International News

Letter from EUROPE

Following the Letter from Europe in the previous **me·trol'o·gist** dealing with *Proficiency Testing,* this one is to inform about *Reference Materials* from a European view.

Reference Materials (RMs) are a key to ensure reliability and comparability of the results of measurement, testing, and chemical analysis. They are a major tool for improving the confidence in, and the mutual recognition of measurement results and certificates in a global market of free exchange of goods and services. RMs usually serve the following purposes:

- Calibrating measurement instruments
- Validating measurement procedures
- Establishing metrological traceability
- Assuring the quality of measurement results
- Testing the performance of a laboratory and its staff.

The following pictures illustrate the broad variety of reference materials and indicate their importance for technology, economy and society.

The definitions of reference materials are given in *ISO Guide 30*:

- Reference Material (RM): Material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.
- Certified Reference Material (CRM): reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

Examples of brands for certified reference materials provided by specific RM-producers are:

- *Standard Reference Material SRM®* (certified reference material provided by NIST), and;
- *European Reference Material ERM®* (certified reference material provided by the ERM cooperation).

From the metrological point of view, a kind of hierarchy can be established based on the uncertainty of the certified values and in relation with their position in the traceability chain:

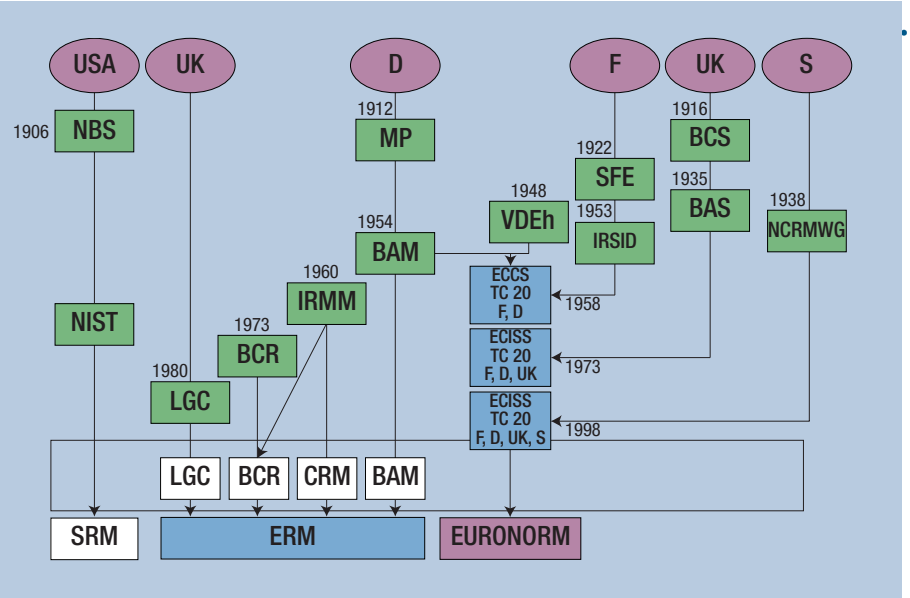
- Primary reference material: a material having the highest metrological qualities and whose value is determined by means of a primary method
- Secondary reference material: a reference material whose chemical composition is assigned by comparison with a primary reference material of the same chemical composition, or with several such primary reference materials
- "In-house" reference materials, QC materials etc.

The uncertainty associated with the property values usually increases from reference material types 1 through 3 as does the length of the traceability chain. In several cases neighboring material types may be situated on the same level of hierarchy.

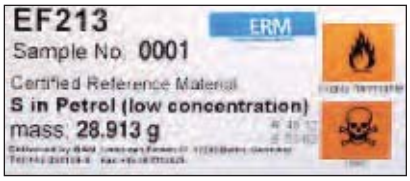
International Developments

CRM-activities started in the US at the National Bureau of Standards (NBS) in 1906. In 1912 the first iron and steel reference materials were certified in Germany by the Royal Prussian Materials Testing Institute MP, predecessor of BAM, the Federal Institute for Materials Research and Testing.

In Europe the production of RM was primarily organized nationally, but as early as 1957 three institutes and enterprises of France (F), Great Britain (UK) and Germany (D) com-



- First CRMs from commercial gasoline
- Covering present legal limits in EU and US
- Offer lower uncertainties (3.5 to 8.8%) than presently available materials



bined their efforts in issuing exclusively iron and steel RM under the common label EURONORM. In 1998 a company from Sweden (S) joined this group.

To overcome national differences, to avoid duplicate work and to improve mutual acceptance, a new class of European Reference Materials (ERM) has been created. With the signature of the memorandum of Understanding on 8th October 2003 the European Reference Materials (ERM®) Initiative was launched by three major reference material producers in Europe: the Institute for Reference Materials and Measurements (IRMM) of the European Commission's Directorate General Joint Research Centre, the Federal Institute for Materials Research and Testing (BAM), Germany, and the Laboratory of the Government Chemist (LGC), UK. The goal of this initiative is the harmonization and further improvement of quality, reliability and performance in chemical analysis. ERM® are certified reference materials, which undergo uncompromising peer evaluation by the ERM Technical Board to ensure highest quality and reliability according to the state of the art. Harmonization and increased reliability through joining efforts in CRM production and dissemination will significantly contribute to strengthen the European Internal Market.

Examples of Reference Materials

To illustrate reference materials and their impact for technology, industry, economy and society some examples from sectors like (a) currency, (b) industry (c) environment, (d) food, (e) international cooperation, are shown with a view from Europe.

Since 2002, Europe has a new common currency: the Euro (€). In order to control and assure the alloy quality of the coins, several ERM have been issued. The following picture shows ERM-EB389, "CuNi25", representing the golden colored partitions of the Euro coins.

The automobile sector is an important industrial factor in all economies. There is a demand for automobiles to be exported also into countries with deviating standards for exhaust emission. Comparable, correct measurements are not only a national or a European goal but a challenge of international implications. To support the detection of sulfur in gasoline, certified reference materials have been developed which cover the present legal limits in the European Union and in the United States. These certified reference materials have two unique features: They are the first CRMs made from commercial gasoline and they offer lower uncertainties than presently available materials.

In addition to CRMs also interlaboratory comparisons are needed to assess reliably the determination of harmful substances, like for example sulfur in diesel fuel.

Toxic components in food endanger the quality of life. Foodstuffs and a large number of other goods cross national borders. European legislation sets out limit values to shelter consumers. RM like ERM-BD272 "Acrylamide in Crisp Bread" enables control.

Likewise, harmful substances in industrial products may detrimentally influence technical functionality and may give harm to man and the environment. Consequently, CRMs

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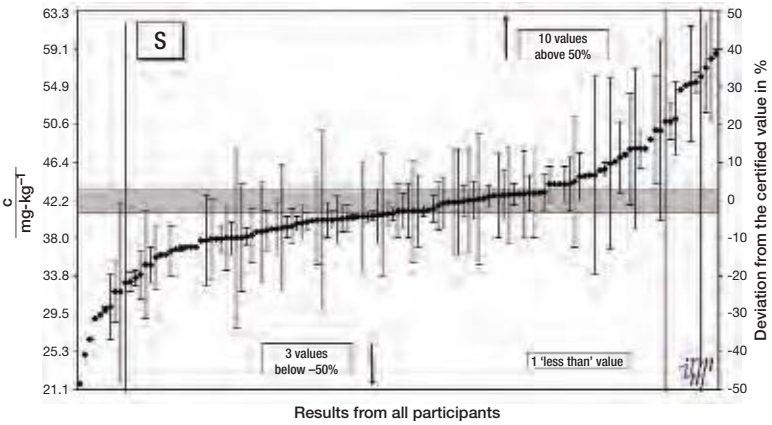
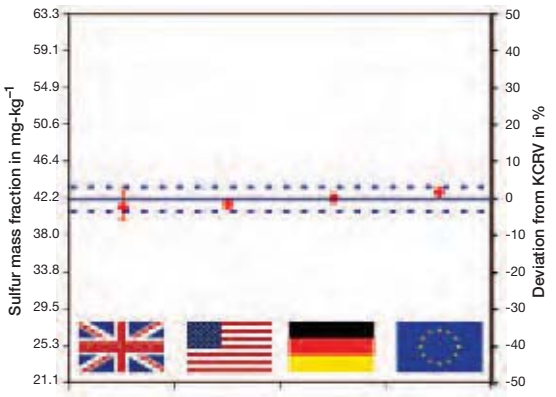
Sulfur in diesel fuel: IMEP–18
Certified value: 42.2 ± 1.3 mg/kg [U = k·u_c (k = 2)]



IMEP–18:
Routine laboratories, different methods
Uncertainties over a broad range
Spread: over 50 %

Low sulfur in fuel: CCQM-K35
KCRV: 42.2 ± 1.3 mg·kg^{-1} [U = k·u_c (k = 2)]



CCQM–K35:
IDMS only
Smaller uncertainties: < 2 %
Spread (RSD): ± 1.7 %

are needed to assess toxicity and environmental benign of industrial products for the benefit of society and economy.

A key event for the worldwide recognition and acceptance of calibration and test certificates was the Mutual Recognition Arrangement (MRA) of 1999 – an international agreement which may be as significant as the famous Meter Convention. Signatories of the MRA express their hope and trust in each others measurement competence. But up to date there are only very few examples for RM that truly bridge continents. The porous material NIST SRM 1917 / BAM-P127 is one of them.

Frequently asked questions about Reference Materials

There is an increasing interest in Reference Materials. So a group of experts from European countries institutes, namely

- BAM Federal Institute for Materials Research and Testing, Germany (Martina Hedrich, Sebastian Recknagel, Thomas Steiger),
- LGC Ltd. United Kingdom (Steve Wood)
- NMi Van Swinden Laboratory, The Netherlands (Adriaan van der Veen)
- SP Technical Research Institute of Sweden (Bertil Magnusson)
- IRMM Institute for Reference Materials and Measurements Joint Research Centre,
- European Commission (Hendrik Emons),

has compiled answers to the following six frequently asked questions in the area of reference materials:

1. What are reference materials used for?
2. What types of reference materials are there?
3. What are the topical developments related to reference materials?
4. How to use a reference material?
5. How to find a suitable reference material?
6. Which international guidance documents are relevant?

1. What are reference materials used for?

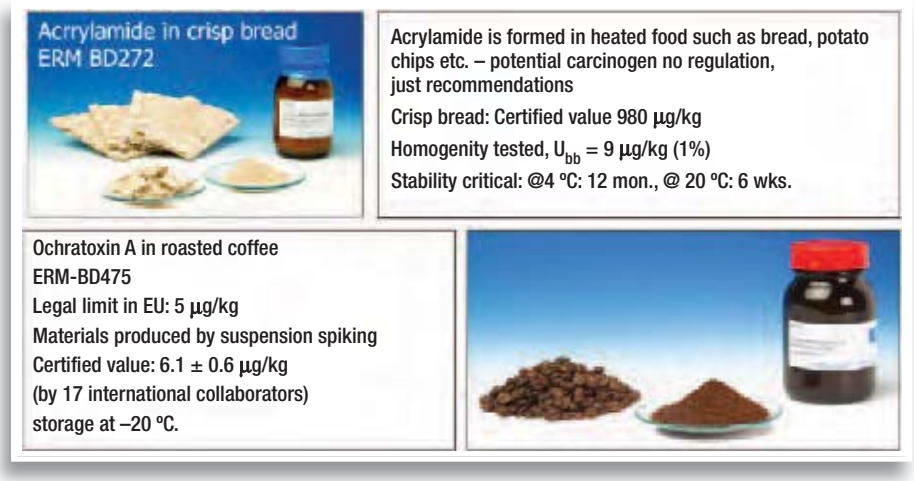
Reference materials are used for a range of functions within measurement processes, including:

- Calibration, i.e. the establishment of a relation between a 'signal' and the quantity intended to be measured. In the simple case, a calibration factor and its uncertainty are calculated from the ratio of the observed and certified values.
- Method development and validation, i.e. to check if the observed value measured on the reference material and the certified value match within the uncertainty (trueness control).
- Establishment of metrological traceability, i.e. to ensure that results are traceable to stated references and are comparable to other results.
- Quality control purposes, e.g. to control the accuracy of a single measurement within the stated uncertainty, to check for long-term stability of an analytical procedure and laboratory performance (establishment of control charts),
- Proficiency testing, either with non-certified RMs or when the certified reference value of the material is used as the assigned value for the PT round.
- Estimation of measurement uncertainty.

2. What types of reference material are there?

Reference materials can be categorized according to a variety of criteria, e.g. field of application, form of material, matrix type, intended use in the measurement process and specified properties. The categorization according to the specified properties is useful for a general overview. Reference materials are available for the following categories of specified properties:

A **Chemical composition**
Reference materials (RMs), being either pure chemical compounds, mixtures thereof, or representative sample matrices, either natural or with added analytes, characterized for one or more chemical or physicochemical properties, e.g. metal RMs (ferrous/non-ferrous and their alloys), environmental RMs (soil, water, bi-



ological materials), gases, solutions (e.g. pH buffers).

B **Biological and clinical properties**
Materials similar to Category A, but characterized for one or more biochemical or clinical functional property, e.g. catalytic activity of an enzyme, taxonomic identity of a microorganism.

C **Physical properties**
Materials characterized for one or more physical properties, e.g. optical properties (refractive index, spectral absorbance), electrical/magnetic properties (e.g. dielectric strength, magnetic susceptibility), radioactivity, thermodynamic properties (e.g. thermal conductivity, thermal resistance), physicochemical properties (e.g. viscosity, density).

D **Engineering properties**
Materials characterized for one or more engineering properties, e.g. sizing, hardness, tensile strength, surface characteristics, impact hardness, elasticity, etc.

E **others**
E.g. materials to determine quality properties of wheat flour like water absorption, processing and dough characteristics.

3. What are the topical developments related to reference materials?

Speciation

Physical (e.g. hardness), chemical (e.g. reactivity) and biological (e.g. toxicity) behaviour of substances depend strongly upon their bonding status. Certification of individual species is a difficult task to achieve and thus only few RMs are currently available. Considerable effort will have to be put into the development of speciation RMs to fill this gap.

Biological reference materials

There is a good choice and variability of reference materials offered for industrial applications or laboratory work with inorganic constituents. In the areas dealing with nutrition, health and life, however, a limited number in relation to the huge variety of tested samples (matrices, investigated properties, etc.) can be found, leaving RMs of this type to be among the most desired and urgently needed ones. Besides the identification of appropriate measurands, stability is a crucial factor here and developing reliable biological RMs with an acceptable period of validity is one of the biggest future challenges for RM producers.

Metrological traceability

Establishing traceability and thus enabling comparability of measurement results is one of the major applications of RMs. But where does the traceability chain end? It may end at this respective RM or it may lead further up the metrological pyramid, linking the measurement results to a national standard or in an ideal case even to the SI units. To enable the user to recognize the end of this chain, a clear statement about metrological traceability needs to be found on each RM certificate. This has rarely been done in the past and is a commitment for the present and the future.

Accreditation

An important trend is the accreditation of reference material producers. While ILAC-G12 was the leading document for an accreditation of this type in the past, it now follows the rules given by *ISO Guide 34* (usually in combination with *ISO/IEC 17025*).

Networking

Although not a new idea, networking of reference material producers has become prominent to split the efforts in producing high quality RMs in order to satisfy the demand of the market and avoid duplicate work. The ERM® program in Europe is a recent example for such a network. Similar initiatives are under discussion in other parts of the world.

4. How to use a reference material?

General

To ensure an effective use of reference materials, it is necessary to obey all instructions concerning intended use, stability (shelf life and storage conditions), sample preparation, minimum sample intake etc. given by the RM-producer on the certificate or in accompanying documentation. A specific RM can only be used

CONTINUED ON PAGE 46

for a single purpose in a given measurement (e.g. calibration or validation/verification). If one CRM is used for calibration another CRM must be used for validation. If an RM is used for e.g. calibration or quality control the user has to choose a material as similar as possible to the test sample. This comprises the matrix composition as well as the content level of the analyte of interest.

Calibration using RMs

Reference materials – pure substances as well as matrix RMs – are often used for calibration purposes. If matrix RMs are used for calibration it has to be ensured that the matrix of the RM is behaving sufficiently similar in the calibration process to the test sample to cope with potential matrix influences for the measurement method used. Calibration can be done using one or several different RMs. The uncertainties associated with the property values of the RMs have to be considered when the the uncertainty contribution due to calibration is evaluated.

Validation – Verification of a measurement result

To verify a measurement result the difference (Δm) between measured (cm) and certified value (cCRM) of the CRM has to be compared with the combined uncertainty ($u\Delta$) of the CRM (uCRM) and the measurement (um). If $\Delta m \leq 2\ u\Delta$ then there is no significant difference between the measurement result and the certified value.

Establishment of metrological traceability

Use of a CRM is a convenient way to demonstrate metrological traceability. If the property value of the CRM is traceable to, e.g., the SI, then the measurement involving it allows a statement concerning the metrological traceability of the results to SI units. However, metrological traceability can only be established when the uncertainty of the property values of the CRM is duly taken into account and if the nature of the analytical sample is sufficiently matched by matrix and analyte level of the CRM.

5. How to find a suitable reference material?

Even in the age of web based technologies and services finding a proper reference material can be a demanding task, in particular for newcomers or for new kinds of materials.

The best choice is to use reference material databases that collect data from several RM producers and provide information in a uniform way. There are some databases covering a broad scope of RM application fields and collecting data from several producers:

• COMAR www.comar.bam.de/

COMAR is a RM database maintained in cooperation of national and international institutes and free of charge to the users. COMAR is focused on certified reference materials covering mainly analytical chemistry, but also physics and materials testing. About 11 000 reference materials are listed here.

• Virtual Institute for Reference Materials (VIRM)

www.virm.net/ The 'Virtual Institute for Reference Materials'

(VIRM) is operated by the Quality Consult association. VIRM offers a large-scale RM database covering all kinds of reference materials. Users (and RM producers) have to register and to pay an annual subscription fee.

• European Reference Materials (ERM®)

www.erm-crm.org/

Three major European reference materials producers (BAM, IRMM, LGC) have established a new trade mark (ERM®) for high quality reference materials. European Reference Materials are certified in an uncompromising peer evaluation by the ERM Technical Committee and the ERM Panel applying ISO Guides 34 and 35.

• Reference materials total information service of Japan (RMinfo)

www.rminfo.nite.go.jp/english/index.html

This site is maintained by NITE and offers a database for Japanese reference materials and links to COMAR and NIST.

There are some databases overarching several producers and focused to special kinds of materials:

• GeoReM

http://georem.mpch-mainz.gwdg.de/

The GeoReM database is hosted by the Max-Planck-Institute (MPI) for Chemistry and is specialized to geological and environmental reference materials.

• Joint Committee for Traceability in Laboratory Medicine (JCTLM)

www.bipm.org/jctlm/

JCTLM offers a database for higher-order reference materials for laboratory medicine and in vitro diagnostics.

• Virtuell Institute for Thermal Metrology (EVITHERM) www.evitherm.org/

The 'Virtual Institute for Thermal Metrology' is operated by the evitherm Society and provides a database for thermal properties. The use is free of charge.

The world's major RM producers maintain websites offering search tools for their reference materials, e.g.:

• BAM, Federal Institute of Materials Research and Testing of Germany

www.bam.de/en/fachthemen/referenzmaterialien/index.htm

• Institute for Reference Materials and Measurements (IRMM)
http//irmm.jrc.ec.europa.eu/html/reference_materials_catalogue/index.htm
• International Atomic Energy Agency (IAEA)
www.iaea.org/programmes/aqcs/database/database_search_start.htm
RMs produced by IAEA's Analytical Quality Control Services (AQCS)
• LGC Limited (formerly Laboratory of the Government Chemist)
www.lgcstandards.com/home/home_en.aspx
LGC Standards is supplier and distributor of reference materials from many producers.
• National Institute of Standards and Technology (NIST)
http://ts.nist.gov/measurementservices/referencematerials/index.cfm
• Nederland's Meetinstituut (NMi)
http://nmi.nl/index.php?pageId=21&lg=e
Reference materials for gas analysis, air quality measurement, density and viscosity
• World Health Organization (WHO)
www.who.int/bloodproducts/ref_materials/en/
Reference materials (International Reference Preparations) of blood products and related biologicals

6. Which international guidance documents are relevant?

Documents dealing with reference materials can be divided into three groups.

Group 1: General terminology

[1] ISO Guide 30 (1992) Terms and definitions used in connection with reference materials
[2] ISO Guide 30:1992(E)/Amd.1:2008
[3] International vocabulary of metrology — Basic and general concepts and associated terms (VIM), JCGM 2008 (http://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2008.pdf)
[4] ISO Technical report 10989 (2008) Reference materials - Guidance on, and keywords used for RM categorization

Group 2: Production of reference materials

[5] ISO-Guide 31 (2000) Reference materials – Contents of certificates and labels
[6] ISO-Guide 34 (2000) General requirements for the competence of reference materials producers
[7] ISO-Guide 35 (2006) Reference materials – General and statistical principles for certification
[8] ILAC – G12 (2000) Guidelines for the Requirements for the Competence of Reference Materials Producers
www.ilac.org/documents/ILAC_G12-2000_guidelines_for_the_requirements_for_the_competence_of_reference_materials_ producers.pdf
[9] ISO 11459, Iron ores – Certified reference materials – Preparation and certification for use in chemical analysis, 1997
[10] ISO/CD Guide 80 (2008) – Guidance for the Production of Reference Materials for Precision Control (PCMs)
[11] Recommendations for the preparation, characterization and establishment of international and other biological reference standards (revised 2004) WHO
www.who.int/bloodproducts/publications/Final_Prep_Stds_Nov2004.pdf
[12] CEN TR 10317:2002 European certified reference materials (EURONORM-CRMs) for the determination of the chemical composition of iron and steel products prepared under the auspices of the European Committee for Iron and Steel Standardization (ECISS)
[13] International Organization for Standardization, "ISO 6142 – Gas analysis – Preparation of calibration gas mixtures — Gravimetric method", ISO Geneva, 2001
[14] International Organization for Standardization, "ISO 6143 – Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures", ISO Geneva, 2001

Group 3: Use of reference materials

[15] ISO-Guide 32 (1997) Calibration of chemical analysis and use certified reference materials (this guide is foreseen to become part of ISO-Guide 33)
[16] ISO-Guide 33 (2000) uses of certified reference materials
[17] EURACHEM-Guide (2002) the selection and use of reference materials - a basic guide for laboratories and accreditation bodies (identical with ILAC G9 (2005))
www.ilac.org/documents/ILAC_G9_2005_guidelines_for_the_selection_and_use_of_reference_material.pdf
[18] NIST Publication 260-100 (1993): Standard Reference Materials - Handbook for SRM Users
http://ts.nist.gov/MeasurementServices/ReferenceMaterials/upload/SP260-100.pdf

Prof. Horst Czichos, EUROLAB Past President
Professor at TFH Berlin
University of Applied Sciences
horst.czichos@t-online.de
+49-30-8013913