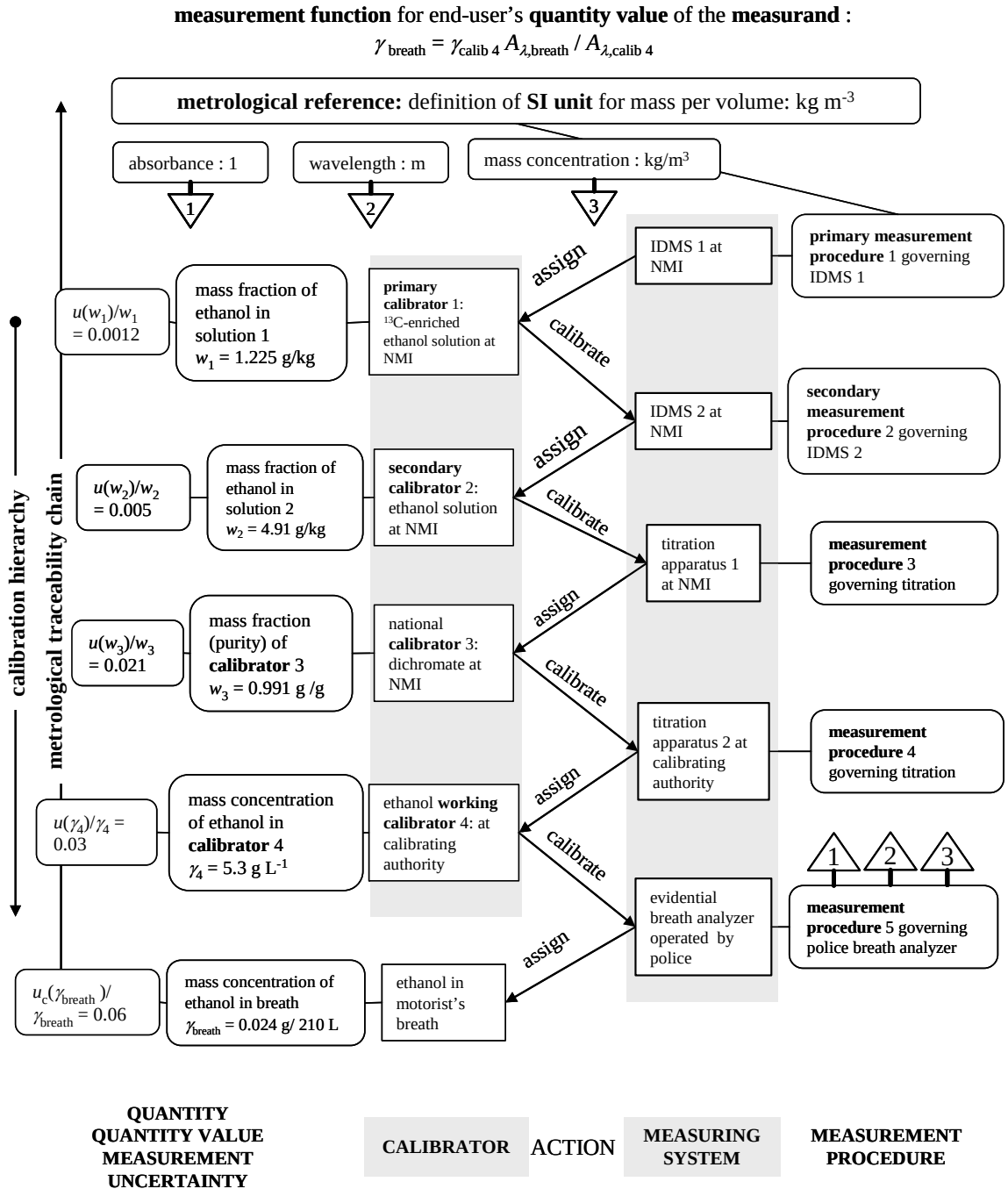

Figure 6: Traceability chain for measurements of breath alcohol with calibration via dichromate titration. IDMS = isotope dilution mass spectrometry. Adapted from [3].

The zigzag of arrows shows the process of calibration and comparison that creates metrological traceability from the SI unit down to a measurement of a motorist's breath. As discussed above the metrological traceability of the measurement of breath ethanol involves other quantities that allow passage from amount per mass units (IDMS) through mass per mass (intermediate standards) to a measurement in mass per volume. Transfer standards and quantities, for example molar masses, must be traceable together with apparatus of given volume, and thermometers, for example. At each stage in the traceability chain therefore, there will be multiple values of quantities that will need to be traceable, both of input quantities to the measurement function and important influence quantities. These are signified by the symbols of different shapes on top of the procedure box.

It should be noted that Figure 6 gives only one way of establishing metrological traceability of a breath alcohol measurement, (although each measurement must have its own unique traceability chain). An alternative route via calibration by gas chromatography has also been devised by Australia's National Measurement Institute.

CRMs as quality control materials

A CRM is often used as a quality control material or to establish recovery or bias. The use of this material, while a proper part of a quality system does not establish metrological traceability. If recovery is to be corrected for, then the value of the CRM must be traceable, but so must any standards used in calibration. It is not recommended to use the same CRM for calibration and as a trueness control material.

So what happens if I do not have a CRM at all?

There are two answers to this question. One addresses what obligations there are on a laboratory making a measurement for which metrological traceability has not been clearly established, and the second concerns how a laboratory can make the best of this situation. The Eurachem guide recently published on traceability writes [4]:

> 7.1.2 In some circumstances it may not be possible to obtain a suitable certified reference 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.

As was pointed out above, a CRM might be a popular way of establishing metrological traceability, but it is not the only way.

A series of measurements for process control in a company in which variability of results is of more interest than the values of those results, means that the use of a consistent in-house standard, whose quantity value has not been established traceable to a higher standard, may be entirely acceptable. The results are not comparable outside the organization, but as long as this is known and recognized, the results stand. So we are back to the extent to which results may be considered comparable.

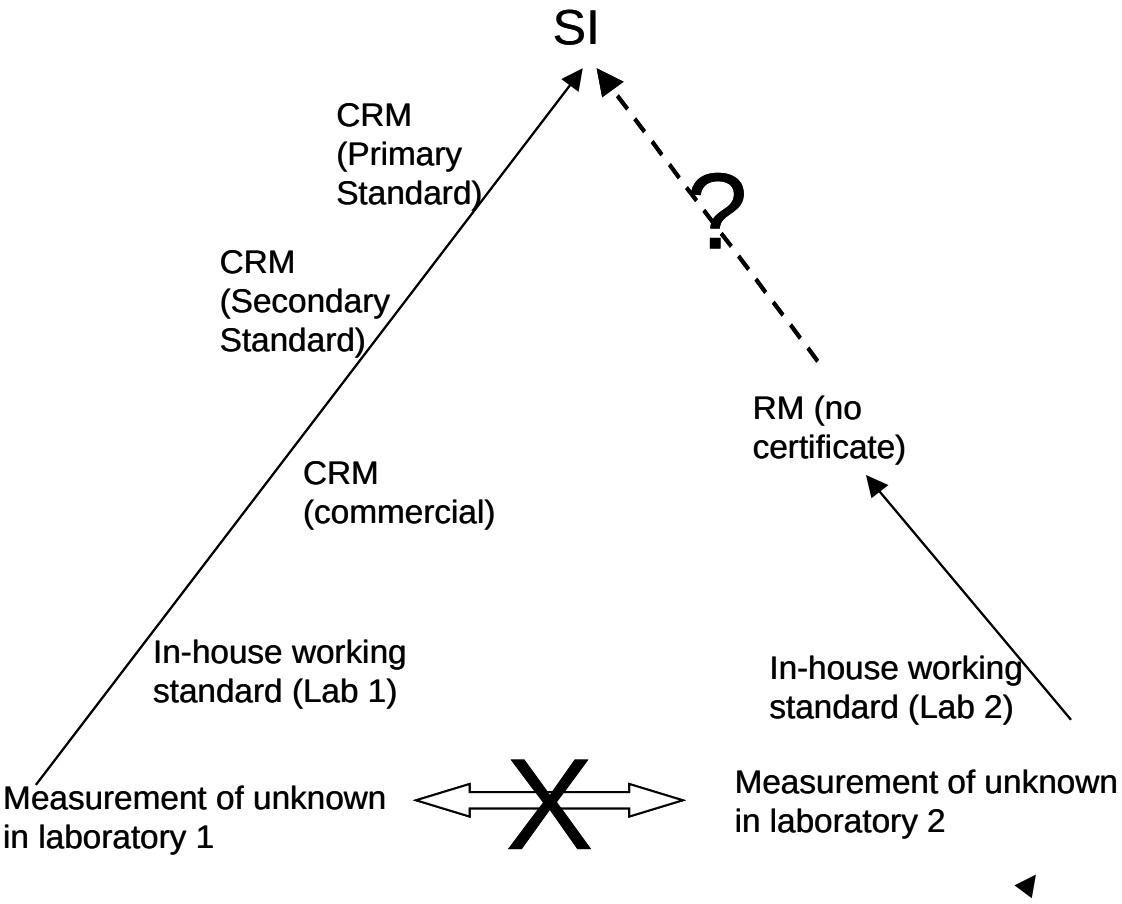

Figure 7: Without a traceable calibrator measurement results obtained in different laboratories cannot be comparable.

There are two approaches to rectifying the situation of Figure 7. First, the reference material used in laboratory 2, must have some provenance. For example, it may have been purchased as analytical reagent grade material from an international chemical supplier. It is unlikely that the un-certified statement of purity and list of impurities on the side of the bottle are entirely inaccurate. It may be possible to perform some checks on the material and with a generous estimate of uncertainty the measurement using this as calibrator could be claimed to be traceable. To what extent this is adequate must be judged by the laboratory and its clients, and perhaps the national accreditation body. What the laboratory cannot do, is to accept the un-certified value as correct with no uncertainty, just because there is not an uncertainty mentioned on the side of the bottle.

A second approach is when a calibrator is prepared from pure material. If a 0.1 mol L^{-1} aqueous solution is made up from solid potassium dichromate and water, wherein lies the metrological traceability? If the purity of the material is certified, and the water may also be accepted as pure, then the solution derives its metrological traceability from the statement of purity, the balances and volumetric glassware used to make the solution, and the relevant atomic weights. If a laboratory has properly calibrated balances and grade 'A' glassware, then as long as the purity of the material can be assured the solution, and measurements made using it as reference should be traceable to the SI derived unit $moll^{-1}$ (assuming mass, volume and amount measurements have been made in SI units). Completely assessing the purity of a material is not a trivial pursuit. In Australia the NMI prepares reference materials of many drugs used in sport and for other purposes. After extensive analysis, including GC, GCMS, IR, NMR, elemental analysis, and DSC the material is certified by an independent committee for identity and purity [5]. Some sub-set of these procedures could be undertaken by a laboratory resulting in a reasonable estimate of the purity with an uncertainty that would reflect the extent of the measurements and checks carried out. Preferable is a measurement that establishes the amount of the material in a given mass, and hence the purity directly. Quantitative NMR is a promising candidate for the analysis of organic compounds, as a standard of the same material is not required [6]. So if a laboratory maintains one or two generic CRMs, we have used sodium

acetate and dimethyl sulfone, the purity of a wide range of compounds can be established. Alternatively, impurities can be measured, for example by GC, and subtracted from 100%. This provides useful information about the number and amounts of the impurities, but there must always be a doubt that the methods used have encompassed all possible impurities. Thus GC will reveal organic impurities having similar properties to the analyte, but will say nothing about inorganic impurities or water.

Interlaboratory comparisons (material certification campaigns) have been used to assign quantity values to reference materials that are then distributed as calibration standards across an industry. Wheat growers have done this with standard grain samples for protein content, under the auspices of the NMI. As some IMEP rounds have shown (International Measurement Evaluation Program. For an example see [7]) consensus does not mean having a correct value, and such schemes must always guard against the intrusion of a bias affecting the whole group.

Conclusions

Nowadays we all take metrological traceability seriously. There have been too many examples of results not being comparable over time and space, arising from either a complete lack of traceability or incomplete estimation of measurement uncertainty (which also invalidates the traceability). An understanding of the existence of multi-stranded traceability chains means we must always pay attention to the metrological traceability of results from balances, thermometers and volumetric equipment. Use of CRMs for calibration is a straightforward way of providing metrological traceability, as long as the uncertainty of the measurement is properly estimated. Making in-house standards from a CRM maintains the metrological traceability, again if the measurement uncertainty is attended to. When no appropriate CRM is available, and if the consequence is that metrological traceability to an international standard is not established, this must be made clear to the client. In-house attempts to assess the purity of non-certified reference materials can allow reasonable claims of metrological traceability.

Acknowledgement

The author thanks the Royal Australian Chemical Institute, Queensland Branch for permission to reproduce the paper which originally appeared in the proceedings of the symposium [8]. Some changes have been made to reflect the international audience of the present journal. He also acknowledges the work of his fellow task group members on IUPAC project 2001-010-3-500, Professor P. De Bièvre (chair), Dr A Fajgelj, and Dr R Dybkær.

References

[1] ISO (1993) International Vocabulary of Basic and General Terms in Metrology (VIM), 2rd Edition, Geneva,.
[2] Emanuele G, Guenther R, Keeling D, Moss J, Bollenbacher A, Scripps reference gas calibration standards system: for carbon dioxide-in-nitrogen and carbon dioxide-in-air, revision of 1999, Scripps Institution of Oceanography, California, 2002.
[3] Besley L, Brittain R, Farrar J, Heng Y, Hibbert D B, Mackay L, Yeomans B (2003) Legal Traceability of Breath Alcohol Measurements, APLMF Symposium on Traceability in Legal Metrology, Kyoto, October 2003.
[4] EURACHEM Guide (2003) Traceability in chemical measurement: A guide to achieving comparable results in chemical measurement. EURACHEM Secretariat. Teddington, UK.
[5] Hibbert D B, Westwood S (2003) Accred. Qual. Assur. 8: Policies and Concepts.
[6] Wells R, Al-Deen T Saed, Hook J, Hibbert D B (2002) J. Agric Food Chem., 50(12):3366-3374.
[7] Papadakis I, Taylor P (2000) Accred. Qual. Assur. **5**(8): 331.
[8] Hilton G, Comino E, Krieger B (eds.)(2005) The Hitchhiker's Guide to Quality Assurance: the Queensland edition. The Royal Australian Chemical Institute, Brisbane.