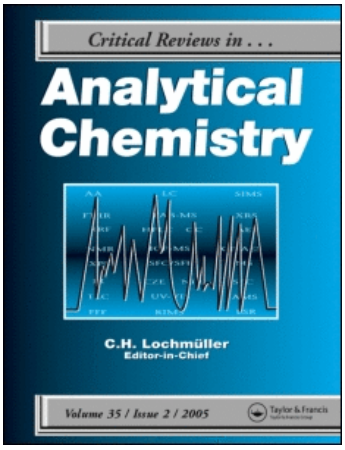

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Prospects for the Production, Research and Utilization of Reference Materials

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Prospects for the Production, Research and Utilization of Reference Materials

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For some time the quality of results of analytical measurements has been in the center of interest of chemical analysts. This is caused by the rising importance of these results in almost all spheres of life. There are many parameters contributing to the achievement of reliable and comparable measurement results. These are, among other things: checks of the competence of the analyst or the laboratory, routine checks of accuracy and precision of measurement results, validation of analytic methods, accreditation of the laboratorys, etc. Reference materials (RMs), particularly (CRMS), constitute a very important tool and are the basis of achieving accurate measurement results by laboratories and also for the verification of results of analytical measurements. All over the world we note a rising demand for various kinds of reference materials, which leads to a wider offer and a continuous increase of the number of producers of such materials.
The paper discusses the most important information available and perspectives of utilization, research, and production of reference materials.

Keywords Reference materials, certified reference materials, production of reference materials, certification report

INTRODUCTION

Since the 1980s, European Commission (EC) has been supporting research programs aimed at improving the quality of physical, biological, and chemical measurements through the use of appropriate reference materials. Problems connected with their production and use in analytical practice, both in Europe and in other geographical regions, are the subject of numerous discussions (1, 2).

The European Union has adopted a comprehensive inspection system (Fig. 1) for protection of the environment from contamination. Member states are obliged to use this system for inspection of the quality of air, waters, ground, food products, etc. Among all these elements playing a role in ensuring high quality of results (shown in Fig. 1), an essential role is played by reference materials (RMs), in particular certified reference materials (CRMs) (3–5). Table 1 presents information about reference materials.

It should be remembered that during the last few years the European Union has been financing up to three projects (in the Vth Framework of the EU) devoted to problems of utilization of RMs in analytical practice (Table 2). The author's own institution was involved in the realization of tasks within these projects; apart from it there was also a project *Centre of Excellence in Environmental Analysis and Monitoring*. Within this project there were also tasks connected with the utilization of RMs.

DEFINITIONS AND CLASSIFICATION OF REFERENCE MATERIALS

RMs are indispensable in any analytical laboratory. Their preparation is expensive and time-consuming. Therefore, we have to differentiate between uncertified RMs and CRMs to perform a rational selection for assumed tasks. It is impossible to prepare reference materials for all measurements because of the great variety of matrices and analytes. Thorough acquaintance with methods and knowledge of available reference materials allow us to make a proper selection. A general repartition of reference materials is presented in Fig. 2 (11). The basic areas of their use include (12–16):

1. Checking the competence of a new analyst or a new laboratory;
2. Routine control of precision and accuracy of analyses;
3. Validation of analytical methods;
4. Quality checks of the performance of a laboratory; and
5. Calibration of instruments and procedures.

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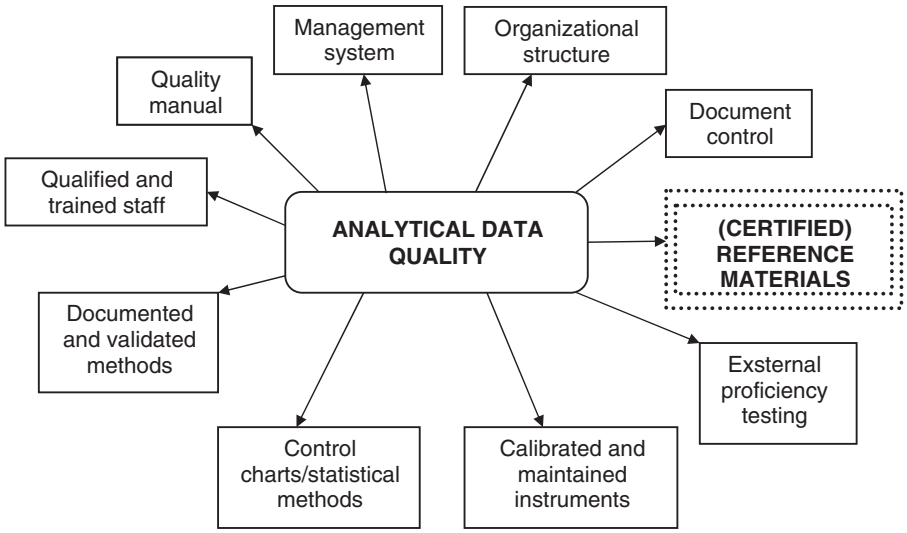


FIG. 1. Inspection system used by the European Union for protection of the environment and pollution prevention (4).

The definitions of the basic terms reference material and certified reference material were formulated for the first time in 1997. Presently, in literature a whole line of terms is used to describe the nature of these materials: reference materials, certified reference materials, materials for quality control, laboratory reference materials, etc. Proper use and a commonly false understanding of terminology related to various types of reference materials is nowadays under critical discussion (4).

The guides, like ISO Guide 30 and Guide Expression Uncertainty in Measurements GUM contain the following definitions of reference materials (14–16):

Reference material (RM)—A material or substance for which the value of one or a greater number of properties were recognized as sufficiently homogenous and sufficiently well defined, so that they can be used for the calibration of an instrument, to evaluate a measurement method, or to assign values to properties of materials. The reference material can be a pure substance or a mixture; it can appear in the form of gas, liquid or solid state (1).

Certified reference material (CRM)—A reference material provided with a certificate, characterized by a value or values of a given property which have been certified according to a procedure assuring reference to precise realization of a unit of measure in which values of the given property are being expressed; each certified value should be accompanied by an uncertainty related to a specific confidence level (1).

Matrix reference material—A material that is characterized by an usually low analyte content level. It is used mainly in testing and validation of analytic procedures and in calibration of measuring instruments. Among matrix reference materials the following types can be distinguished: primary reference materials, materials for quality control, laboratory reference materials, and secondary reference materials.

Matrix-free reference material—A reference material whose matrix content does not influence the determination result. Such materials are used for the calibration of analytic instruments. Among matrix-free reference materials the following can be distinguished: pure substances and standard solutions.

Primary reference material (PRM)—A certified reference material of the highest metrological quality (measuring coherence with SI units). Such material is developed by national metrological institutes, approved by authorized national institutions, and verified during international comparative measurements.

Secondary reference material (SecRM)—A material for which the value of the characteristic parameter is determined by comparison with the appropriate value for the primary reference material of the same kind (17).

Laboratory reference material (LRM)—The so-called working reference material or material used in quality control, prepared by accredited institutions. Reference values are determined through tests conducted by means of at least one analytical procedure which has undergone a validation procedure. Such materials are accompanied by a description of the method of achieving measuring coherence and the value of the estimated measuring uncertainty. They are prepared mainly for use in inter-laboratory tests and for internal quality control.

In analytical praxis a wide range of RMs is used and the amount of such materials available on the market is rising steadily. However, taking into account their significance in quality control and in ensuring high quality of analytical results, a shortage of them still persists.

Available RMs are, still above all, such as:

- soils, precipitates, and water with certified metal content;

TABLE 1
Where to find information about reference materials (RMs) (certified and non-certified) (6–8)

No.	Abbrev.	Institution	Country	www.page
1.	BSC	Brammer Standard Company Inc.	USA	http://www.brammerstandard.com/
2.	BAS	Bureau of Analysed Samples Ltd.	England	http://www.basrid.co.uk/bas.htm
3.	CCRMP	Canadian Certified Reference Materials Project	Canada	http://www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/ccrmp/ccrmp-e.htm
4.	COMAR	Code d'Indexation des Matériaux de Référence	Germany (secretary)	http://www.comar.bam.de/
5.	CMI	Czech Metrology Institute	Czech Republic	http://www.cmi.cz/
6.	BAM	Federal Institute for Materials Research and Testing	Germany	http://www.bam.de//
7.	FV	Ferroetalon Vaskut	Hungary	http://2theta.com/nabidka/refmat/modry.htm
8.	GSJ	Geological Survey of Japan	Japan	http://www.aist.go.jp/GSJ/
9.	GUM	Central Office of Measures	Poland	http://www.gum.gov.pl/en/site/
10.	IRMM	Institute for Reference Materials and Measurements	Belgium	http://www.irmm.jrc.be/
11.	IGS	Institute of Geological Science	England	http://www.see.leeds.ac.uk/research/igs/index.htm
12.	IChTJ	Institute of Nuclear Chemistry and Technology	Poland	http://www.ichtj.waw.pl/
13.	IPO	Institute of Industrial Organic Chemistry	Poland	http://www.ipo.waw.pl/
14.	IAEA	International Atomic Energy Agency	Austria	http://www-naweb.iaea.org/nahu/nmrm/
15.	JAC	Japan Society for Analytical Chemistry	Japan	http://www-naweb.iaea.org/nahu/nmrm/nmrm2003/producer/jac.htm
16.	KRISS	Korea Research Institute of Standards and Science	Korea	http://www.kriss.re.kr/
17.	LGC Standards	Laboratory of the Government Chemist (*LGC Standards*)	England	http://www.lgc.co.uk
18.	CENAM	National Center of Metrology	Mexico	http://www.cenam.mx/
19.	NIES	National Institute for Environmental Studies	Japan	http://www.nies.go.jp/
20.	NIST	National Institute for Standards and Technology	USA	http://www.nist.gov/

(Continued on next page)

TABLE 1
Where to find information about reference materials (RMs) (certified and non-certified) (6–8) (Continued)

No.	Abbrev.	Institution	Country	www.page
21.	NMI	National Measurement Institute	Australia	http://www.measurement.gov.au
22.	NMIJ	National Metrology Institute of Japan	Japan	http://www.nmij.jp/
23.	NRCCRM	National Research Centre for Certified Reference Materials	China	http://www.nrccrm.org.cn
24.	NRCC	National Research Council of Canada	Canada	http://imb-ibm.nrc-cnrc.gc.ca/crmp
25.	NRC-INMS	National Research Council of Kanada, Institute for National Measurement Standards	Canada	http://www.inms-ienm.nrc-cnrc.gc.ca/
26.	NWRI	National Water Research Institute	Canada	http://www.nwri.ca/nlet/crm-e.html
27.	RTC	Resource Technology Corporation	USA	http://www.rt-corp.com/
28.	SCP	SCP Science	Canada	http://www.scpscience.com/regions/en_can/default_can.asp
29.	SMU	Slovak Institute of Metrology	Slovakia	http://www.smu.gov.sk/eng/main.html
30.	USGS	U.S. Geological Survey	USA	http://www.usgs.gov/
31.	VI-RM	Virtual Institute for Reference Materiale	Italy (bureau)	http://www.virm.net/

- vegetable and animal tissues, food products with certified metal content;
- soils and sediments with certified contents of organic impurities (pesticides, hydrocarbons, dioxin, and others);
- animal tissues with certified contents of organic impurities (pesticides, hydrocarbons, and others)
- materials containing microorganisms (microbiological reference materials);
- geological materials (rocks, ores, minerals);
- fuel (coal, crude oil) with certified content of sulphur and metals;
- industrial products and raw materials (cement, glass and fertilizers, minerals, and metallic ores) with certified properties; and
- materials which represent physico-chemical quantities, pH, viscosity, etc.

PRODUCTION OF REFERENCE MATERIALS

The production of reference materials is a difficult and time-consuming process. The preparation process and the characteristics of a reference material consist of various kinds of stages which include (17–23):

- estimation of the most important needs and confirmation of demand;
- literature search and project plan;
- acquisition of resources for the future reference material and their processing;
- testing homogeneity;

TABLE 2
Information on the subject of European projects connected with reference materials (9, 10)

Acronym	Full project name	Realization period
TRAP-NAS	Training on the production and use of reference material in newly associated states)	2002–2003
VI-RM	The European virtual institute for reference materiale)	2003–2005
QUA-NAS	Improving the infrastructure for metrology in chemistry in the candidate new member states)	2003–2005
CEEAM	Centre of Excellence in Environmental Analysis and Monitoring	2003–2005

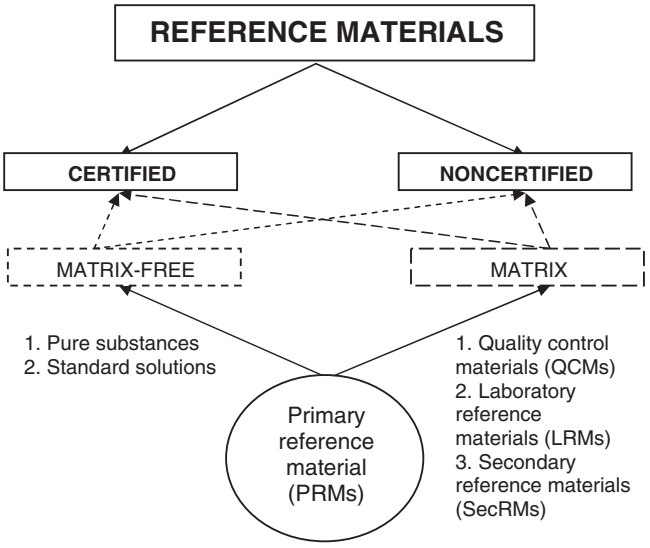


FIG. 2. Classification of reference materials used in chemical analysis (8).

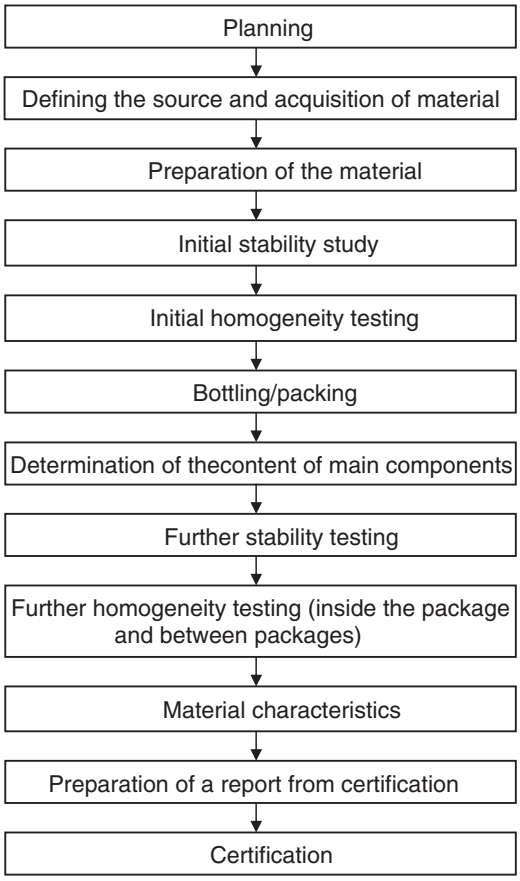


FIG. 3. Main stages in the production of reference materials.

- studying stability;
- characteristics; and
- preparation of a report from the certification and the certification itself.

The main stages leading to the production of CRMs are shown schematically in Fig. 3 (21, 24). Each of them is shortly discussed below.

Estimation of the Demand for Reference Material

This is the fundamental, first step in the production of a new RM. It is very important that the future RM be profit-yielding (evaluation of potential demand for the produced RM) and that there be demand for such material in the analytical environment.

Planning the Production of Reference Material

The production of a new reference material can last at times from 3 to 5 years; therefore, the basis of success lies in proper and complete planning. A detailed plan for the production project is essential before commencing research on the new RM: what is needed, what shall be done, and within what period, etc. It is important to confirm that the production of the future RM will be technically feasible.

Quest for Raw Material for the Future Reference Material and its Processing

Detailed qualification of the source of acquisition of material with the required properties and values is not easy and in the initial search stage may require of the producer some consultation with extraneous persons. The final choice of the source of supply of raw material often depends upon the ultimate required amount of material. Usually, from 100–200 kg of the ordered raw material are used; after processing, some 1000 to 5000 completed samples of the reference material are produced. The delivery and processing of such a great amount of material requires specialized equipment and expert knowledge.

The majority of materials will require different processing to obtain a new RM suitable for use. Processing may require desiccation, crushing, milling, sieving, stirring, mixing, shifting, etc. The material thus processed must be thoroughly mixed, divided into individual portions, and packed into containers suitable for the specific kind of material so that its physical stability and certified value (C_{CRM}) will be preserved for a long period of time.

Homogeneity Testing

Testing of homogeneity is an essential step at the RM preparation and certification stage (25, 26). It is important that the RM packaged into bottles or vials be subjected to tests which ensure that it is homogeneous and that the reference value (C_{CRM}) measured in part of the packages be comparable to that in

another sample of packages and that it lies within the admissible uncertainty threshold (27, 28).

In connection with this, two kinds of homogeneity can be distinguished:

- within-bottle homogeneity—homogeneity of material inside one package of a given material and
- between-bottle homogeneity—homogeneity in different units of a given material charge.

The samples for homogeneity tests should be taken at random, so that each sample had the chance of being included in the test lot. An experiment plan should be adopted that k samples of the material are taken and for each sample n equal determinations are performed. It is recommended to perform the determination in random succession, in order to avoid a possible systematic variability with time. Besides, the values of k and n ought to be sufficiently large, to enhance the detection of in homogeneity at a previously established level of significance.

The reference materials can be prepared in the form of:

- solutions, in such cases they are homogeneous by virtue of physical (thermodynamic) laws. The main purpose of testing their homogeneity is detection of any impurities, inclusions or irregularities,
- mixed powders, ores, alloys, etc. which by nature are an inhomogeneous composition. The reference materials must undergo tests for an evaluation of their homogeneity level before being put on the market.

Stability Study

A stability study of the candidate for future RM in planned storage and deposition conditions is an important part of its pre-production stage (26). A valuable reference material is such which remains stable under the influence of deposition, storage, transportation, and use.

Two types of stability of reference materials can be distinguished (28):

- long-term stability and
- short-term stability (e.g., stability during transportation).

A stability test requires "quick" measurement methods, small mass of samples, and high repeatability of measurements. The tests are carried out at different temperatures, times, and storage conditions.

Resistance to light, humidity and temperature can be checked by repeating the storage in various environments and analyzing them afterwards in normal laboratory conditions after fixed periods of time. The degradation reactions which occur in normal conditions in the laboratory will be speeded up two-fold for each temperature increase by 10°C (in accordance with the Arrhenius equation). The acceleration of the sample testing stage at elevated temperatures usually consists of simulating conditions and observing the samples during a long (fixed) period of time. Commonly, most stability tests require that the samples be put in a freezer at a temperature of −20°C , in a refrigerator at 4°C, at an ambient temperature of 20°C, and in a drier at +40°C and subsequently analyzed after a period of 0, 1, 3, 6, and 12 months. Sometimes, materials sensitive to conditions of storage, e.g., microbiological samples, are not sufficiently durable to be used as RMs and for this reason they are stored at a temperature of −70°C (28–32).

The type of container in which the reference material is kept can also play a great role in preservation of material properties. If the container is chosen inappropriately, it can interact mutually with the reference material itself and unfavorably influence the length of its lifespan. A long period of chemical stability of any RM also has to be controlled through its admissible storage period.

Checking the stability of RMs can be also discussed at two levels:

- classical (long-term) and
- isochronous.

In the case of the classical method of checking the stability of RMs, it is determined on the basis of comparison of results obtained for samples stored in recommended conditions and for reference samples—most often stored at a lowered temperature, e.g, −40°C. Such tests are conducted shortly before expiration of the previously accepted stability threshold limit and on their basis a decision is taken on extending the stability period.

The isochronous method of checking the stability, in turn, is based on concluding the stability of the RM on the basis of analyses of samples kept during a short period of time (several weeks) and at various temperatures (generally higher than the recommended storage temperature) (29).

Characteristics of the Reference Material

From a technical point of view, several approaches (described in ISO Guide 35) can be used to characterize the future reference material (33, 34, 21).

Suitable information can be obtained by performing measurements using:

- one definitive method*;
- two or more independent reference methods used by one institution;
- a network of institutions having appropriate authorization, using methods with confirmed accuracy; and
- an approach using "a specific method" (interlaboratory tests).

Depending on the type of RM, its planned range of exploitation, competence of laboratories, and the kind of method in use, one of the proposals may be chosen as appropriate. The producer of the RM should, if only possible, ensure the conformance of

11. INSTRUCTIONS FOR USE

The following notes are a guide to the user of these reference materials for the determination of the rate earth elements. U and Th elements in calcareous soil. The material consist at a soil sample in glass bottles, containing about 70 g at dry powder. Before a bottles is opened, it should be shaken manually for 1 min so that the material within in is re-homogenised.

The analytical sample for analysis should be taken as it is. The correction to dry mass should be made by taking a separate portion of 1 g and drying in an oven at 105ºC for 2-3 h until constant mass is attained (successive weighings should not differ by more than 1 mg). The mean moisture content (as calculated from 11 sets of data) found in the certification campaign was (5.6±1.3) %.

Although no effects are expected at room temperature, it is recommended that the bottles be kept closed at < 20ºC in a refrigerator, in the dark. The material picks up moisture when in prolonged contact with humid air. Therefore, after having been opened, the bottle with remaining material should be stored in a dry empty dessicator. Spoilage by moulds may occur at moisture contents exceeding 8-18 % by mass and ruins the whole sample.

FIG. 4. Exemplary fragment of a report on certification, containing instructions for proper use of the reference material ERM® -C690 (calcareous soil) (37).

the method of performing the characteristics with requirements presented in the ISO/IEC No. 35 Guide.

Definitive method—a solid method based on well-defined theoretical grounds, which has been tested experimentally; it has been established that systematic errors connected with the method are insignificantly small with simultaneously high precision. There exists only a small group of such methods which are used in specialist laboratories (5).

Certification and Preparation of a Certification Report

A consecutive stage in the production of a RM is its certification (33, 35).

Certification of a RM is a procedure leading to the issue of a certificate, in the result of which the value(-es) of one or many properties of the material or substance is established in a process which ensures measuring coherence, with exactly reproduced units in which the values of the properties are expressed.

The ISO/IEC No. 35 Guide mentions three main procedures of reference material certification (36–38):

1. measurement by one absolute method in one laboratory,
2. measurement by one or more independent standard methods performed in one laboratory, and
3. a measurement performed by a network of specialist laboratories, using one or more methods with documented accuracy.

After completing the certification tests and obtaining an appropriate collection of results, a report should be prepared from the performed certification, containing the following information:

1. name and address of the certifying institution;
2. title of the report;
3. description and name of the reference material;
4. confirmed estimated certified values and their uncertainties;
5. certification date and admissible storage period;
6. source of supply of reference material;

During tests of a future matrix-free reference material - ethen – 3 measurements were carried out in order to determine the amount of analyte (oxygen) liberated from glass fibres stored at room temperatures. A series of data was obtained:

Lp.	ethen [ng/cm]
1.	2,46
2.	2,12
3.	2,056
average	**2,212**

$$U = k\frac{s}{\sqrt{n}}$$

n - number of measurements
s - standard deviation
k – expansion coefficient

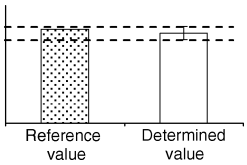
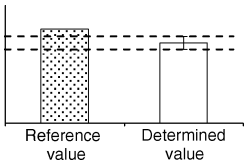
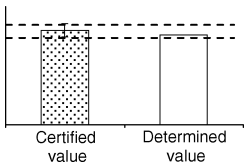
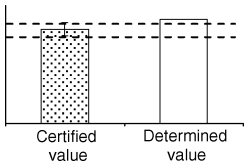
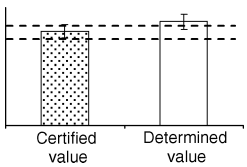
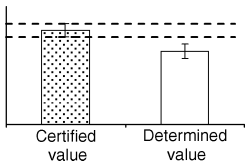
k = 2
s = 0,069
n = 3
U(k=2) = 0,079 [ng/cm]

Proper way of recording the value of the measured quantity together with the measurement uncertainty:

(2,212 ± 0,079) ng/cm.

FIG. 5. The example of the proper way of recording the value of the measured quantity together with the measurement uncertainty.

TABLE 3
Possible methods of graphical comparison of a reference value (certified) with the determined value

Conditions	Grpahical presentation	Conclusions
Reference value without given uncertainty value (is not a certified value) Determined value with given uncertainty value		Determined value consistent with the reference value
		Conclusion not possible
Determined value without given uncertainty value		Determined value consistent with certified value
		Conclusion not possible
Determined value with given uncertainy value		Determined value consistent with certified value
		Determined value inconsistent with certified value

7. supplier of the reference material;
8. exploitation and limitations during the use of the reference material;
9. stabilities and instructions related to transportation and storage conditions of the reference material;
10. instructions (directions) for proper use of the reference material (Fig. 4);
11. method of preparation of the reference material for use;
12. report (declaration) on the homogeneity and stability of the reference material;
13. method of certification of the reference material;
14. list of laboratories participating in the production process of the reference material;
15. measurement techniques used for the certification of the reference material;
16. names of analysts, researchers and names of participating

laboratories;
17. signatures or names of persons officially responsible for the certification.

Some RMs need a more specific report on the subject of preparation and certification of material, containing the following information:

- source (origin) of the material;
- detailed preparation procedure; and
- measurement techniques used to test homogeneity, stability, and for certification.

A present, internet databases are available containing reports and certificates as well as offers to buy CRMs. Some of these are, among others:

- www.erm-crm.org
- www.comar.bam.de
- www-naweb.iaea.org/nahu/nmrm2003/browse.htm
- www.virm.net
- www.refmat.org.pl

ESTIMATION OF UNCERTAINTY

The result of a most meticulously performed measurement or observation is burdened with uncertainty. That is why an analysis of measurement uncertainties is an essential element of planning and production of RMs as well as realization and processing of the results obtained. Therefore, it has been taken as obligatory to determine the uncertainty of measurements as an international agreement between institutions concerned with measurements and introduced by national offices.

The GUM guide (19) contains the following definition of uncertainty:

Uncertainty—a parameter connected with the result of a measurement, characterizing the dispersion of values and which may be in a substantiated way attributed to the measured quantity.

Among the most common sources of uncertainty during the determination of the certified value of RMs, are:

1. incomplete definition of the measured quantity,
2. imperfect realization of the definition of the measured quantity,
3. unrepresentative sampling,
4. incomplete knowledge of the effect of environment on the measurement,
5. inaccurate values attributed to standards and RMs,
6. inaccurate values of constants and other parameters obtained from external sources for the measurement and used in data-processing procedures, and
7. changes in repeated observations of a quantity in apparently identical conditions.

Such a great number of possible sources of uncertainty during the production process of the future RM causes the measurement result to be only an approximation of the value of the measured quantity (the measurement result is complete only when given together with the uncertainty). A faultless record of the value of a measured quantity has the following form (Fig. 5):

(value of the measured quantity $\pm$ expanded measurement uncertainty) unit.

COMPARISON OF A MEASUREMENT RESULT WITH THE VALUE CERTIFIED FOR A GIVEN REFERENCE MATERIAL

One of the main problems coming out during the use of RMs is the interpretation of calculated values of determinations. The interpretation can be carried out by comparing (graphically or by calculation) the measurement result with the value certified for the specific RM.

1. Graphical comparison of the measurement results with the value certified for the RM.

A very practical approach seems to be a graphical comparison of the (certified) reference value with the value obtained in the result of measurement (determined). Possible situations, dependent upon the information about both compared values, together with conclusions resulting from such a comparison, are presented in Table 3.

2. Comparison by calculation of the measurement with the certified value for the RM.

After carrying out a measurement with the use of certified material, calculate the absolute difference between the average determined value and the value certified according to Eq. [1]:

$$\Delta_m = |C_m - C_{CRM}|, \quad [1]$$

where Δ_m is the absolute difference between the average measured value, and the certified value $C_m$is the average determined value, and C_{CRM} is the certified value.

In accordance with the description in "ISO instructions on expressing uncertainty in measurements (GUM)", each measurement is characterized by uncertainty u(Section 4). This means that every result should be investigated within limits of that uncertainty. Also the certified value must be examined only with allowance for uncertainty u_{CRM} given in the certificate.

A calculation is to be made of the complex uncertainty of the measurement result and the certified value, according to Equation [2]:

$$u = \sqrt{u_m^2 + u_{CRM}^2}, \quad [2]$$

where u is the complex uncertainty of the result and the certified value,u_m is the uncertainty of the measurement result, and u_{CRM} is the uncertainty of the certified value.

The uncertainties of certified values u_{CRM} are given in each certificate (Figs. 6, 7). Besides, the certificate should contain an annotation with an explanation of the method of how to

AFLATOXIN G1 IN ACETONITRILE		
	Mass fraction	
	Certified value [1] [µg/g]	Uncertainty [2] [µg/g]
Aflatoxin G1	3.78	0.13

1) This value was derived from the gravimetric preparation of the material corrected for the purity of the aflatoxin G1 used. The value is traceable to the International System of Units (SI).
2) Estimated expanded uncertainty U with a coverage factor k = 2, corresponding to a level of confidence of about 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement (GUM), ISO, 1995. Uncertainty contributions arising from characterisation as well as stability assessments were taken into consideration.

FIG. 6. Table from a report on certification of reference material ERM® -AC 059 (37) containing an expanded uncertainty, the certified value (C_{CRM}) and the expansion coefficient. the standard uncertainty of the certified value (u_{CRM}) is obtained by dividing the expanded uncertainty (in this case 0.13 μg/g) by the expansion coefficient (in this case 2; indicated in a circle) (37).

PORK FAT		
Chlorobiphenyl IUPAC No. (Congener name)	Mass fraction	
	Certified value [1] [µg/kg]	Uncertainty [2] [µg/kg]
28 (2,4,4'-Trichlorobiphenyl)	29.6	2.1
52 (2,2',5,5'-Tetrachlorobiphenyl)	25.5	1.8
101 (2,2',4,5,5'-Pentachlorobiphenyl)	30	4
118 (2,3',4,4',5-Pentachlorobiphenyl)	30.2	2.7
138 (2,2',3,4,4',5'-Hexachlorobiphenyl)	32	4
153 (2,2',4,4',5,5'-Hexachlorobiphenyl)	30.8	2.4
180 (2,2',3,4,4',5,5'-Heptachlorobiphenyl)	29.8	2.5
Sum PCBs	207	11

[1] Certified values calculated as the unweighted mean of the means of the 7 accepted sets of results. Traceable to GC.

[2] Estimated expanded uncertainty *U* with a coverage factor *k* = 2, corresponding to a level of confidence of about 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement (GUM), ISO, 1995. Uncertainty contributions arising from characterisation as well as from homogeneity and stability assessment were taken into consideration.

FIG. 7. Table from a report on certification of reference material ERM® -BB446 (37), containing expanded uncertainties (indicated in a circle), certified values (C_{CRM}, indicated in a rectangle) and the expansion coefficient.

The content of chromium in potable water was checked (37). Reference material ERM®-CA011a has been used. $C_{CRM} = (48 \pm 3)\mu g / L$ $k = 2$ - expansion coefficient given in the certificate $u_{CRM} = \frac{3}{2} = 1{,}5\mu g / L$ It was obtained in the result of performed measurements: $(39 \pm 4{,}2)\mu g / L$ $\Delta_m = \lvert C_m - C_{CRM} \rvert = \lvert 39 - 48 \rvert = 9\mu g / L$ $u = \sqrt{u_m^2 + u_{CRM}^2} = \sqrt{2{,}1^2 + 1{,}5^2} = 2{,}58\mu g / L$ $u_\Delta = 2u = 6{,}65\mu g / L$	The content of magnesium in potable water was checked (37). Reference material ERM®-CA010a has been used. $C_{CRM} = (4{,}2 \pm 0{,}2)\mu g / L$ $k = 2$ - expansion coefficient given in the certificate $u_{CRM} = \frac{0{,}2}{2} = 0{,}1\mu g / L$ It was obtained in the result of performed measurements: $(3{,}9 \pm 0{,}3)\mu g / L$ $\Delta_m = \lvert C_m - C_{CRM} \rvert = \lvert 3{,}9 - 4{,}2 \rvert = 0{,}3\mu g / L$ $u = \sqrt{u_m^2 + u_{CRM}^2} = \sqrt{0{,}15^2 + 0{,}1^2} = 0{,}18\mu g / L$ $u_\Delta = 2u = 0{,}36\mu g / L$
The condition must be satisfied: $\Delta_m \le u_\Delta$	
$9\mu g / L \le 6{,}65\mu g / L$ The average value differs considerably from the certified value.	$0{,}3\mu g / L \le 0{,}36\mu g / L$ The average value does not differ considerably from the certified value.
CONCLUSIONS	
INCONSISTENCY !!!	**CONSISTENCY**

FIG. 8. The exemplary comparison between the measurement results the certified value for the reference material.

determine the uncertainty of certified values. In the majority of cases explicitly the coefficient is expansion given.

$$u_\Delta = 2u, \quad [3]$$

where U_Δ is the expanded uncertainty of the difference between the result and the certified value.

$$\Delta_m \leq u_\Delta \quad [4]$$

If the above condition [4] is satisfied, we may conclude that there is no considerable difference between the measurement result and the certified value (Fig. 8).

SUMMARY

The accuracy and precision of measurements form the basis of correct functioning in industry, commerce, and medicine all over the world. Harmonization of the measurement system can be achieved by enforcing various standards and directions (39–41). In many cases varying measurement results are obtained, even when laboratories use the same research method. To avoid such situations, it is necessary to use quality control systems, personnel training, a good management structure of laboratories, validation of methods (e.g., control diagrams), evaluation by external quality control (e.g., participation in interlaboratory comparisons), but above all by the use of CRMs (41–43).

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