Establishing traceability to SI for elemental analysis: reporting from a difficult but worthwhile journey

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In *SE* 14/4, I asked the question "traceable: what does it really mean?" I concluded the short essay with an extract from a recent ILAC document:

"It is recognised in some economies calibrations performed by verifying authorities appointed under their economies legal metrology frameworks are also accepted. Legal metrology laboratories should also be encouraged by Accreditation Bodies and through their international and regional organisations to seek accreditation to ensure competence and safeguard proper traceability of their measurement and calibration results and to make their competence transparent to third parties."

I went on to comment "But if the NMIs do not become accredited to ISO 17025 their NMI status may become threatened, as other more dynamic and possibly commercial organisations offer products that better match users' quality system accreditation requirements".

Shortly after *SE* 14 /4 landed on the desks of the 21,000 or so readers across Europe, Dr Heinrich Kipphardt, from BAM in Germany contacted me. I had cited a presentation he gave in my essay. He felt that the topic was worthy of further discussion and provided the following, excellent, essay that we are very pleased to print.

Peter J. Jenks
RM Column Editor

In a recent contribution to the "RM column"[1] I was cited by P. Jenks with a poster[2] dealing with the topic of reference materials to establish traceability in analytical chemistry. I am grateful to the editor of *Spectroscopy Europe* and P. Jenks for the opportunity to contribute with an additional viewpoint on the discussion of this complex and developing topic.

Traceability is defined 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".[3] In chemical analysis the "stated reference" is closely linked to Reference Materials, since reference materials are the physical embodiment of abstract values. The questions which need to be addressed are:

- What is the state of the current practice?
- What is needed? How can the needs be fulfilled?
- Who can do that?

In chemistry high purity materials put on a balance have a long tradition as stated references. In the case of elemental analysis, typically a high purity metal is bought from a supplier together with a "certificate of analysis", which has been issued on the basis of values for measured metallic impurities obtained by using an instrumental method (such as GD MS) in a semi-quantitative mode. There is nothing wrong with this, and the information given is fit for purpose in many applications. The problem is, that when used for calibration in chemistry, this information is often misinterpreted as a statement for the total purity. When important impurity contributions from other metals, and especially, from non-metals (O but also H, S, C and halogens) are simply ignored, this can lead to a wrong statement for the total purity and to an underestimation of the uncertainty as exemplified in Table 1. Total purity and a corresponding uncertainty statement is what matters.

At BAM a project was launched to overcome the lack of SI (Système International d'Unites) traceable standards of high metrological quality for elemental analysis by establishing a system of high purity materials with known (because measured) mass fraction for the matrix element. The target uncertainty according to GUM[4] is 0.01% rel., which is typically one order of magnitude lower than the uncertainty, which can be obtained from methods of analysis having the potential to achieve smallest combined uncertainties (e.g. IDMS). Since this target uncertainty cannot be achieved by a direct measurement of the matrix component (e.g. by electrogravimetry, coulometry), an indirect approach is carried out. For that, the mass fractions of all elements, except the matrix element, in the high purity metal are measured and their sum is subtracted from the ideal purity of 100%. Metrological practice is applied including consistency checks, redundancy and conservative uncertainty estimates. Conceptual and technical information is given in References 5–10. For copper and iron, only values for the impurity of fluorine are missing; Sn, Pb, Ga, W and others are in the pipeline. Finally, calibration solutions will be prepared from the metrologically-certified high purity metals. Together with the certificate, there will be a certification report available, which transparently demonstrates how the certified value was obtained.

Typically only small batches of less than 1 kg are going to be certified, because the starting material is very expensive and has limited availability. Therefore, the material will be directly available to other NMIs (National Metrology Institutes) only. However, these standards must be transferred to the field laboratories for daily use, where large amounts of material are needed and usually larger uncertainties can be tolerated. It is planned to achieve this by co-operation with commercial suppliers of calibration solutions.

From formal decree between PTB and BAM the materials produced by BAM are the "National Standards for Elemental Analysis" in Germany. Since the time of single nation solutions in science and commerce is largely over, this project aims to contribute to a European or even world-wide har-

Table 1. Mass fraction of copper in two different materials based on (a) the nominal metallic impurities as stated by the supplier, (b) based on the measurement of all metallic impurities and (c) based on the measurement of all impurities.

	BAM-B-primary-Cu-1		BAM-A-primary-Cu-1	
"nom. metallic purity"	m6N	0.999 999	m4N	0.999 9
"metallic purity"	$m5N_7$	0.999 997 ± 0.000 002	$m4N_{78}$	0.999 978 ± 0.000 010
total purity	$t3N_{44}$	0.999 44 ± 0.000 17	$t4N_{69}$	0.999 969 ± 0.000 010

monisation, which until now is not existent.

As a first step, the project contributes to a scientific co-operation between EMPA, IRMM, PTB and BAM. By citing me in Reference 1 with Reference 2, the incorrect impression might arise that the European Commission substantially funds this co-operation. Although this co-operation has content, aims and partners with a very European dimension, these activities are funded only from the budgets of the participating institutes.

For this project, only NMIs are accepted partners, because of their neutrality and also to avoid even the suspicion of commercial interests, which would be in conflict with metrological care. Moreover, this restriction enables us to have the certification process fully under our control and under our full responsibility. From own experience, the certification process is expensive and the direct financial pay back of selling these materials is expected to be marginal, compared to the certification costs. However, even if difficult to quantify, it is believed that the money wasted by decisions based on wrong chemical measurement results is many orders of magnitudes higher than the certification costs.[11] This why I believe that providing metrological standards to establish traceability is a typical task for (publicly-funded) NMIs.

Concerning the statement "CRMs produced by a calibration laboratory that has been accredited to ISO 17025 by UKAS is no more or no less a CRM than one produced by a NMI" by P. Jenks[1] in *Spectroscopy Europe* 14/4, I would like to point out that section 5.6 "Measurement Traceability" of ISO 17025[12] says: "NOTE 3: Calibration laboratories that maintain their own primary standard or representation of SI units based on fundamental physical constants can claim traceability only after these standards have been compared, directly or indirectly, with other similar standards of national metrology institutes". In this context I would also like to add, that the major part of BAM's Division I "Analytical Chemistry; Reference Materials" is accredited according to ISO 17025.

References

1. P.J. Jenks, *Spectroscopy Europe* **14(4),** 27 (2002).
2. H. Kipphardt and R. Matschat, poster at "Towards an Integrated Infrastructure for Measurements", Warsaw, June (2002) and http://europa.eu.int/comm/research/growth/warsaw/posters/pano-14-ct-14.pdf.
3. *International Vocabulary of basic and general terms in Metrology (VIM)*. ISO, Geneve (1993).
4. *Guide to the expression of uncertainty in measurement*. ISO, Geneve (1993).
5. R. Matschat, M. Czerwensky, S. Pattberg, H.-J. Heinrich and S. Tutschku, *Mat. Trans. (JIM)* **43,** 90 (2002).
6. H. Kipphardt, T. Dudzus, K.A. Meier, S. Recknagel, M. Hedrich and R. Matschat, *Mat.Trans. (JIM)* **43,** 98 (2002).
7. R. Matschat, M. Czerwensky, S. Pattberg and H.-J. Heinrich, *Phys. Stat. Solidi (a)* **189,** 107 (2001).
8. S. Pattberg and R. Matschat, *Fresenius J. Anal. Chem.* **364,** 410 (1999).
9. S. Pattberg, Dissertation, Humboldt-Universität, Berlin (1999).
10. R. Matschat, M. Czerwensky, M. Hamester and S. Pattberg, *Fresenius J. Anal. Chem.* **359,** 418 (1997).
11. B. King, *EUR 19074*. CEC, Bruxelles (1998).
12. *ISO 17025*. ISO, Geneve (1999).