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Certification of Geological Reference Material

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Abstract: This articel aims to provide a short information on the preparation and certification of geological reference materials. It summarises the key issues and the principles in area of planning of the project, procedures for sample preparation, methods for homogeneity and stability testing, certification exercise, assigning of uncertainty and gives information for final form of certificate according to ISO Guide 31, 2000.

Key words: certified reference material, homogeneity testing, stability testing

Introduction

Certified reference materials play an important role in geological laboratories to help analysts monitor their laboratory performance, verify the quality of produced data, and thus improve the comparability of measurement results. New analytical techniques with increased precision of measurement and legislative and trading requirements have caused that laboratories are becoming increasingly interested for new reference materials of higher quality.

Guidance for the preparation of reference materials is given in ISO Guides (ISO Guide 31, 2000; ISO Guide 34, 1996; and ISO Guide 35, 1989) and guides on the preparation of reference materials are also available (European Commission Document, BCR/01/97, 1997; B. Brookman et al., 1998).

According to ISO Guides 35 **Certified Reference Material (CRM)** is 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 realisation 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.

Preparation of reference material

Laboratory (producer) which intended to prepare CRM may submit a proposal for a project to Slovak Institute of Metrology which according to the Law No. 142/2000 for metrology has responsibility as a certification body for certification of RMs. The proposer in proposal have to take into account for which purpose or use should be CRM prepared. In the planning and during the designing of the project the producer has to identify a kind of matrix material to be collected, identification of suitable source and procedure for sample preparation, amount of material needed, definition of parameters, range to be certified, choice of the methods for homogeneity, stability and characterisation studies. The next part of the project is designing for ensuring storage, labelling, packing of CRMs, transport arrangement, post distribution services and design of a certificate.

After the identification of a suitable source of material producer has to decide about the amount of the material which should be collected. The amounts of material depend on the number of samples needed for commercial use, homogenity, stability study and what amount is needed for certification exercise.

The producer should take care of selecting a suitable processing procedure in order to prevent any contamination of material, change or degradation in the form, ensure that its final form achieve the required homogeneity and is sufficiently stable.

Typical procedures for processing of geological reference material are drying, crushing, grinding, quartering, sieving, testing of grine size and bottling. Before processing of geological reference material it is necessary to perform petrography – mineralogical characterisation and preliminary chemical analysis to obtain basic information about candidate RM.

The meaningful aspect that should be considered in the process of certification of geological RMs is that in generaly, certified compounds are related to dry matter and therefore the dry sample mass has also to be assessed. The moisture content has to be determined on a separate subsample to enable analytical results to be expressed on a dry sample weight basis. Choice of several competent and experienced laboratories which are able to perform the certification measurements play important role in the process of characterisation of RM. Performance of the participating laboratories is possible to assess through proficiency test on the samples which have approximately the same chemical and mineralogical composition as tested candidate reference material.

Homogeneity testing

The first step in the preparation of geological RMs is conducted with a homogenity test. The homogeneity test

is performed prior to certification on a reasonable number units (bottles) randomly selected from batch of bottles of candidate reference material that has been packed in its final form. There are two kinds of homogeneity study. Between unit variation (between – bottle homogeneity study) and within – bottle homogeneity study. From between – bottle homogeneity study is determined between – bottle variation as one important component of uncertainty which must be included in the total uncertainty of CRM (Thomas P. J. Linsinger et al., 2001). Within – bottle homogeneity study is necessary to determine a minimum representative sample portion which will be identical in terms of their certified properties and uncertainties.

The measurements for both homogeneity study should be carried out under best repeatability conditions, in one laboratory, in such a way to minimise possible drift in measurements. Applied measurement method should be selected for its good repeatibility. Recommended number of samples (depending on the type of material and repeatability of the method) is from 8 to 30 (European Commission Document, BCR/01/97, 1997). Analysis of variance (ANOVA) according to ISO Guide 35 should be used for statistical evaluation of homogenity study. An example for between – bottle homogeneity study is showed in Fig.1. This model is an ideal case where subsampling from selected bottles and multiple measurements after transformation is possible (Adriaan M. H. van der Veen et al., 2001).

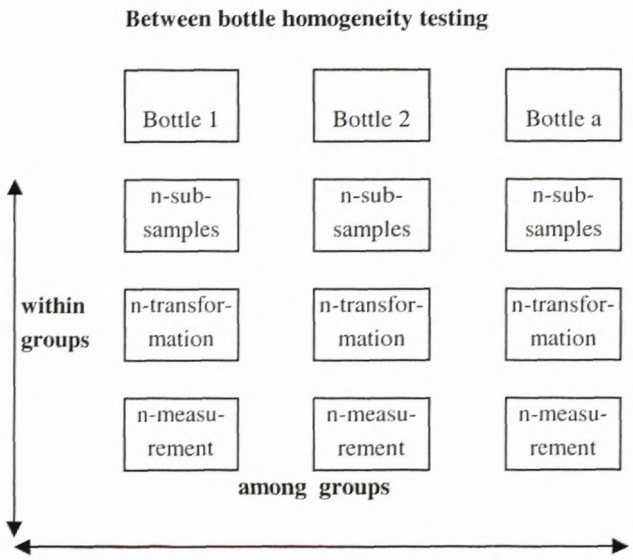

Fig.1 Between – bottle homogeneity study

Stability testing

The stability testing is second crucial point in characterisation of CRM. This testing can be performed when homogeneity of candidate reference material has been demonstrated. There are two types of stability testing, long term stability and short term stability. Long term stability gives an information about material that was exposed storage conditions and short term stability is associated with realistic conditions of transport.

The selection of testing condition will depend on the structure of the geological material and knowledge of behaviour of components of interest.

The frequency of testing for long term stability trials is usually 0, 3, 6 and 12 months and for a short term study is shorter period not longer than 4 weeks. Stored temperature of samples for long term stability is in general at room temperature and various temperatures (e.g., +4 °C, room temperature and 35 - 40 °C) are selected for short term study.

The measurement method applied for stability study, where the samples are analysed at different times should be choosen on the basis of its production of highly repeatable measurements.

Certification excercise

For the characterisation of geological matrix reference materials there are two approaches, first by a single method and second through the series of analysis carried out by multiple methods and laboratories. Second approach is mostly used through organized interlaboratory programme. The most important aspect for successful certification of candidate RM is that the organiser of interlaboratory programme should check if a group of competent and experienced laboratories in the area of analysis of geological materials is available to perform the certification measurements and if several independent methods are available. According to ISO Guide 35 the minimum number of participating laboratories is 15 or more.

The organiser should send to each participant one unit of RM with sufficient amount of material to allow the participant carry out minimum two replicate determinations, which should be made on separate test portion for all requiered certified properties and to use method of its choice. If the results from interlaboratory programme are to serve as a final confirmation of the homogenity of an RM, two units should be send to allow meaningful statistical processing of the results. For statistical treatment of data there exist many programmes and ISO guides which offer assistance. The results generated from Interlaboratory programme should be subjected to careful examination, outlieres thoroughly investigated and finally from these data certified value and its uncertainty are estimated.

The most important aspect in characterisation of RM is assigning final uncertainty of a CRM in which all sources of uncertainty should be considered. According to Guide to expression of uncertainty in measurement (GUM, 1993) the final uncertainty is expressed as:

$$u_{CRM} = [u^2_{char} + u^2_{bb} + u^2_{lts} + u^2_{sts}]^{1/2}$$

where:

– u_{char} is uncertainty of characterisation of the batch which was described in publication by Pauwels et al., 1998 and which includes standard uncertainties which are exclusively laboratory dependent, common to all of laboratories, such as the effect of between-bottle variation or use common calibrant and standard uncertainty common to groups of laboratories (labs using the same measurement procedure),

– u_{bb} is between-bottle uncertainty,
– u_{lts} is uncertainty for long term stability,
– u_{sts} is uncertainty for short term stability.

At the end of certification procedure the producer should prepare a report, which should include a full account of the procedures used for the preparation and certification of the RM and prepare records for issue of certificate according to ISO Guide 31, 2000. The certificate should include minimum following information:

– name and address of the certifying organization,
– title of the document,
– name of material,
– sample number,
– description of RM,
– intended use,
– instruction for correct use of RM,
– state of homogeneity, stability,
– certified property values and their uncertainties,
– ucertified values,
– values obtained by idividual laboratories or methods,
– date of certification,
– date of expiration,
– signatures or names of certifying officers.

Conclusion

The preparation and certification of reference material consists of several principal componets. The producer of RM should start with responsible planning of the project, thorough knowledge mineralogical and chemical composition of the material, methods used for sample preparation, homogenisation and bottling of the material. The choice of highly repeatible methods applied for homogeneity and stability study, selection appropriate groups of competent laboratories for performing of the determination of properties of the interest, knowledge of the statistical methods which are used for assignment of the certified values and their uncertainties, all of this is needed for successful and complex realisation of the preparation and certification of RM.

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