Application Note 7

European Reference Materials

Prolonging the validity of reference material certificates

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Certificates of certified reference materials have limited viability, either because of unknown behaviour of opened samples or a general limitation of liability.
This application note explains the information users should collect in order to continue using a CRM beyond the validity date stated on the certificate.

INTRODUCTION

ISO 17034 requires reference materials (RM) producers to specify a period of validity on their certificates. Reaching this validity period of the certificate does not necessarily mean that the material has degraded. This application note explains the background and concept of the validity dates on certificates and the conditions under which users can continue using the certified reference material (CRM).

VALIDITY PERIOD OF THE CERTIFICATE VERSUS SHELF LIFE OF A MATERIAL

It is important to note that the validity period of a certificate is not the same as the shelf life of a material. The validity period of the certificate refers to the certified values of a specific unit of a CRM. Expiry of the validity means that the RM producer can no longer guarantee the certified value of this material. It does not necessarily suggest the existence of evidence that the material has degraded and that the certified value is not valid anymore.

REASONS FOR LIMITING THE VALIDITY PERIOD OF CERTIFICATE

Unknown behaviour of unopened samples

RMs, particularly matrix RMs are often produced in batches and are intended to last several years. A processing technique that would likely ensure the stability of the certified value over these years is chosen. Reference material batches are often unique, even in the case of replacements made from slightly different raw material and using somewhat different processes. This means that, unlike in the production of food or pharmaceuticals, RM producers often do not have stability data of previous batches on which to base the assessment of validity. The stability studies performed during the CRM production give some indication, but due to their limited duration (1-2 years), they cannot guarantee stability indefinitely. Therefore, RM producers must implement a stability monitoring scheme for all certified values that are likely to change. This means that RM producers should confirm the stability of the certified values while being distributed. This limited knowledge of future behaviour prevents RM producers from consistently guaranteeing the validity of their certificates.

Unknown behaviour of opened samples

RM producers take special precautions to ensure the stability of their materials. Stabilising steps could involve filling under argon to avoid oxidation or using perfectly tight containers (ampoules). This special protection is violated when opening the samples. RM producers usually do not have data on the stability of opened samples, as this could multiply the necessary resources spent for stability testing. Also, RM producers have no control over the actual storage conditions at their customers' premises. In principle, this means RM producers cannot guarantee the stability of the certified values of opened samples. However, based on general knowledge on similar materials and their knowledge of the certified properties, RM producers can be sufficiently confident about the stability of the certified values for a limited period of time.

General limitation of liability

The JRC procedures state that if a certified value is found to have changed, customers with valid certificates should be notified of the time of the last stability test that confirmed the stability of the certified value. Limiting the shelf life means that not all customers, since the release of the material, need to be informed.

PROLONGING THE VALIDITY PERIOD OF CERTIFICATE

As RM producers cannot control the storage conditions at their customers' premises and

usually do not have data on the stability of opened samples, they cannot issue certificates with extended shelf life or prolong the validity of certificates that had earlier been distributed.. However, users can decide to continue using their CRMs if they have evidence that the material is still stable. To do this, users should apply the following two steps.

Step 1: Information about the probable stability status

At this stage, it should be checked whether the certified values on the certificate are still stable. This is only a preliminary stage and cannot replace stage 2. The following questions are relevant:

a) Have the stated storage conditions been met?
All certificates state storage conditions for the CRMs which must obviously be met. Deviation from these storage conditions, especially towards higher temperatures, generally invalidates the certificate.
Note that also, storage at a lower temperature can lead to degradation, through freeze-thaw cycles, condensation, concentration by freezing etc.

b) Is a statement of limited stability on the certificate?
For some materials, the stability of opened or reconstituted materials has been tested, and dedicated information is stated on the certificate. It is generally not possible to use the material longer than the period given on the certificate.

c) Is the material still on sale?
The fact that the producer still sells a material shows that unopened samples stored under the same conditions are still stable. However, as stated above, this does not necessarily mean that samples after repeated use are still stable.

d) Should the material still be stable?
A technical assessment should answer the question whether the material should still be stable. This depends on the stability of the certified values, as well as on the stability of the matrix. In the simplest case, the trace metal mass fraction in copper is not expected to change. If a new surface is generated for every measurement, the material should be stable. On the other hand, more labile compounds like vitamins are more likely to change.
This assessment should also take into consideration the matrix: for example, the trace metal ions in a calibration standard in nitric acid will not change, but the concentration can vary due to evaporation leading to instability of the certified values.

Step 2: Collection of data that demonstrate the stability of the certified values

This is, in fact, the crucial question, as a) and b) give the conditions under which the material could still be stable, c) and d) provide an indication that the material could still be stable, but only the following point proves that the material is still stable. Such data can be

Quality control charts
If the material is used in quality control charts and no trend in the data is visible, then the material is still stable. While it is possible that the change of the certified values is matched by a drift in the method, this is very unlikely.

Comparison with data from other CRMs
If the results on the material agree with the certified values and another CRM has been measured at the same time, the material is still stable. The reasoning is that the second CRM demonstrates the accuracy of the method and therefore the agreement of the measurement results with the certified values confirms stability.
This is also true if the CRM in question is used for calibration: If the results of another CRM agree, then obviously the calibration standard is still valid.
Similar reasoning applies when the CRM is measured together with a sample of a proficiency test where a satisfactory result was obtained: the satisfactory result in the PT demonstrates the accuracy of the method and the agreement of the measurement results with the certified value demonstrates the stability of the CRM.

DOCUMENTATION OF THE PROLONGATION OF THE SHELF LIFE

After the stability of the certified values has been ascertained using the data collected in step 2, the prolongation of the validity must be documented. The new validity date is written on the certificate of analysis (of course duly signed and dated) and the reason for the prolongation of the validity is added to the certificate (for example a printout of the quality control chart). In this way, it is clearly documented when and on which basis the validity of the certificate has been prolonged and who takes over the responsibility for the prolongation.