

# **Reference materials —**

## **Part 3: Guide to the uses of certified reference materials**

# Committees responsible for this Published Document

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- British Gas plc
- Chemical Industries' Association
- Consumers' Association
- Department of Trade and Industry (Laboratory of the Government Chemist)
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- Ministry of Defence
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- Royal Society of Chemistry
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## National foreword

This Part of PD 6532 has been prepared under the direction of the Quality, Management and Statistics Standards Policy Committee. It is identical with ISO Guide 33:1989 *Uses of certified reference materials* published by the International Organization for Standardization (ISO).

Three Parts of this Published Document have been published and these may be summarized as follows.

Part 2 *Guide to the contents of certificates of reference materials* (identical with ISO Guide 31:1981). This Part provides guidance on the preparation of clear and concise certificates of reference materials that summarize the information needed by the user of the reference material. The information that should be provided on a certificate is listed under a series of headings. Each heading is further explained and examples are provided where necessary.

Part 3 *Guide to the uses of certified reference materials* (identical with ISO Guide 33:1989). This Part provides guidance on the uses of certified reference materials (CRMs). The proper uses, and potential misuses, of CRMs are explained. Recommendations are presented for the assessment of the precision and trueness of a measurement process by the use of CRMs. The use of CRMs for the definition and realization of conventional measurement scales is discussed, including temperature, pH, octane number, soluble solids content (refractometric), turbidity, hardness and the Roga test for the classification of hard coals.

Part 4 *Guide to general and statistical principles for the certification of reference materials* (identical with ISO Guide 35:1989). This Part provides guidance on the concepts and practical aspects of the certification of reference materials. The roles of reference materials in quantitative measurements are described and important technical aspects of the certification of reference materials are considered including the measurement uncertainty associated with certified values. Commonly used methods for the certification of reference materials are discussed.

A further Part is in the process of being drafted and this is as follows.

Part 1 *Guide to terms and definitions used in connection with reference materials* (identical with ISO Guide 30:1992). This Part will recommend terms and the meanings that should be assigned to them, used in connection with reference materials. Particular attention will be given to terms that are used in reference material certificates and corresponding certification reports.

**Additional information.** The auxiliary “must” is avoided in British Standards and only the verb form “shall” is normally used to express mandatory requirements. The text of this Published Document reproduces the original ISO Guide 33 in which “must” and “shall” are employed extensively. As indicated by its title, this Published Document is a guide and the use of “shall” and “must” do not indicate mandatory requirements.

### Cross-references

| International Standard | Corresponding British Standard                                                                                                                                                                      |
|------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| ISO Guide 35:1985      | PD 6532 <i>Reference materials</i><br>Part 4:1992 <i>Guide to general and statistical principles for the certification of reference materials</i><br>(Identical)                                    |
| ISO 5725:1986          | BS 5497 <i>Precision of test methods</i><br>Part 1:1987 <i>Guide for the determination of repeatability and reproducibility for a standard test method by inter-laboratory tests</i><br>(Identical) |
| ISO 5163:1977          | BS 2637:1978 <i>Motor and aviation-type fuels — determination of knock characteristics — motor method</i><br>(Identical)                                                                            |
| ISO 5164:1977          | BS 2638:1978 <i>Motor fuels — determination of knock characteristics — research method</i><br>(Identical)                                                                                           |
| ISO 7027:1984          | BS 6068 <i>Water quality</i><br>Part 2 <i>Physical, chemical and biochemical methods</i><br>Section 2.13:1984 <i>Determination of turbidity</i><br>(Technically equivalent)                         |

There are no corresponding British Standards to ISO 3534:1977, ISO 2173:1978 or ISO 335:1974 to which informative reference is made in the text, but this does not adversely affect the validity of the standard.

### Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 16, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.



## Introduction: “Proper use” and “misuse” of CRMs

Today’s world of modern technology requires a vast number of certified reference materials (CRMs) in widely diverse fields and the demand for such materials is expected to increase. The preparation of a CRM is a time-consuming, meticulous and expensive endeavour and consequently it has not always been, and will continue not to be, possible to satisfy the demand for all types and quantities of CRMs. For this reason, CRMs must be used properly, i.e. effectively, efficiently and economically.

Certified reference materials must be used consistently to ensure reliable measurements. However, in doing so, the magnitude of the supply of that RM, its relative cost, its availability (accessibility) and the measurement technique, be it destructive or non-destructive, must be considered. Also important to the user is the fact that the misuse of an RM may not provide the intended information.

Misuse of CRMs differs from incorrect use. The user of a CRM is expected to be familiar with all information pertinent to the use of the CRM as specified by the producer. He should comply with such factors as the period of validity of the CRM, the prescribed conditions for storage of the CRM, instructions for the use of the CRM, and specifications for validity of the certified properties of the CRM. A CRM should not be used for a purpose other than that for which it was intended. Nevertheless, from time to time, when a user must resort to applying a CRM in an incorrect manner because of the unavailability of a suitable CRM, he must be fully cognizant of the potential pitfalls and therefore assess his measurement output accordingly.

There are many measurement processes where CRMs are in general use but are replaceable by a host of working standards such as homogeneous materials, previously analysed materials, pure compounds, solutions of pure elements, etc. Some examples are where only a “rough” estimate of the trueness or precision of a method is sought, where “blind” unknown check samples are used routinely in quality control programmes, and where only the variation in trueness or precision of a method with some parameter such as time, analyst, instrument, etc., is being evaluated. The first example illustrates the use of a CRM where the well-defined certified value and uncertainty of the CRM is under-utilized. The others illustrate the case where a series of “one-time” trueness and precision assessments are compared with one another. There is no need to base that comparison on a well-defined certified value and uncertainty of a CRM. The advantages in using CRMs are that the user has the means to assess the trueness and precision of his measurement method and establishes metrological traceability for his results.

Whether the use of CRMs in these procedures is in fact “misuse” depends largely on the availability and relative cost of the CRMs. Where CRMs are in short supply or very expensive, their use would indeed be misuse. However, for CRMs in ample supply or where similar CRMs are available from one or more producers, it is strongly recommended that CRMs always be used instead of working standards because of the resultant enhanced confidence in the measurement output.

It is important that users remain aware that the preparation of working standards for use instead of CRMs has an associated cost based on factors such as material cost, facility usage charges, personnel labour rates, etc., in which the material cost is in general the lowest. For some CRMs such as the complex compositional materials certified for chemical composition, the cost of preparing working standards to match the composition of real samples can exceed that of available CRMs. In these cases, the use of CRMs is recommended.

The user should be aware of the potential misuse of CRMs as “blind” unknown check samples in quality control programmes. Where there are only a few CRMs in an area of expertise, they are easily recognized and they may therefore not satisfy the intended purpose. Moreover, the same CRMs should never be used for both calibration purposes and as “blind” unknown check samples in a measurement process.

The misuse of CRMs can occur also when the user does not fully take into account the uncertainty in the certified property. The overall uncertainty of a certified property of a CRM can have contributions from the inhomogeneity of the material, the within-laboratory uncertainty and, where applicable, the between-laboratories uncertainty. The level of homogeneity defined for a CRM by the producer is dependent on both the statistical design used to evaluate it and the repeatability of the method of measurement. For certain CRMs, the level of homogeneity is valid for a test portion defined by mass, physical dimension, time of measurement, etc. The user must be aware that the use of a test portion that does not meet or exceed that specification could severely increase the contribution of the inhomogeneity of the CRM to the uncertainty of the certified property to the point where the statistical parameters of certification are no longer valid.

The variation in the repeatability of different methods has another implication for the user. Since the degree of inhomogeneity of a CRM is dependent on the repeatability of the method of measurement, it is possible that a user, in applying a method capable of better repeatability, could detect inhomogeneity in that CRM. In such cases, the observed inhomogeneity is already accounted for in the statistical parameters for the certified property and therefore the statistical tests presented in this Guide remain valid but the scientific basis for using that particular CRM to give a true assessment of the user's method must again be questioned.

It is well known that the methods of measurement of a property are not capable of equal repeatability. Accordingly there could arise instances where the user may wish to assess a method that has greater repeatability than that or those used in the certification of the CRM. In such cases, the statistical tests presented in this Guide remain valid but the scientific basis for using that particular CRM to give a true assessment of the precision (and possibly the trueness) normally expected from the user's method must be questioned. It is recommended that the user resort to a CRM of lesser uncertainty, if available.

For RMs certified by a “definitive” method, the user should not assume that his method is capable of matching the precision and trueness reported for the CRM. It is unreasonable therefore to apply the statistical procedures in this Guide for assessing the trueness and precision of a method by application to a CRM using the certification parameters for a property reported by the producer. The user, as a consequence, must either experimentally establish or make estimates based on available information for those parameters that are more appropriate. Similarly, where a user applies a method to an RM that has been certified by a single different method, the user must not assume that the certification parameters for the certified property are applicable to his method except in cases where the trueness and precision capable by both methods are known to be comparable.

One of the important considerations in selecting a CRM for use either in assessing the trueness and precision of a method or in the calibration of instruments in a method is the level of uncertainty required by the end-use of the method. Obviously the user should not apply a CRM of greater uncertainty than permitted by the end-use. This Guide states that the uncertainty of the replicated measurement of a CRM is twice the between-laboratories standard deviation of the certification programme, when this parameter is known, or four times the repeatability of the method on the CRM. These values represent the lowest level of uncertainty achievable with this CRM and may be used as a guide in determining whether it satisfies the uncertainty requirement of the end-use.

The selection of CRMs must take into account not only the level of uncertainty required for the intended purpose but also their availability, cost, and chemical and physical suitability for the intended purpose. For example, the unavailability or high cost of one CRM could force a user to resort to using another CRM of greater uncertainty than the preferred one. Also, in chemical analysis, a CRM of greater, but still acceptable, uncertainty in the certified property may be preferred over another CRM because of better matching with the composition of real samples. This could result in minimizing “matrix” or chemical effects in the measurement process which are capable of causing errors far greater than the difference between the uncertainties of the CRMs.

In conclusion, CRMs are meant to fulfil many purposes. Accordingly, a CRM used properly for one purpose in one laboratory may be misused for another purpose in another laboratory. It is recommended to the user that he consider the suitability of a CRM for his intended purpose on a case-by-case basis.