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A careful look at traceability in chemical measurement

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Abstract

A traceable procedure in chemical measurement is taken to comprise a series of 'calibrations' in each of which the output quantity is calculated from several input quantities with known uncertainties. The starting points are the units of the SI. The endpoint is the analytical result. There is evidence that few analytical procedures conform to that prescription. Problems arise because neither (a) the recovery of the analyte nor (b) the matrix-matching between the treated test solution and calibrators can be guaranteed to be perfect. This gives rise to a continuum of analytical procedures in which the proportion of the true uncertainty of the result found by a traceability chain is mostly less than 100%.

Definition: metrological traceability[1]: *property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty.*

A common problem for analytical chemists stems from the varied nuances attaching to the word 'traceability'. In an everyday sense it just means that we make all measurements in terms of (usually) SI units, and express the results accordingly. Sometimes traceability is used largely in the sense of covering the whole measurement quality system[2]. The prevalent paradigm of metrological traceability is deeper: it is based on the idea that measurement comprises a tree of comparisons called 'calibrations'[3,4]. ('Calibration' will be used only in this specific sense throughout this paper.) Each of these calibrations in a measurement procedure involves successive stages, in which several input quantities determine an output quantity *via* a specific mathematical relationship. For example, in a titration, the inputs could be two readings on a burette and the output quantity would bethe volume delivered. If the uncertainties of all of the input quantities in a calibration are known, the uncertainty of the output quantity can be found by the mathematical theory of error propagation. Usually the starting points for the chain of calibrations are units of the SI plus, in the instance of chemical measurement, an element or stoichiometric compound of known purity or a certified matrix reference material. The ultimate calibration provides the measurement result and its uncertainty. An unbroken chain of such calibrations shows that the result is metrologically traceable. Traceability in this sense is held to be essential for ensuring the comparability of results from difference sources and for the estimation of uncertainty.

It is clear *a priori* that this model of an unbroken chain of calibrations can be appropriate only under two conditions: (a) that there are no unknown factors influencing the calibrations, and (b) that no groups of influence factors interact in unknown ways. In chemical measurement it would usually be

impossible to guarantee these conditions. Indeed there is evidence that most chemical measurements conducted for practical use do not comply with this doctrine of a complete chain of calibrations.

If we found that on average an experimentally-estimated uncertainty associated with a result exceeded a value calculated under the premise of unbroken traceability, we would be entitled to reject that premise. And such a tendency is common, even dominant, in chemical measurement. It can be observed simply by conducting an interlaboratory exercise in which a measurement procedure is applied to portions of an effectively homogeneous test material in each of the participant laboratories. In the great majority of cases, individual estimates of standard uncertainty tend to fall short of the between-laboratory standard deviation by roughly one half[5]. In other words, the results deviate from each other to a degree that the individually-estimated uncertainties cannot account for. Traceability must therefore be broken in these cases. (*Note*: some readers may prefer to think of the traceability as being 'incomplete' rather than 'broken'. The words are used as synonymously here.)

There are at least two aspects of a chemical measurement where we can readily see that traceability is incomplete. The first is in the chemical treatment of the test portion that transfers the analyte into a new matrix, usually a solution (the 'test solution'), that is suitable for presentation to an instrument. For various reasons this process is often incomplete. The second aspect occurs in the comparison of the test solution with solutions containing known concentrations of the analyte ('calibrators'). Unless the test solution and the calibrators are matrix-matched, the analytical signal will be affected and the comparison will generate an incorrect result. Exact matrix matching is virtually impossible in routine chemical analysis—each test material is unique. Of course there are well-known techniques for compensating for both of these effects but, except in very simple instances (such as the determination of a trace constituent in very pure water), or under conditions of the most scrupulous care, we cannot know the success of these corrective actions. We cannot therefore estimate via a traceability chain the whole of the uncertainty involved in the great majority of procedures used in everyday analysis.

From this we can infer that, in terms of traceability, there exists a continuum of chemical measurement procedures. At one extreme there are methods that conform (or very nearly so) to strict traceability, such as the aforementioned analysis of pure water. In that instance, virtually 100% of the true uncertainty could in principle be encompassed by an uncertainty estimated via calibrations. Most other procedures will result in a smaller—sometimes considerably smaller—percentage of traceable uncertainty.

Incomplete traceability in no way renders a measurement result invalid or meaningless—it simply means that the uncertainty cannot be estimated fully by considering 'calibrations'. In such instances the between–laboratory standard deviation is a good estimate of uncertainty.

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[1] JCGM 200:2012 *International vocabulary of metrology – Basic and general concepts and associated terms (VIM) 3rd edition 2008 version with minor corrections*. Paragraph 2.41 (6.10)
[2] NIST document: http://www.nist.gov/traceability/traceability_toc.cfm. Paragraph 1.A.5
[3] Eurachem/CITAC Guide: *Traceability in chemical measurement*. 2003.
[4] P de Bièvre, R Dybkaer, A Fajgelj and D B Hibbert. *Pure Appl. Chem*. 2011, **83**, 1873-1935
[5] M Thompson and S L R Ellison. *Accred. Qual. Assur*. 2011, **16**, 483-487.

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Graphical abstract

The standard idea of a traceable analytical result is called into question.