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Solid mineral fuels — Guidelines for the validation of alternative methods of analysis

Combustibles minéraux solides — Lignes directrices pour la validation de variantes analytiques

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Foreword

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This document was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

Solid mineral fuels — Guidelines for the validation of alternative methods of analysis

1 Scope

This document describes procedures for validating alternative methods of analysis for coal and coke either directly by comparison with the relevant International Standard method or indirectly by comparison with reference materials that have been exhaustively analysed using the relevant International Standard method.

The statistical analysis methods used are parametric, i.e. their use is possible only when the characteristic is expressed as a simple number on an approximately linear scale. The results from some methods, for example the Gray-King coke type, are not so expressed and the methods given here need to be used only if the data are converted to a parametric scale.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 5725-6:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 6: Use in practice of accuracy values*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
accuracy
closeness of agreement between a test result and the acceptable reference value

Note 1 to entry: The term accuracy, when applied to a set of results, describes a combination of random components and a common systematic error or bias component.

3.2
bias
difference between the expectation of the test results and an accepted reference value

Note 1 to entry: Bias is a systematic error as contrasted to random error. There may be one or more systematic error components contributing to the bias. A larger systematic difference from the accepted reference value is reflected by a larger bias value.

3.3
precision
closeness of agreement between independent test results obtained under prescribed conditions

Note 1 to entry: Precision depends only on distribution of random errors and does not relate to the accepted reference value.

Note 2 to entry: The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results. Higher imprecision is reflected by a larger standard deviation.

Note 3 to entry: "Independent test results" means results obtained in a manner not influenced by any previous result on the same or similar material.

3.4
trueness
closeness of agreement between the average value obtained from a large series of test results and an accepted reference value

Note 1 to entry: The measure of trueness is usually expressed in terms of bias.

4 General

An International Standard method is a measurement method that has been subjected to a standardization process to satisfy various requirements. Among these requirements, taken from ISO 5725-6:1994, Clause 8, are the following:

— The method shall be applicable to a wide range of levels of characteristics to cover most materials that are internationally traded.

EXAMPLE A method for the determination of sulfur content in coal is applicable to as many internationally traded coals as possible.

— Equipment, reagents and personnel shall be available on an international basis.

— The costs of performing the tests shall be acceptable.

— The precision and trueness of the measurement method shall be acceptable for the users of the results.

Many analytical methods for coal and coke are based on traditional combustion or wet-chemical analysis and the results are highly dependent on the test conditions. They are frequently time-consuming, labour- and skill-intensive and unsuited to automation. However, they meet the requirements of International Standard measurement methods, both in being internationally available and in providing acceptable levels of trueness and precision in international coal trade.

Other, non-standard methods of analysis are in use when

a) most of the material tested comes from the same source and the variation of its characteristics is relatively small. In such cases a simpler, less expensive method may be adequate;

b) an instrumental or automated version of the standard method provides much cheaper analysis of large numbers of samples. Such equipment may be much more expensive than the standard equipment or of a highly proprietary nature;

c) an instrumental method based on an analytical principle different from that of the standard method is available. Such methods have similar characteristics to 4 b) above.

In some cases, if it is possible to write a generic description of the method and the equipment is widely available, methods of types 4 b) and 4 c) above can be developed as International Standards. If an International Standard method already exists for analysis of a particular parameter, the new alternative method should be tested against the established method to ensure that it provides results that are comparable for trueness and accuracy. This is part of the process of issuing the alternative method as an International Standard.

Even if the equipment is widely available, it might not be possible to convert the method into an International Standard because of the proprietary nature of the equipment, speed of development and rapid obsolescence of such equipment.

The commercial pressure for cheaper, more rapid analysis has, however, meant that many analyses are carried out on equipment of this type. Some users develop their own in-house methods or use such methods for contractual purposes if agreed between both parties, provided that they can be ensured that the alternative method produces results that are comparable for accuracy and trueness with the International Standard method.

The purpose of this document is to give guidelines for such a validation, as applied to methods for testing of coal and coke. It is not intended to infer that the use of such alternative methods complies with the relevant International Standards nor is it for use in writing alternative International Standards. If the intention is to develop a new method into an International Standard, the procedures given in ISO 5725-6 should be used.

To summarize, alternative methods requiring validation range from simplified versions of the International Standard method to proprietary automated instrumental methods using principles entirely different from those of the International Standard method.

5 Preliminary work on the alternative method

5.1 General

Before any detailed comparison with the International Standard method is undertaken, it is necessary to investigate the performance characteristics of the alternative method. When buying specific commercial equipment, information on these aspects should be sought from the manufacturer. Many of the characteristics given below are applicable only to methods where the sample is in liquid form for the determination. For direct determination on solids (e.g. ash), little preliminary work is possible. Some of the main performance characteristics are given below, drawn from Reference[3].

5.2 Selectivity and specificity

Selectivity of a method refers to the extent to which it can determine particular analyte(s) in a complex mixture without interference from the other components in the mixture. A method that is perfectly selective for an analyte or group of analytes is said to be specific. The applicability of the method should be studied using various samples, ranging from pure standards to mixtures with complex matrices. Standard addition of pure analyte to coal/coke solutions should be used. In each case, the recovery of the analyte(s) of interest should be determined and the influences of suspected interferences stated. Any restrictions in the applicability of the technique should be documented in the method.

5.3 Range and linearity

The working range for a method is determined by examining samples with different analyte concentrations and determining the concentration range for which acceptable accuracy and precision can be achieved. While the working range of the analyte in solution may be determined using pure analyte or synthetic matrices containing analyte, the true range and linearity cannot be determined until a detailed comparison with the International Standard method is made on fuel samples.

5.4 Sensitivity

This is the difference in analyte concentration corresponding to the smallest difference in the response of the method that can be detected. It is represented by the slope of a calibration curve and can be determined by a least-squares procedure, or experimentally, using fuel samples containing various concentrations of the analyte.

5.5 Limit of detection

The limit of detection of an analyte is determined by repeat analysis of a blank test portion and is the analyte concentration whose response is the equivalent to the mean blank response plus three standard deviations. Its value is likely to be different for different types of sample.

5.6 Limit of quantitation

This is the lowest concentration of analyte that can be determined with an acceptable level of accuracy and precision, i.e. it is usually the lowest point on the calibration curve (excluding the blank). It should be established using an appropriate standard or sample; it should not be determined by extrapolation.

NOTE Within this document, “accuracy” is known as “trueness”.

5.7 Ruggedness

This is sometimes called robustness. Each time a method is used, small variations are inevitably introduced in the procedure, which may or may not have a significant influence on the performance of the method. The ruggedness of a method is tested by deliberately introducing small changes to the method, for example mass of sample and temperature of combustion, and examining the consequences. A large number of factors may need to be considered, but because most of these will have a negligible effect, it is normally possible to vary several at once.

5.8 Accuracy

The accuracy of a method is the closeness of the obtained analyte value to the true value. The overall accuracy can only be established by analysing suitable reference materials or comparison with the International Standard method (see Clause 7). For intermediate stages (i.e. solution finishes), an estimation of accuracy can be obtained by spiking test portions with chemical standards. The value of spiking is limited; it can only be used to determine the accuracy of those stages of the method following the spiking.

5.9 Precision

The precision of a method is a statement of the closeness of agreement between mutually independent test results and is usually stated in terms of standard deviation. It is generally dependent on analyte concentration, and this dependence should be determined and documented. It may be stated in different ways depending on the conditions for which it is calculated. Repeatability is a type of precision relating to measurements made under repeatability conditions, i.e. same method, same material, same operator, same laboratory, different time but within a narrow time period. Preliminary estimations of precision of the alternative method may be made, for example, by comparing the results of duplicate samples for the ruggedness tests.

6 Defining the alternative method to be validated

Once the preliminary work on the alternative method (see Clause 5) has shown that it is likely to be suitable for the intended purpose, the test conditions for the method should be chosen and clearly and unambiguously defined in a manner similar to the way in which International Standard methods are defined. Critical test parameters vary with the type of test and cannot be exhaustively listed in this document. Examples of some parameters commonly found in coal and coke analysis are as follows:

a) mass of sample and solid reagents, plus critical range;

b) condition of sample, moisture content, particle size, particle size range;

c) accuracy of measuring equipment for temperature, mass, volume;

d) purity of reagents, accuracy of solution concentration;

e) furnace temperature, with critical dimensions of the hot zone where relevant;

f) length of time of combustion/heating;

g) atmosphere in the furnace/oven;

h) in spectroscopic determinations, cell path length, wavelength;

i) calibration procedures.

When automated instruments are operated under pre-set conditions, these conditions should be defined as closely as possible; all variable settings of the instrument should be defined. Particular attention should be paid to those instruments whose settings can be altered by modification of a computer program where any change might not be immediately apparent to the operator. Some method of checking that the program has not been altered from the standard conditions should be devised.

The test procedure should be written, again in a manner similar to that of an International Standard, so that subsequent operators are able to follow the method identical to that used during validation.

7 Procedure

7.1 Measurement of precision and trueness

7.1.1 Precision

Measure the precision of results in terms of the standard deviation of a set of analyses carried out under repeatability conditions. The precision of the alternative method is measured directly by making replicate analyses of samples.

If the alternative method is to be validated using reference samples, then calculate the standard deviation of the International Standard method from the repeatability limit given in the International Standard method.

If a direct comparison is to be made between the two methods, then determine the precision of the International Standard method directly by analysing samples in replicate. This will be a more accurate measure than that calculated from the International Standard because the precision of the two methods on the analysis of the same fuels is compared, rather than a precision determined at the time of development of the International Standard on fuels whose identity is unlikely to be known.

7.1.2 Trueness

Estimate the trueness either by comparing the results obtained by analysing a reference material using the alternative method with the reference value (see 7.2) or by comparing results on the same fuels using both the alternative and International Standard methods (see 7.3).

Measurement of trueness can only be an estimate, the errors of which are measured by considering the variability of the differences between the results. The greater the variability, the greater the estimation error, the more results that are compared, the lower the estimation error.

Two different statistical analysis methods (A and B) are given in this document.

Method A (see 7.2.2.1 and 7.3.2.1 for details) is recommended as the most rigorous. Decide before starting on the maximum tolerable bias, MTB, and design the test to be sufficiently sensitive to detect that bias, should it exist. Carry out a sufficient number of analyses to make the statistical test powerful enough to conclude either that

a) the bias is significantly greater than zero and not significantly less than MTB, or

b) the bias is significantly less than MTB and not significantly greater than zero.

In a simpler test (method B; see 7.2.2.2 and 7.3.2.2 for details), compare a fixed number of results and, unless the mean difference fails a null hypothesis test, it can be concluded that no bias exists between the two methods. If the estimation error is too great, however, it is also possible that a bias at an unacceptable level could exist. To obviate such an ambiguous conclusion, use method A.

The difficulty with method A is in deciding what value to assign for MTB. However, with method B, it is necessary to a make a judgement, after the result, as to what bias levels are tolerable. For either method, therefore, it is necessary to consider the practical implications of any possible bias and to make a rational judgement on what level is unacceptable.

7.2 Comparison with reference materials

7.2.1 Sources of reference materials

Coal and coke reference materials samples are widely available commercially. Before use, investigate the traceability, authority and methods of analysis. Obtain details of homogeneity trials, stability trials, the methods used for certification and the uncertainty and variations in the stated analyte values from the producer and use them to judge the pedigree. In order to compare the alternative method with the International Standard method, use only reference materials that have been analysed using the International Standard method. Where an International Standard method contains a major element of choice, quote the subclauses from the International Standard giving details of that variation.

Reference materials should be clearly labelled and stored under the specified conditions and should be safeguarded against contamination or loss of determinand.

Select reference materials to be of the same type of fuel and to have the same analyte concentration ranges as those which are to be analysed routinely by the alternative method. Some factors which should be considered are coal rank, coke type or manufactured fuel type.

Where the range of fuels to be tested is very wide or reference materials of the appropriate type cannot be obtained, test the method against the International Standard method (see 7.3 or 7.4).

Two methods are given for the estimation of trueness. The recommended method, method A, requires the specification, before any analysis is done, of the greatest bias (the maximum tolerable bias) that the user is prepared to risk; testing continues until an unambiguous conclusion is reached. In a simpler method, method B, a fixed number of analyses is performed and a conclusion drawn from the result. In the latter method, there is a possibility that an alternative method is considered to be unbiased even though there is a risk that it is biased to an unacceptable extent.

7.2.2 Estimation of trueness

7.2.2.1 Method A

Decide on a value for the maximum tolerable bias, B (see 7.1.2).

Calculate the standard deviation of the International Standard, s_{ISO}, method using Formula (1):

$$s_{ISO} = \frac{r}{2\sqrt{2}} \tag{1}$$

where

s_{ISO} is the standard deviation of the International Standard method under repeatability conditions;

r is the repeatability limit for the International Standard method.

Calculate the value of g using Formula (2):

$$g = \frac{B}{s_{ISO}} \tag{2}$$

Using Table 1, calculate the number of replicate tests, n, necessary to identify the MTB.

Table 1 — Values for factor g for calculating the number of analyses required

	0	1	2	3	4	5	6	7	8	9
0	—	—	—	4,170	2,728	2,195	1,872	1,659	1,506	1,389
10	1,295	1,218	1,154	1,099	1,051	1,009	0,972	0,938	0,907	0,880
20	0,855	0,832	0,810	0,790	0,772	0,755	0,739	0,724	0,710	0,696
30	0,684	0,672	0,660	0,649	0,639	0,629	0,620	0,611	0,602	0,594
40	0,586	0,579	0,571	0,564	0,558	0,551	0,545	0,539	0,533	0,527
50	0,521	0,516	0,511	0,506	0,501	0,496	0,491	0,487	0,483	0,478
60	0,474	0,470	0,466	0,463	0,459	0,455	0,451	0,448	0,445	0,441
70	0,438	0,435	0,432	0,429	0,426	0,423	0,420	0,417	0,414	0,411
80	0,409	0,406	0,404	0,401	0,399	0,396	0,394	0,392	0,389	0,387
90	0,385	0,383	0,380	0,378	0,376	0,374	0,372	0,370	0,368	0,366
NOTE	The number of sets required corresponding to a given g factor is the sum of the column and row headings.									

Analyse the reference material using the alternative method n times.

Calculate s_{ALT} using Formula (3):

$$s_{ALT} = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{(n-1)}} \tag{3}$$

where

$\sum x$ is the sum of all the results;

$\sum x^2$ is the sum of the squares of the results;

n is the number of the results.

Recalculate g and hence n. If the new value for n is greater than the number of analyses already done, then carry out additional analyses to reach n. Continue with this process until enough analyses have been carried out.

Calculate the value of the mean difference of the analytical values from the reference value, $\bar{d}$, using Formula (4):

$$\bar{d} = \frac{\sum x_i}{n} - R \tag{4}$$

where

x_i is the analytical value of the ith determination;

R is the reference value.

Calculate the statistic, t_c, from Formula (5):

$$t_c = \frac{\bar{d}\sqrt{n}}{s_{ALT}} \tag{5}$$

Compare with the value of t_t from Table 3 at $(n - 1)$ degrees of freedom.