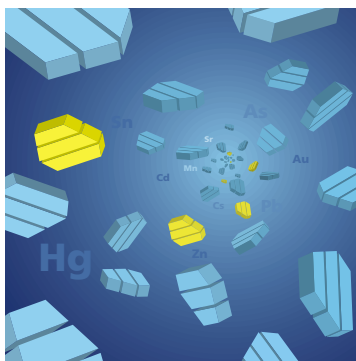


Certified Reference Calibration Standards

The Reference Material as a Transfer Standard in the Traceability Chain

Most results of chemical analytical measurements are directly related to reference materials which are used for the calibration of the measurement process. Two decisive pre-conditions must be fulfilled in order to obtain a result that is traceable to the SI (Système International d'Unités). First, the reference material itself must carry an SI-traceable value and an attached uncertainty. Second, the whole measurement procedure – from sampling to calculation of the result – must be fully validated and the uncertainty must be evaluated according to common rules (GUM, Eurachem guide). While the analyst has to validate his procedure and to evaluate his measurement uncertainty by himself, he may take for granted that the value declared on the label of the reference material is traceable to the SI. Thus, the reference material plays a most important role as it serves as a transfer standard in the traceability chain.



to assure a suitable quality of reference materials which should be clearly indicated in a certificate, (figure 1).

There have been several discussions on how the traceable value has to be assigned to the reference material and who is responsible for the assignment. However, there is still no generally accepted guideline at

present. In fact, one has to face a contradictory situation today. On the one hand, there is a growing demand for reference materials which carry traceable values. On the other hand, assigning a traceable value means putting much effort into a primary measurement.

For a private company, this may not be economically feasible. Thus, not all the produced reference materials will carry traceable values. Several studies at LNE (Laboratoire National d'Essais,

Figure 1:
ISO-Guides content

Commercially available Reference Materials

Reference materials are available from a large number of producers. Among them are private companies, federal research laboratories, and metrology institutes. ISO has set up several rules

ISO Guide No.	Content
17025	General requirements for the competence of testing and calibration laboratories
30 (1992)	Terms and definitions used in connection with reference materials
31 (1996)	Contents of certificates of reference materials
32 (1997)	Calibration of chemical analysis and use of certified reference materials
33 (1989)	Use of certified reference materials (under revision)
34 (1996)	Quality system guidelines for the production of reference materials
35 (1989)	Certification of reference materials – General and statistical principles (under revision)

Contents:

- **Certified Reference Calibration Standards for Spectroscopy and Titrimetry**
- **Certification Procedure: Teamwork between Private Companies and Federal Institutes**
- **Concept for the Value Assignment**

France) and EMPA (Swiss Federal Laboratories for Materials Testing and Research) have shown that even the values declared for monoelemental standard solutions, which are used for calibration and which are relatively simple materials with respect to their matrices, are often not traceable.

An Effective Solution

As the need for reference materials will keep growing, a division of tasks may be the most effective solution. Federal institutes and private companies will focus on their unique skills and core activities. While a private company may be able to produce a reference material very efficiently on a large scale, they may not be equipped for the assignment of a traceable value. In many cases, the declared value has been regarded as a traceable value by most analysts. Federal institutes, especially the metrological institutes, are well-equipped to assign a traceable value because normally it is one of their core tasks to provide the link to the SI by performing a primary measurement. However, they often may not be equipped well enough for an efficient production. Regarding the large number of

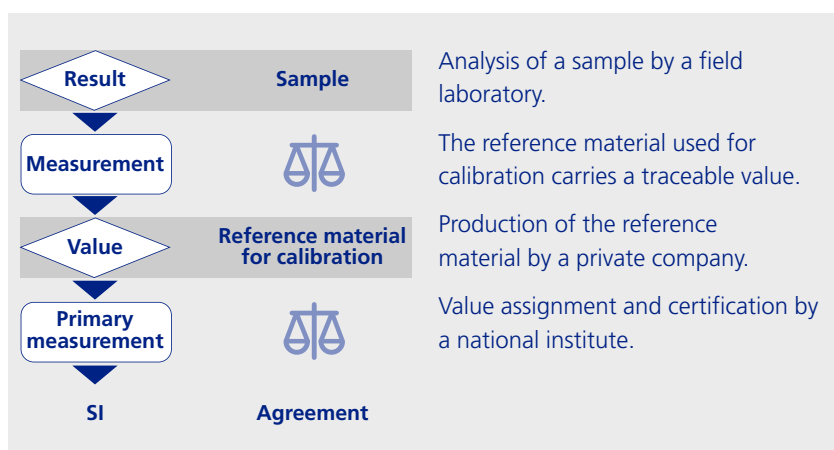
reference materials that are already available, one could state, that there is already enough production capacity. There is, however, a lack of capacity for a traceable value assignment. As a consequence, it would be more effective to combine the different skills in a complementary way (figure 2).

Concept for the Value Assignment of Reference Materials

The way described above was chosen by EMPA and FLUKA Chemie GmbH almost five years ago. From the beginning, BAM (Federal Institute for Materials Research and Testing) was involved as a partner. A suitable quality assurance system was required from each partner. An ISO DIS 9001:2000 certification is in place at EMPA and FLUKA. BAM and EMPA are accredited according to ISO/IEC 17025. The production and certification of a monoelemental standard solution is shown in the flow chart, (figure 3).

After having agreed to the criteria of EMPA for the value assignment, FLUKA produces the reference material according to ISO guide 34 and eventually further requirements defined by EMPA. EMPA controls the batch for its homogeneity and approximate content before the material is released for bottling and packaging. The certification analysis is performed by EMPA and BAM using randomly chosen bottles. Two different methods of measurement are applied. The results are combined to the certified value. Long term stability tests are carried out by EMPA in parallel. A certificate is provided only when all criteria, including stability, are met. Ten titrimetric standards and twelve elemental standard solutions have been certified.

Figure 2:
A complementary way
for value assignment



Example: Certification of Potassium Hydrogen Phthalate

A certification analysis is shown for potassium hydrogen phthalate which is used as an acidimetric standard. For certification EMPA applies a volumetric acid-base titration. BAM provides a coulometric value. Both methods are performed at a high level of precision. The resulting values are combined to the certified value according to common rules. In this case the homogeneity is investigated simultaneously to the content assessment using the randomly chosen samples. The result of the homogeneity test is considered in the calculation of the combined standard uncertainty, (figure 4).

The certified value is provided in a certificate according to ISO guide 31. Part of the certificate is the certification report which includes a description of the whole certification process, details of the applied methods and reference materials, the full calculation of values and uncertainties, and the identification of people involved.

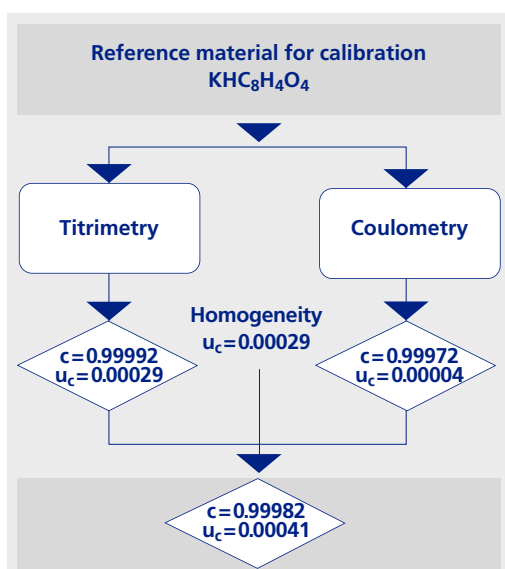
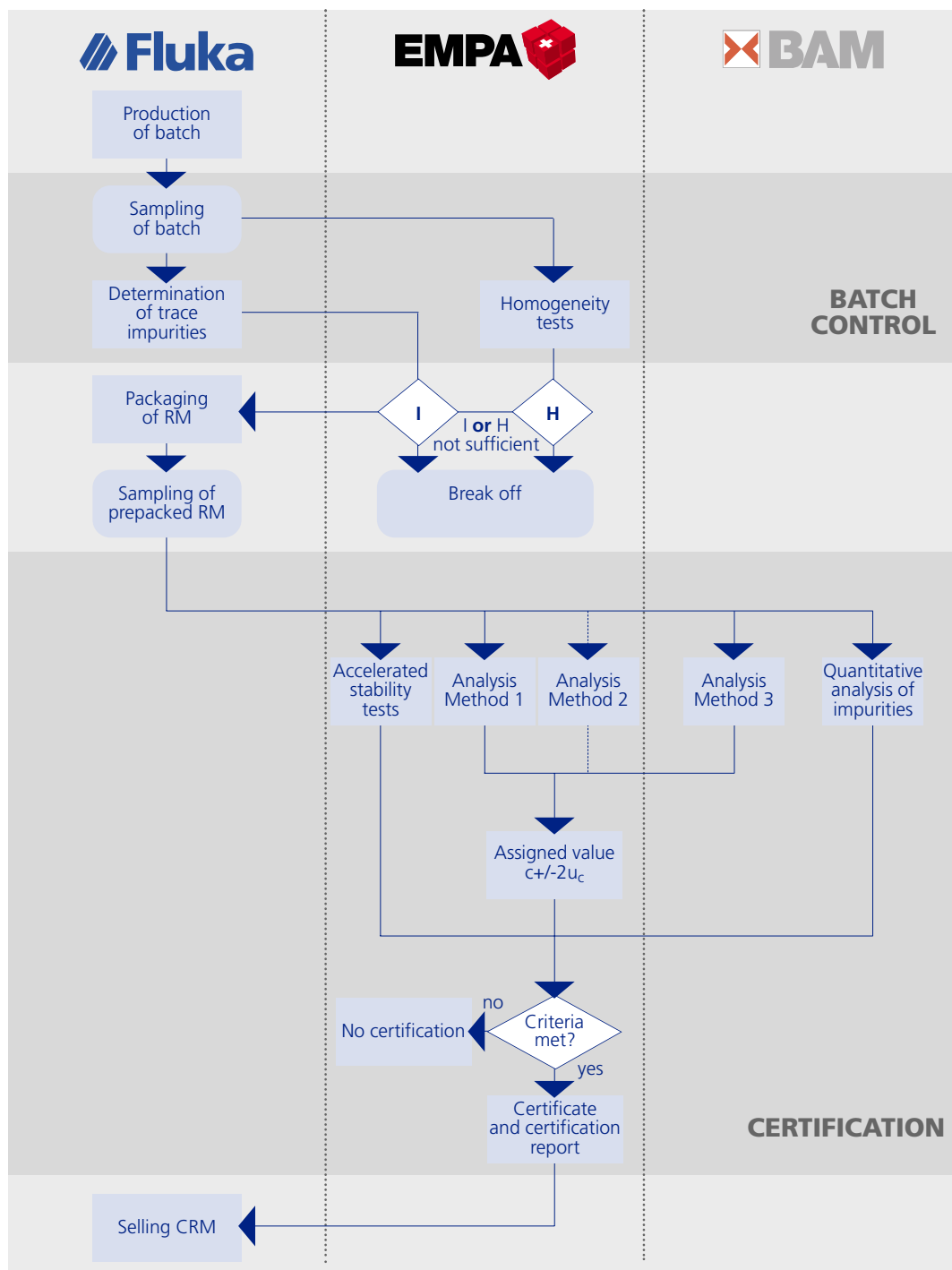


Figure 4:
Assignment of a traceable value in mol/mol
to the titrimetric standard $\text{KHC}_8\text{H}_4\text{O}_4$

Figure 3:
Production and Certification
of a Monoelemental Standard
Solution



Product Programme

Besides the titrimetric substances, Fluka Chemie GmbH also offers certified ion standard solutions, certified also by EMPA and BAM. These reference materials are intended for use in the preparation of standard solutions for AAS, ICP spectrometry or spectrophotometry.

Product No. Ion Standard Solutions (each 1000 mg/kg)

06159	Aluminium
11078	Arsenic (As III)
20896	Cadmium
21062	Calcium
27014	Chromium (Cr VI)
27571	Cobalt
61155	Copper
44907	Iron
15283	Lead
63038	Magnesium
72226	Nickel
96460	Zinc

Product No. Standard Titrimetric Substances

17971	Arsenic trioxide
12353	Benzoic acid
21067	Calcium carbonate
15194	Lead nitrate
60357	Potassiumhydrogenphthalate
60386	Potassiumiodate
71363	Sodium carbonate
71387	Sodium chloride
71804	Sodium oxalate
93440	Tris hydroxymethyl aminomethane

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