BRITISH STANDARD

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15239:2005

# Solid mineral fuels — Evaluation of the measurement performance of on-line analysers

ICS 75.160.10

British Standards

# National foreword

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The UK participation in its preparation was entrusted to Technical Committee PTI/16, Solid Mineral Fuels, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep UK interests informed;
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## Summary of pages

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# INTERNATIONAL STANDARD

# ISO 15239

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# Solid mineral fuels — Evaluation of the measurement performance of on-line analysers

*Combustibles minéraux solides — Évaluation de la performance de mesure des analyseurs en ligne*

Reference number
ISO 15239:2005(E)

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# Foreword

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ISO 15239 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

# Introduction

There are now many instruments in use which have been developed to enable the rapid on-line measurement of solid mineral fuels for a range of parameters that indicate coal quality. The principles on which they are based differ from those currently in use for sampling and analysis and, in effect, constitute a completely different approach to the measurement of solid mineral fuel quality.

This standard has been developed to specify methods by which the measurement performance of such analysers can be evaluated.

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# Solid mineral fuels — Evaluation of the measurement performance of on-line analysers

## 1 Scope

This International Standard sets out practices for the evaluation of the measurement performance of all types of on-line analysers for solid mineral fuel.

It presents information on the different types of analyser currently available and describes procedures for the evaluation of various aspects of measurement performance, appropriate methods of test and techniques for the statistical assessment of the data collected.

## 2 Normative references

The following referenced documents are indispensable for the application 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 1213-2, *Solid mineral fuels — Vocabulary — Part 2: Terms relating to sampling, testing and analysis*

ISO 1988, *Hard coals — Sampling*

ISO 2309, *Coke — Sampling*

ISO 3534-1, *Statistics — Vocabulary and symbols — Part 1: Probability and general statistical terms*

ISO 5069 (all parts), *Brown coals and lignites — Principles of sampling*

ISO 13909 (all parts):2001, *Hard coal and coke — Mechanical sampling*

## 3 Terms and definitions

For the purposes of this document, the definitions given in ISO 1213-2, ISO 3534-1 and ISO 13909-1 and the following apply.

**3.1**
**accuracy**
closeness of agreement between an observation and the “true” value

[ISO 1213-2:1992]

**3.2**
**analyser dynamic precision**
closeness of agreement between analyser values, obtained from solid mineral fuel interrogated by the analyser under dynamic conditions and determined by a comparative test method which eliminates random errors attributable to the reference test method

**3.3**
**analyser test method**
method of analysis which gives, for a solid mineral fuel process stream, values arising from the operation of the on-line analyser, which are estimates of the true values for specified measurands

**3.4**
**analyser value**
value of a specified measurand in a test unit that is obtained from a test carried out by an analyser test method

**3.5**
**backscatter geometry**
arrangement of an interrogation process in which a source of incident energy and a detector system are on the same, or adjacent, sides of the solid mineral fuel passing through the interrogation zone

**3.6**
**bias**
systematic error which leads to the average value of a series of results being persistently higher or persistently lower than those which are obtained using a reference test method

[ISO 13909-1]

**3.7**
**bias of scale**
bias that varies as a function of the range of values measured

**3.8**
**bias of location**
bias that is constant and independent of the range of values measured

**3.9**
**comparative dynamic precision**
closeness of agreement between analyser values obtained from solid mineral fuel interrogated by the analyser under dynamic conditions and those determined by a comparative test method, which includes random errors attributable to the reference test method

**3.10**
**comparative test method**
method of testing in which analyser values are compared with corresponding reference values

**3.11**
**comparison period**
period of time, during which a test unit is interrogated by an analyser to give an analyser value and is sampled by a reference test method to obtain a reference value, for a measurand

NOTE The period can be based on the typical time to produce a particular mass of solid mineral fuel, e.g. a trainload, or on a period which coincides with operations, e.g. a shift, or some other period that is convenient to, or preferred for, a specific evaluation procedure.

**3.12**
**interrogation process**
procedure which elicits from the solid mineral fuel process stream a measurable response related, specifically or by inference, to the quantity of the measurand

**3.13**
**interrogation volume**
volume of the solid mineral fuel process stream in which the detected response to the interrogation process originates

**3.14**
**interrogation zone**
part of the analyser installation through which the solid mineral fuel process stream passes and in which it is subjected to the interrogation process

**3.15**
**mainstream configuration**
configuration in which the whole of the process stream to be analysed is presented to, although not necessarily analysed by, an on-line analyser

**3.16**
**on-line analyser**
instrument for the measurement, continuously, of one or more quality indicators of solid mineral fuel while it is undergoing processing or handling, to give data rapidly and automatically

**3.17**
**precision**
closeness of agreement between independent results obtained under stipulated conditions

[ISO 3534-1:1993]

NOTE For the purposes of this International Standard, the index of precision used is $\pm ts$, where $t$ is the value of Student's $t$ (95 % confidence level, two-sided) and $s$ is the standard deviation of the observations about the mean value.

**3.18**
**reference test method**
method of sampling, sample preparation and analysis which is expected to give, for a solid mineral fuel process stream, values which are unbiased estimates of the true values for specified measurands

**3.19**
**reference value**
value of a specified measurand in a test unit that is obtained from a test carried out by a reference test method and which serves as a reference for comparison with an analyser value

NOTE For the purposes of this International Standard, reference values are considered to be conventional true values.

**3.20**
**sample**
quantity of fuel, representative of a larger mass, for which the quality is to be determined

[ISO 13909-1]

**3.21**
**static repeatability**
closeness of agreement between replicate analyser values obtained from a reference standard in the interrogation zone of the analyser

**3.22**
**sub-stream configuration**
configuration in which a part of the process stream to be analysed is diverted by means of a suitable sampling system for presentation to an on-line analyser

**3.23**
**test unit**
quantity of solid mineral fuel chosen for the determination of analyser and reference values

**3.24**
**transmission geometry**
arrangement of an interrogation process in which a source of incident energy and a detector system are on opposite sides of the solid mineral fuel passing through the interrogation zone.

# 4 Symbols and abbreviations

## 4.1 Mathematical

### 4.1.1 Primary

| | |
|---|---|
| $\beta$ | regression coefficient (slope) |
| $C$ | Cochran's criterion |
| $d$ | difference between pairs of values (other than duplicates) |
| $D_1$ | duplicate 1 reference test method value |
| $D_2$ | duplicate 2 reference test method value |
| $\overline{D}$ | mean of duplicate reference test method values |
| $\delta$ | test statistic (see D.16) |
| EIV | errors in variables |
| $E(\rho)$ | expected number of runs |
| $F$ | $F$-distribution |
| $f_{\mathrm{SDR}}$ | static/dynamic response factor |
| $L_{\mathrm{C}}$ | confidence level |
| $n$ | number of values in a set |
| $P$ | precision |
| $Q$ | test statistic (see D.16) |
| $R$ | reference test method value |
| $R_1$ | reference test method 1 value |
| $R_2$ | reference test method 2 value |
| $r$ | linear correlation coefficient |
| $\rho$ | run |
| $S_1$ | reference standard 1 value |
| $S_2$ | reference standard 2 value |

| | |
|---|---|
| — $s$ | standard deviation |
| — $s_{\mathrm{g}}$ | the expected (guaranteed) value of precision of the analyser at one standard deviation |
| — $s(\rho)$ | standard error of number of runs |
| — $\sigma$ | population standard deviation |
| — $t$ | Student's *t*-distribution |
| — $V$ | variance |
| — $\nu$ | degrees of freedom |
| — $X_{\mathrm{A}}$ | analyser test method value |
| — $x$ | any value in a set |
| — $x_{\mathrm{dup}}$ | difference between pairs of duplicate values |
| — $\chi^2$ | chi-squared distribution |
| — $Z$ | test statistic (see D.16) |
| — $z$ | normal deviate |

### 4.1.2 Subscripts

| | |
|---|---|
| — A | set of analyser test method values |
| — c | critical value |
| — d | set of differences |
| — dup | set of duplicate differences |
| — Dy | set of dynamic calibration values |
| — D1 | set of duplicate reference 1 test method values |
| — D2 | set of duplicate reference 2 test method values |
| — $\overline{\mathrm{D}}$ | set of means of duplicate reference test method values |
| — g | guaranteed value |
| — $i$ | *i*th value |
| — max | maximum value |
| — 0 | time zero |
| — R1 | set of reference test method 1 values |
| — R2 | set of reference test method 2 values |

| | |
|---|---|
| — St | set of static calibration values |
| — S1 | set of reference standard 1 values |
| — S2 | set of reference standard 2 values |
| — $\tau$ | time |
| — 1 | set 1 |
| — 2 | set 2 |

### 4.2 Other abbreviations

| | |
|---|---|
| — GHz | gigahertz |
| — keV | kilo-electron volt |
| — MeV | mega-electron volt |
| — RF | radiofrequency |

## 5 Principle

The performance of an on-line analyser, which has been set up and calibrated, is evaluated by procedures that address three main aspects of analyser operation. These are the stability of the instrumentation, the validity of the calibration and the precision of measurement under operational conditions. Instrument stability is assessed by static measurements made, in replicate, at operationally significant intervals of time. The installed calibration is confirmed by making simultaneous comparative measurements with the analyser and a reference method of analysis over a range of measurand values which encompasses at least the spread of values encountered in normal operations. Operational performance is evaluated by comparison of analyser values with reference values obtained from separate reference procedures.

## 6 Analyser installations

### 6.1 General

There are many types of analyser, based on a variety of measurement principles and possible installation configurations, which have been designed to measure one or more indicators of quality in a range of products that occur in solid mineral fuel process streams.

The measurement principles on which analysers are based may be divided into four classes, as outlined in 6.2.

### 6.2 Analyser types

#### 6.2.1 Absorption/scattering processes

The majority of on-line analysers for solid mineral fuel depend upon the existence of a quantitative relationship between the measurand and the degree of absorption and/or scattering of a beam of electromagnetic radiation or neutrons incident upon the solid mineral fuel flowing through the interrogation zone of the analyser. Incident electromagnetic radiation, in the X-, gamma, microwave or optical energy regions, or neutron radiation may be used; source, sample and detector may be arranged in transmission or backscatter geometry.

### 6.2.2 Excitation processes

A second group depends on a quantitative relationship between the measurand and the emission of specific electromagnetic radiation, (X- or gamma rays) arising as a result of excitation by an outside source of X-, gamma or neutron radiation.

### 6.2.3 Natural radiation emission

In this class, the gamma radiation emitted by naturally occurring radioisotopes, present in the measurand in relatively constant proportions, is measured.

### 6.2.4 Property changes

A few analysers depend upon an effect of the measurand on a selected electrical or physical property that is measurable on line.

NOTE Annex A gives information on techniques for on-line analysis.

## 6.3 Methods of presentation

The solid mineral fuel to be analysed may be transported through or past the analyser on a conveyor belt or other supporting platform, or within the confines of a container, chute or pipe. In most designs, the analyser detection system is physically non-invasive and non-contacting with the solid mineral fuel.

The condition of the solid mineral fuel presented to the analyser varies, among the methods of analysis, from material as it occurs in the process stream, to crushed, mixed and possibly dried material which has been carefully profiled.

The solid mineral fuel may be presented to the analyser as a bulk solid or as a fuel-water slurry.

Two basic installation configurations for on-line analysers are possible (see Figure 1). The choice between the two for any particular application depends on the type of analyser appropriate to the measurand and certain parameters of the product and the plant, such as particle size and flow rate.

## 6.4 Installation configurations

### 6.4.1 Mainstream

A mainstream configuration is a system in which the whole of the process stream for which the analytical information is required is presented to the analyser. The system can contain conditioning steps, such as mixing and profiling, prior to interrogation by the analyser.

### 6.4.2 Sub-stream

A sub-stream configuration is a system in which a portion of the process stream is diverted to the analyser by means of a suitable sampling process. The diverted portion of the stream may be subsequently subjected to sample preparation procedures, such as crushing, dividing and conditioning before presentation to the analyser. After interrogation the sub-stream is normally returned to the main process stream.

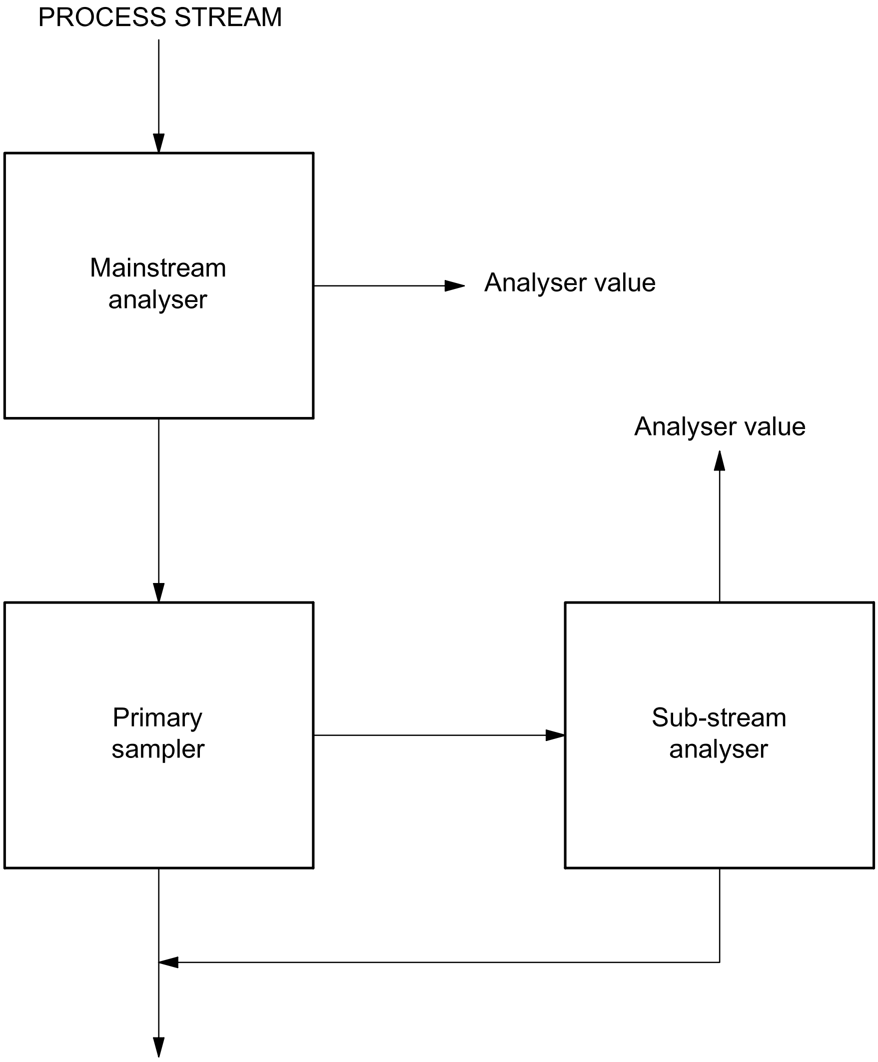


**Figure 1 — Analyser configurations**

## 7 Evaluation techniques

The procedures described in this International Standard are designed to allow the evaluation of analyser performance in a range of situations and conditions of operation.

They are intended to be applied to an analyser after it has been set up and calibrated as recommended by the manufacturer, with all instrumental parameters at their normal operational values for the particular installation.

In order to make a full evaluation of on-line analyser performance, it is necessary to address three interdependent aspects of analyser operation:

- instrument stability;
- calibration confirmation;
- operational measurement performance.

Since some of the measurement errors that are attributable to the analyser occur only as a result of operations on, or interactions with, the moving process stream, it is essential for a full evaluation of measurement performance to carry out tests under dynamic conditions.

Nevertheless, information from static tests, although more limited in its nature, is useful for monitoring some aspects of analyser performance on a routine basis.

An understanding of the sources of variance that contribute to the errors of measurement of the analyser and of any reference system with which it is compared, is necessary for the proper design of tests and the evaluation of the results. Sources of variance are discussed in Annex B.

The procedures used vary with the situation but have many features in common. General considerations for the design and operation of comparative tests are given in Annex C and techniques for the statistical analysis of the data in Annex D.

The principal steps involved in an evaluation are as follows:

- decide which aspect of analyser operation is to be evaluated (see Note);
- choose an appropriate method of test and design a scheme of operation;
- carry out the test procedure;
- apply appropriate statistical treatment to the data obtained from the test.

NOTE Frequently a situation will require more than one aspect to be considered (see Clause 11).

## 8 Instrument stability

### 8.1 General

It is a pre-requisite to accurate measurement by an on-line analyser that the instrumentation be stable and contribute as little as possible to the total error of measurement. Errors arising from the instrumentation may be random or systematic.

An estimate of random variations attributable to the instrumentation is obtained by determining the static repeatability. A significant increase in this value with time is an indicator of changes in instrumental characteristics that may need investigation and could lead to a worsening of the measurement performance of the analyser. Static repeatability is also an indicator of the limiting value of accuracy achievable (base-line performance).

Systematic instrumentation changes, which could affect the calibration if they are sufficiently large, are indicated by changes in the level of response from reference standards. These changes can provide the information needed to compensate for systematic instrumentation errors. In some analysers this process is carried out automatically at intervals and a correction applied.

Random and systematic variations originating in the instrumentation can be measured simultaneously by a relatively simple procedure that is amenable to routine use.

### 8.2 Objectives

The test methods and methods of data analysis described in 8.3, 8.4 and 8.5 are designed to achieve three objectives:

- to establish benchmarks against which subsequent tests for variations due to instrument instability may be compared;

- to determine and monitor the contribution made to the overall measurement performance of the analyser by random variations in response originating in the instrumentation;
- to monitor systematic changes in response, originating in the instrumentation, which may affect calibration.

## 8.3 Test conditions

Test conditions require

- a measurement period that will return an adequate precision to allow the testing of the significance of any changes from previous measurements,
- a minimum of 10 periods (see note).

NOTE A larger number of periods will increase the precision, but with diminishing returns; a practical maximum is probably about 20.

## 8.4 Test procedure

Make an initial set of consecutive replicate measurements under the chosen test conditions with a reference standard (see Notes 1 and 2) in the interrogation zone of the analyser. If it is required to detect systematic changes, repeat with a second reference standard that offers a different level of response from the first one. Designate these as measurements made at time 0. The levels of response from the standards chosen for the detection of systematic changes should be representative of those which are obtained from values of measurands close to each end of the calibration range. This will ensure that any shift of the calibration line and/or change in slope is signalled.

After an interval, repeat the above procedure. Designate these as measurements made at time $\tau$. A suitable interval depends upon the usual operating programme of the analyser. The repeat test should normally be part of a regular check routine at intervals of a shift or a day, for example. A special check should be undertaken after any system changes (see Clause 11).

NOTE 1 Information on suitable reference standards is given in Annex E.

NOTE 2 Evaluation of instrument stability might not be possible with some designs of analysers that cannot accept a reference standard. In others, a suitable response might be available from the empty interrogation zone.

## 8.5 Data analysis

### 8.5.1 General

Consider measurements made at time 0 to be benchmarks against which subsequent measurements made at time $\tau$ are compared.

If, at time $\tau$, the instrumental parameters in use when the benchmark performance was established have changed, normalize the data obtained for the test at time $\tau$ with respect to those changes.

### 8.5.2 Measurement precision

**8.5.2.1** For each set of observations calculate the following values:

- variance, $V_{\mathrm{S1}}$ and $V_{\mathrm{S2}}$ (see D.2);
- standard deviation, $s_{\mathrm{S1}}$ and $s_{\mathrm{S2}}$ (see D.3);
- precision, $P_{\mathrm{S1}}$ and $P_{\mathrm{S2}}$ (see D.4).

**8.5.2.2** Test the following for significance:

- ratio of the variances, $V_{\mathrm{S}1,0}$ and $V_{\mathrm{S}1,\tau}$ (see D.5);
- ratio of the variances, $V_{\mathrm{S}2,0}$ and $V_{\mathrm{S}2,\tau}$ (see D.5).

### 8.5.3 Changes in response level

**8.5.3.1** For each set of observations, calculate the following:

- mean values, $\overline{S_1}$ and $\overline{S_2}$ (see D.6);
- differences of the means, $\overline{S_{1,0}}$ and $\overline{S_{1,\tau}}$ $\overline{S_{2,0}}$ and $\overline{S_{2,\tau}}$ .

**8.5.3.2 Test the following for significance:**

- difference of the means, $\overline{S_{1,0}}$ and $\overline{S_{1,\tau}}$ (see D.7);
- difference of the means, $\overline{S_{2,0}}$ and $\overline{S_{1,\tau}}$ (see D.7).

## 8.6 Results and interpretation

Record the following information:

- the date of the test;
- the identity of the reference standard(s) used;
- relevant instrument parameters;
- the conditions of the test;
- the values of the individual observations;
- the values calculated in 8.5;
- the results of the significance tests.

The calculated value of $P$ indicates the base-line performance of the analyser, i.e. a lower limiting value for operational accuracy over a similar measurement period. In practice, this value cannot be achieved since other sources of variation, outside the analyser instrumentation, also contribute to operational accuracy.

When an acceptable initial value for variance has been determined (see 11.2) or re-established (see 11.4), designate it $V_{\mathrm{S}1,0}$. If a subsequent determination of variance, $V_{\mathrm{S}1,\tau}$, is not significantly different from $V_{\mathrm{S}1,0}$, then the instrumentation may be considered to be stable with respect to its contribution to random errors in the measurement of operational accuracy. If this is not the case, examine the instrumentation for the cause of the change.

When acceptable initial values for variance have been determined or re-established, designate the mean values of the observations as $\overline{S_{1,0}}$ and $\overline{S_{2,0}}$ . If, in a subsequent determination, at time $\tau$, there is no significant difference between $\overline{S_{1,0}}$ and $\overline{S_{1,\tau}}$ ,or between $\overline{S_{2,0}}$ and $\overline{S_{2,\tau}}$ , then it can be concluded that the instrumentation response has not changed in a way that will affect the calibration. If one or both differences are significant, then there has been a change that could affect the calibration. Whether it will translate to a detectable change in the calibration depends on the size of other sources of error outside the instrumentation and the precision with which the calibration is defined. Consider confirmation of the calibration (see Clause 9).

# 9 Calibration

## 9.1 General

Since on-line analysers can only make measurements by reference to values obtained by some other method, the establishment and maintenance of a sound calibration is vital to accurate measurements.

The procedures described under 8.3 and 8.4 provide information that can be used to make corrections to the calibration line for errors due to instrumentation variations. However they offer no help in detecting systematic changes due to other sources, such as changes in the quality of the fuel, in its presentation or in the reference sampling and analysis scheme. This can be achieved only by undertaking a test described in this section.

A particular problem may occur with a well-controlled system that maintains product quality within a narrow range of values. It can be very inconvenient or even difficult to obtain, under dynamic conditions, a range of values that is wide enough to define a calibration with adequate precision. In that case, this International Standard describes a procedure (the static calibration), that is based on samples obtained other than under dynamic conditions.

## 9.2 Objective

To confirm that a previously installed calibration remains valid and appropriate to the current operating conditions.

## 9.3 Dynamic calibration

### 9.3.1 Test conditions

Test conditions include

- a two-instrument test scheme set up in accordance with the principles outlined in C.2,
- a comparison period that is of sufficient duration to allow enough reference sample increments to be taken to achieve a high degree of reference sample precision (see C.5 and C.6),
- a set of reference samples that adequately covers the full range of values to be expected under operating conditions,
- a minimum of 15 comparison periods (see C.5).

It might not always be possible to obtain a full range of expected values within a continuous test period. If this is the case, data obtained from further test periods may be added to the initial data provided that stability of the instrumentation has been shown to be satisfactory (see Clause 8) and the new data are consistent with it. (See ISO 13909-8:2001, 11.5, for tests of homogeneity of data).

### 9.3.2 Test procedure

For each comparison period defined in the conditions of test, collect duplicate reference samples as described in ISO 13909-7:2001, Clause 7 and log the corresponding data, $X_{\mathrm{A}i}$) from the analyser. Ensure that the collection of samples and data are properly synchronised and that sets of data all relate properly to their respective comparison periods. Prepare and analyse the duplicate test samples to give reference duplicate values ($D_{1i}$ and $D_{2i}$).

## 9.4 Static calibration

### 9.4.1 General

The response of an analyser to solid mineral fuel presented under static conditions is unlikely to be the same as that presented dynamically. In order to check the calibration using static samples, it is necessary first to compare the analyser response under static and dynamic conditions and determine a correction factor designated the static/dynamic response. This correction can then be applied to estimate the relationship between analyser and reference values under dynamic conditions.

### 9.4.2 Test conditions

Test conditions include

- a two-instrument test scheme set up in accordance with the principles outlined in C.2,
- a measurement period that will minimize variations due to instrumentation,
- a minimum of 10 reference samples for static/dynamic response,
- a minimum of 15 samples of the product that adequately cover the full range of values to be expected under operating conditions for static test.

### 9.4.3 Test procedure

#### 9.4.3.1 Static/dynamic response

Collect reference samples under normal operating conditions. Log the corresponding analyser readings, $X_{\text{ADy},i}$. Prepare a static calibration sample from each reference sample. The quantity and condition of the static calibration samples will depend on the design of the on-line analyser. Typically, for an on-belt ash analyser for instance, about 5 kg of air-dried coal crushed to a top size of 1 mm is suitable. It is important that all samples in a set be prepared in the same manner using the same equipment. Present the static calibration samples to the analyser and log the analyser readings, $X_{\text{A}i}$. Determine the static/dynamic response factor ($f_{\text{SDR}}$; see D.8).

#### 9.4.3.2 Static test

Collect a set of samples, not necessarily under dynamic conditions. From each sample prepare a static calibration sample and duplicate analysis test samples.

Present each static calibration sample to the analyser, under static conditions, for the chosen measurement period. Log the data, $X_{\text{A}i}$, and analyse each duplicate test sample, $D_{1i}$ and $D_{2i}$. Correct the results by adding the $f_{\text{SDR}}$ (see 9.4.3.1) to each static analyser value.

## 9.5 Data analysis

### 9.5.1 General

Calculate the following:

- mean duplicate reference values $\overline{D}_i$;
- differences, $d_{\text{i}}$, between the analyser values $X_{\text{A}i}$ (corrected in the case of static test) and the mean duplicate reference values $\overline{D}_i$.

### 9.5.2 Visual assessment

Plot a graph of the analyser values, $X_{\mathrm{A}i}$, against the mean duplicate reference sample values $\overline{D}_i$, and assess visually for the presence of possible outliers and other problems (see D.9.2).

It is recommended that other graphical procedures outlined in D.9 also be carried out before a full statistical analysis of the data is undertaken.

### 9.5.3 Outliers

Check for outliers by the statistical procedure of Cochran's criterion (see D.10.2). Consider possible outliers identified in this way for removal in accordance with the criteria defined in D.10.3. Remove those values that meet the criteria.

### 9.5.4 Independence of differences

Test the list of differences for independence between observations: (see D.11).

If the test is satisfactory, continue with the test for bias. Otherwise, discard the data and examine the scheme for possible causes. Modify the test scheme if appropriate and repeat the test.

### 9.5.5 Tests for bias

Calculate the slope of the linear regression of the analyser values, $X_{\mathrm{A}i}$, on the mean duplicate reference values $\overline{D}_i$ using an "errors-in-variables" (EIV) method (see D.12.1)

Calculate the variance of this slope (see D.12.2)

Test for existence of significant bias of scale (see D.13)

If there is no significant bias of scale, test for bias of location (see D.14)

## 9.6 Results and interpretation

Record the following information:

- date of the test;
- identity of the product;
- relevant instrument parameters;
- conditions of the test;
- values of the individual observations;
- results of the tests in 9.5.

Tests for bias of scale and total bias are made with reference to the current calibration that is described in this test by the relationship $X_{\mathrm{A}i} = \overline{D}_i$. In the case of commissioning tests (see 11.2), the current calibration is the preliminary calibration installed in accordance with the manufacturer's instructions. Otherwise it is a calibration installed following a previous test of this kind.

If there is a significant change in bias of scale or of bias of location, which cannot be attributed to systematic instrumentation variations (see 8.6), examine the reference method scheme for possible sources of variation which have arisen since the previous confirmation of the calibration. Changes in solid mineral fuel quality are also potential sources of systematic error to be considered. If the additional source of error cannot be identified and eliminated, install a new calibration based on the relationship found between analyser and reference values in the current test.

## 10 Operational measurement performance

### 10.1 General

When the analyser calibration has been established and the absence of significant bias demonstrated, the precision of the measurement under operational (dynamic) conditions becomes the manifestation of the accuracy of measurement of the analyser.

Depending on the particular application, one or both of two performance indicators may be considered for its evaluation:

- analyser dynamic precision (initial performance testing);
- comparative dynamic precision (maintenance of measurement performance).

### 10.2 Determination of analyser dynamic precision

#### 10.2.1 Test methods

The analyser dynamic precision is the definitive measure of analyser performance and is determined by either of two comparative test methods (see C.2) that eliminate the errors due to the reference test method from the result.

- The two-instrument test: this is the less complex test but it is susceptible to error if there is any calibration bias present. Such errors will report to the analyser precision.
- The three-instrument test: this test requires a second, independent reference sampling system and eliminates bias errors. However, care must be taken to ensure that all the relevant constraints on the test procedure are fully met.

NOTE Provided that one of the reference test methods used is that which will also be used in subsequent routine operations, it will also allow the measurement of comparative dynamic precision (see 10.3).

#### 10.2.2 Objectives

The test methods described in 10.2.1 are designed to achieve two objectives:

- determination of the definitive measurement performance of the analyser;
- its comparison with a guaranteed value.

#### 10.2.3 Test conditions

Test conditions include the following:

- two- or three-instrument test scheme set up in accordance with the principles outlined in C.2;
- comparison period chosen with reference to the conditions of the specified guaranteed performance. (Note that if this application is required and if the performance guarantee is to be checked, the period should be chosen with reference to the conditions of the specified performance. However, due regard should be paid to the need to constrain the precision of the reference test method to be similar to the expected value for the analyser; see C.5 and C.6);

- minimum of 15 periods for a two-instrument test and a minimum of 40 periods for a three-instrument test (see C.5).

#### 10.2.4 Test procedures

##### 10.2.4.1 Two-instrument test

Collect duplicate reference samples as described in 9.3.2.

##### 10.2.4.2 Three-instrument test

Collect reference samples, from both reference test methods, for each comparison period defined in the conditions of test and log the corresponding data from the analyser, $X_{\mathrm{A}i}$. Ensure that the collection of samples and data are synchronised and that the sets of data all relate properly to their respective comparison periods. From each reference sample, prepare and analyse a single test sample ($R_{1i}$ and $R_{2i}$ ).

#### 10.2.5 Data analysis

##### 10.2.5.1 Two-instrument test

###### 10.2.5.1.1 Visual assessment

Plot a graph of analyser values, $X_{\mathrm{A}i}$, against the mean duplicate reference values $\overline{D}_i$ .

Assess visually for the presence of possible outliers and other problems (see D.9.2).

It is recommended that the other graphical procedures outlined in D.9 also be carried out before a full statistical analysis of the data is undertaken.

###### 10.2.5.1.2 Outliers

Check each set of values for outliers by the statistical procedure of Cochran’s criterion (see D.10.2). Consider possible outliers identified in this way for removal in accordance with the criteria defined in D.10.3. Remove those values that meet the criteria.

###### 10.2.5.1.3 Precision

Calculate the following:

- differences, $x_{\mathrm{dup}i}$, between the duplicate reference values $D_{1i}$ and $D_{2i}$;
- variance of these differences, $V_{\mathrm{dup}}$ (see D.15);
- means of the duplicate reference values, $\overline{D}_i$ ;
- differences, $d_i$, between the analyser values, $X_{\mathrm{A}i}$, and the mean duplicate reference values, $\overline{D}_i$ ;
- variance of these differences, $V_{\mathrm{d}}$ (see D.2);
- variance due to the analyser, $V_{\mathrm{A}}$ , calculated as $V_{\mathrm{A}} = V_{\mathrm{d}} - V_{\mathrm{dup}}$;
- analyser standard deviation, $s_{\mathrm{A}}$.

#### 10.2.5.1.4 Performance guarantee

Test for significance the difference between the performance indicator of the analyser, $s_{\text{A}}$, and the manufacturer's declared guarantee, $s_{\text{g}}$ (see D.16).

### 10.2.5.2 Three-instrument test

#### 10.2.5.2.1 Visual assessment

Plot graphs of

- analyser values, $X_{\text{A}i}$ , against reference 1 values, $R_1$;
- analyser values, $X_{\text{A}i}$ , against reference 2 values, $R_{2i}$;
- reference 1 values, $R_{1i}$ , against reference 2 values, $R_{2i}$.

Assess visually for the presence of possible outliers and other problems (see D.9.2).

It is recommended that the other graphical procedures outlined in D.9 also be carried out before a full statistical analysis of the data is undertaken.

#### 10.2.5.2.2 Outliers

Check for outliers by the statistical procedure of Cochran’s criterion (see D.10.2). Consider possible outliers identified in this way for removal in accordance with the criteria defined in D.10.3. Remove those values that meet the criteria.

#### 10.2.5.2.3 Precision

Using the technique of Grubbs' estimators, determine the following for the analyser and the two reference methods:

- the variance, $V_{\text{A}}$, $V_{\text{R1}}$, $V_{\text{R2}}$ (see D.17);
- the standard deviation, $S_{\text{A}}$, $S_{\text{R1}}$, $S_{\text{R}}$ (see D.17);
- the precision, $P_{\text{A}}$, $P_{\text{R1}}$, $P_{\text{R2}}$ (see D.17).

#### 10.2.5.2.4 Performance guarantee

Test for significance the difference between the performance indicator of the analyser, $s_{\text{A}}$, and the manufacturer's declared guarantee, $s_{\text{g}}$ (see D.16).

### 10.2.6 Results and interpretation

Record the following information:

- date of the test;
- identity of the product;
- relevant instrument parameters;
- conditions of the test;

- values of the individual observations;
- values calculated in 10.2.5;
- results of the performance guarantee tests.

In the absence of bias, the precision, $P_{\mathrm{A}}$, is the measure of the accuracy of the analyser, for the test units interrogated during the chosen comparison period. $P_{\mathrm{R1}}$ and $P_{\mathrm{R2}}$ are the corresponding values of precision for the two reference test methods.

## 10.3 Determination of comparative dynamic precision

### 10.3.1 General

The comparative dynamic precision of the analyser is a less rigorous measure of analyser performance and is determined by a comparative test method that includes the errors due to the reference test method. This involves a simpler procedure than for analyser dynamic precision; it is more readily applied to regular monitoring of measurement performance.

### 10.3.2 Objectives

The test method and methods of data analysis described in 10.3 are designed to achieve two objectives:

- determination of an indicator of measurement performance;
- testing it for significant change from a previous value.

### 10.3.3 Test conditions

Test conditions include

- a two-instrument test scheme set up in accordance with the principles outlined in C.2,
- a comparison period which produces a value of consequence for operations (see C.5),
- a minimum of 15 comparison periods (see C.5).

### 10.3.4 Test procedure

Collect reference samples from the reference test methods for each comparison period defined in the conditions of test and log the corresponding data from the analyser. Ensure that the collection of samples and data are properly synchronised and that the sets of data all relate properly to their respective test units. From each reference sample, prepare and analyse a single test sample.

### 10.3.5 Data analysis

#### 10.3.5.1 Visual assessment

Plot a graph of analyser values, $X_{\mathrm{A}i}$, against reference values, $R_i$.

Assess visually for the presence of possible outliers and other problems (see D.9.2).

It is recommended that the other graphical procedures outlined in D.9 also be carried out before a full statistical analysis of the data is undertaken.

#### 10.3.5.2 Outliers

Check for outliers by the statistical procedure of Cochran's criterion (see D.10.2). Consider possible outliers identified in this way for removal in accordance with the criteria defined in D.10.3. Remove those values that meet the criteria.

#### 10.3.5.3 Precision

Calculate the following values:

- differences, $d_i$ , between the analyser values, $X_{Ai}$, and the reference values $R_i$;
- variance of the differences, $V_d$ (see D.2);
- standard deviation of the differences, $s_d$ (see D.3);
- comparative precision, $P_d$ (see D.4).

#### 10.3.5.4 Comparison with a previous value

Test, for significance, the ratio of the variances, $V_{d,0}$ and $V_{d,\tau}$ (see D.5) where $V_{d,0}$ is the value of variance measured by this method in a previous test and $V_{d,\tau}$ is the value of variance measured by this method in the current test.

If this is the first routine monitoring measurement, compare the variance $V_{d,\tau}$ with an estimate of $V_{d,0}$ obtained from one of the methods for determination of analyser dynamic precision (see 10.2).

When a two-instrument test has been used to determine analyser dynamic precision, see 10.2.5.1.3:

$$V_{d,0} = V_d$$

When a three-instrument test has been used to determine analyser dynamic precision, see 10.2.5.2.3:

$$V_{d,0} = V_A + V_{R1}$$

### 10.3.6 Results and interpretation

Record the following information:

- date of the test;
- identity of the product;
- relevant instrument parameters;
- conditions of the test;
- values of the individual observations;
- values calculated in 10.3.5;
- results of the comparison tests.

The comparative precision, $P_d$, is a combination of the random errors arising from the analyser test method and the reference test method.

If there is a significant difference between the current variance and a previous value that cannot be attributed to random instrumentation variations (see 8.6), the reference test method should be examined for possible sources of variation which have arisen since the previous test. Determination of the variance of the reference method, ($V_{dup}$; see D.15), will provide data for comparison with previous values.

Changes in solid mineral fuel quality should also be considered as a source of increased random error that may appear in either the analyser results or the reference method results, or both.

If there are no obvious reasons for the increase in error and the reduced apparent performance of the analyser cannot be accepted, consider conducting another test for analyser dynamic precision to identify the system responsible.

## 11 Application

### 11.1 General

The procedures described in Clauses 8, 9 and 10 cover a wide range of tests to be applied, as appropriate, to a range of situations which can occur during the operation of on-line analysers. The appropriate tests for the various situations are listed in 11.2 to 11.6. Some of the test procedures may not be applicable to a limited number of analysis techniques.

### 11.2 Commissioning (acceptance) tests

On completion of an installation, carry out the procedures a) to c); if a performance guarantee has been given by the manufacturer, carry out procedure d) as well:

a) establish benchmarks for instrument stability (Clause 8);

b) confirm preliminary calibration (Clause 9);

c) determine analyser dynamic precision (10.2);

d) check manufacturer's declared guarantee (10.2.5.1.4 or 10.2.5.2.4).

### 11.3 Routine tests

Carry out the following procedures, at intervals and preferably within a statistical process control procedure, as part of the normal operational programme for the analyser:

a) check instrument stability (Clause 8);

b) check comparative dynamic precision (10.3).

### 11.4 After changes in analyser system

When the analyser system has been changed, e.g. by the repair or renewal of an electronic component, carry out the following procedures:

a) re-establish benchmarks for instrument stability (Clause 8);

b) confirm or renew calibration (Clause 9);

c) check comparative dynamic precision (10.3).

### 11.5 After changes in reference sample system

Whenever a change in components or design of the reference sampling system, which could possibly affect the precision of the reference method, has been made, carry out the following procedures:

a) check instrument stability (Clause 8);

b) check comparative dynamic precision (10.3).

### 11.6 After changes in coal quality

When there has been a significant change in solid mineral fuel quality, e.g. by the introduction of a new source of supply, carry out the following procedures:

a) check instrument stability (Clause 8);

b) confirm or renew calibration (Clause 9);

c) check comparative dynamic precision (10.3).

# Annex A
(informative)

# On-line analysis techniques for solid mineral fuels

## A.1 General

This annex describes the basic techniques in use and their application to on-line analysis of solid mineral fuels.

## A.2 X-ray backscatter

The parameter measured is ash.

The intensity of low energy (normally less than 30 keV), X-radiation reflected (incoherently scattered) from the solid mineral fuel is a measure of the average atomic number which itself correlates reasonably with the ash. The analysis requires that the solid mineral fuel be of small particle size (less than 5 mm), well conditioned and carefully presented in a sub-stream configuration. The method is applicable to bulk solids and coal slurries. It is perturbed by iron content variations in the ash but may be combined with X-ray fluorescence measurements (see A.3) for iron to improve accuracy.

## A.3 X-ray fluorescence

The parameters measured are potassium, iron, sulfur, calcium and silicon.

The solid mineral fuel is interrogated by suitable low energy X-radiation that excites X-rays characteristic of specific elements (X-ray fluorescence). The intensity of these emissions is measured and related to the element concentrations. Particle size, sample homogeneity and sample presentation conditions are critical, especially for the lower atomic number elements and a sub-stream configuration is necessary.

## A.4 Gamma ray backscatter

The parameter measured is ash.

In principle, this test is similar to X-ray backscatter, but the use of higher-energy radiation (generally up to about 100 keV) allows the interrogation of solid mineral fuel of maximum particle size up to 50 mm. It may be applied to a sub-stream, but is mostly used in a mainstream configuration, directly on a conveyor belt. The method is applicable to bulk solids; some profiling of the bed of solid mineral fuel may be needed and a minimum bed depth of 100 mm is required. It is perturbed by iron variations in the ash but some compensation can be effected by selective multi-channel signal measurements.

A variant technique using 662 keV radiation and depending on multiple scattering to render it sensitive to ash variations enables the monitoring of bulk solid mineral fuel up to 300 mm particle size in greater bed depths, directly on a belt or within a chute.

## A.5 Gamma ray forward scatter

The parameter measured is ash.

Measurement of forward (coherently) scattered gamma radiation, using incident radiation of less than 100 keV, provides another technique for the on-belt, mainstream measurement of the ash of bulk solids up to 25 mm particle size, which is not so sensitive to bed depth but is perturbed by iron variations.

## A.6 Dual energy gamma ray transmission

The parameter measured is ash.

The intensity of unscattered gamma radiation (less than 100 keV) transmitted through a layer of solid mineral fuel is dependent on its ash and mass per unit area. Correction for the latter effect is available by simultaneously measuring the transmitted intensity of higher energy gamma radiation that is insensitive to ash. This allows direct on-belt measurement of solid mineral fuel up to 200 mm top size which is unaffected by bed depth to a minimum of about 50 mm. It is less sensitive to ash than scattering techniques but perturbed by iron variations.

## A.7 Pair production

The parameter measured is ash.

Interrogation by high-energy (greater than 1,02 MeV) gamma radiation results in the emission of 0,511 MeV gamma radiation (via electron/positron pair production) which correlates strongly with average atomic number and hence ash. Less sensitive to iron variations, it is applied to coal up to 50 mm top size, flowing at a rate of a few tons per hour, constrained within a vertical tube in a sub-stream configuration.

## A.8 Natural gamma radiation emission

The parameter measured is ash.

The mineral matter in coal contains a small and reasonably constant proportion of naturally occurring radioisotopes that emit high-energy gamma radiation. The intensity of this emission provides a measure of the mineral matter in the coal and hence the ash. The technique is applied directly to coal up to 300 mm top size on a belt. It is relatively unaffected by changes in mineral composition but may require compensation for belt mass loading variations.

## A.9 Prompt gamma neutron activation analysis

The parameters measured include carbon, hydrogen, nitrogen, sulfur, chlorine, oxygen, aluminium, silicon, iron, calcium, potassium and titanium and derived values such as ash, heat content, sulfur dioxide emission rates and slagging and fouling factors.

Irradiation of bulk coal by neutrons gives rise to the prompt emission of gamma rays with energies (1 MeV to 10 MeV) that are characteristic of most of the elements in the coal. Most instruments depend on thermal neutron capture interactions, but these are of low efficiency for carbon and negligible for oxygen. The two latter elements can be better determined from gamma rays arising from higher energy neutron inelastic scatter interactions. Coal up to 100 mm top size and at flow rates up to 400 t per hour is presented within the confines of a chute. The technique may also be adapted to determine sulfur content of coal in slurries.

## A.10 Microwave transmission/phase shift

The parameter measured is moisture.

The degree of attenuation and extent of phase shift of microwaves in the 2 GHz to 10 GHz region transmitted through a bed of coal are functions of the mass per unit area and moisture content. The method is applicable to sub-stream or mainstream (on-belt) configurations of coal up to 50 mm top size. Unless the bed depth and density are constrained, a compensating signal for mass per unit area is required. Magnetic material has a strong effect and is a potential source of error.

## A.11 Microwave backscatter

The parameter measured is moisture.

Microwaves backscattered from a bed of coal also correlate with moisture content. The method is applicable to mainstream configurations (on-belt) but profiling of the coal surface is required. A minimum bed depth of 50 mm is required and the maximum particle size is restricted to 30 mm. Magnetic material has a strong effect and is a potential source of error.

## A.12 Neutron moderation

The parameter measured is moisture.

The degree to which high-energy neutrons are moderated (reduced to thermal energies by elastic scattering) by solid mineral fuel is a function of its moisture, providing that it also has low and constant organic hydrogen. The intensity of the thermal neutrons flux arising from neutron-irradiated solid mineral fuel contained within a sub-stream configuration is measured. The technique is normally applied to coke up to 100 mm top size.

## A.13 Capacitance change

The parameter measured is moisture.

The electrical capacitance of coal at radiofrequencies depends on its moisture. Arrangements in which the coal passes through the RF field, either in a chute in sub-stream configuration or on a belt (mainstream) provide appropriate signals. It is applicable to bulk coal up to 25 mm top size but is subject to several perturbing effects.

## A.14 Bulk density measurement

The parameter measured is ash.

For some coals, there is a correlation between ash content and bulk density. Density may be measured using an on-belt weighing system for a constant volume of coal or by the attenuation of transmitted high-energy gamma radiation. Accuracy is generally low but adequate for some control purposes. It is applicable to coal up to 300 mm top size.

## A.15 Optical radiation scattering

The parameter measured is ash.

The optical reflectivity of high ash content slurries (tailings) correlates reasonably with ash. Measurement of the radiation, reflected from slurries up to about 1 mm top size, provides values adequate for the control of fine coal cleaning plant.

## A.16 Infra red absorption

The parameter measured is moisture.

At certain wavelengths, infra-red radiation is specifically absorbed by moisture and the intensity of radiation reflected from a suitably presented bed of coal correlates with the moisture content. It is applicable to coal up to a few millimetres top size.

NOTE The heat content of solid mineral fuel can also be determined by correlation with ash and moisture values obtained from any combination of techniques that provide these data.

# Annex B
(informative)

# Sources of measurement variance

## B.1 General

Measurement errors arise as a result of variations that may occur in the reference and analyser measurement procedures. Unless a test method designed to evaluate analyser performance is carefully constructed, errors due to the reference procedure may be attributed to the analyser procedure. An appreciation of the potential sources of measurement variance is necessary for the proper design of the test method and interpretation of the results.

## B.2 Reference test methods

To obtain accurate results from the analyser and to measure its precision properly, the reference values should be determined by a method that is free from bias and as precise as possible.

If the procedure is not based on stopped-belt sampling, carried out as described in ISO 13909 or ISO 1988, it should employ a sampling procedure that has been demonstrated to be free from bias by the methods described in ISO 13909.

The magnitude of the errors attributable to reference test methods is best assessed as the total variance associated with the procedure and may be determined as described in ISO 13909 or by some other appropriate statistical technique.

Sources of error in reference test methods may be conveniently assigned to four areas:

- product variability: a function of the inhomogeneity of the solid mineral fuel stream flowing through the system and the largest contributor to the total variance;
- sample extraction: arising from operations, such as reduction and division, undertaken on the individual increments before aggregation into the sample. There may be as many as four sequential stages to sample extraction, each contributing its own extraction variance;
- sample preparation: arising from operations undertaken to convert the sample into the test sample for analysis. These include particle size reduction, mixing, sample division and drying;
- testing: includes the application of the laboratory test procedure and the calculation and reporting of the result.

## B.3 Analyser test methods

Sources of error in analyser test methods may be conveniently assigned to six areas:

- product variability: a function of the inhomogeneity of the solid mineral fuel stream;
- sample extraction: arising from operations, such as handling and division, undertaken on the individual increments before presentation to the analyser. This source applies only to analysers arranged in a sub-stream configuration;

- interrogation: due to changes in the presentation of the solid mineral fuel, such as result from profiling or bulk density variations, or to the proportion of measurand within the interrogation volume caused by vertical or lateral segregation;
- instrumentation: due to intrinsic or environmental instability of the electronics. Analysers that use radioisotope sources also have the variations due to counting statistics;
- calibration: due to limitations in the quality of the calibration or inadequacy of its algorithms to account for all effects on instrument response. A calibration may also be outmoded by changes in coal quality after its definition (coal type effect);
- reporting: errors in the transfer of the result.

## B.4 Test procedure artefacts

Incorrect synchronisation of the analyser measurement period with the reference test method sampling can lead to error in accuracy and precision that will be assigned to the analyser.

# Annex C
(normative)

# Comparative test methods

## C.1 General

This annex describes the principal factors to be considered in the design and execution of a comparative test.

A comparative test is based on the comparison of a set of analyser values with one or two sets of reference values obtained from the same test units. Since reference values are themselves subject to measurement errors, care has to be taken to see that a test method is designed to allocate errors to their proper sources (see Annex B).

Comparative test methods are used to confirm calibrations (see Clause 9) and to determine operational measurement performance (see Clause 10).

There are two basic designs for test methods suitable for the requirements of this International Standard. They are designated as the two-instrument test and the three-instrument test.

## C.2 Basic test design

### C.2.1 Two-instrument test

A two-instrument test is used to confirm calibrations (see Clause 9), or to measure operational performance (see 10.2 and 10.3). It returns one analyser value and one or duplicate reference samples, representative of each chosen test unit or sub-lot. For calibration and the determination of analyser dynamic precision, duplicate reference samples are required. For comparative dynamic precision, only a single sample is needed. Figure C.1 gives an outline of the basic steps required in the design of a test for confirmation of calibration or determination of analyser dynamic precision. Figure C.2 shows the steps required to measure comparative dynamic precision.

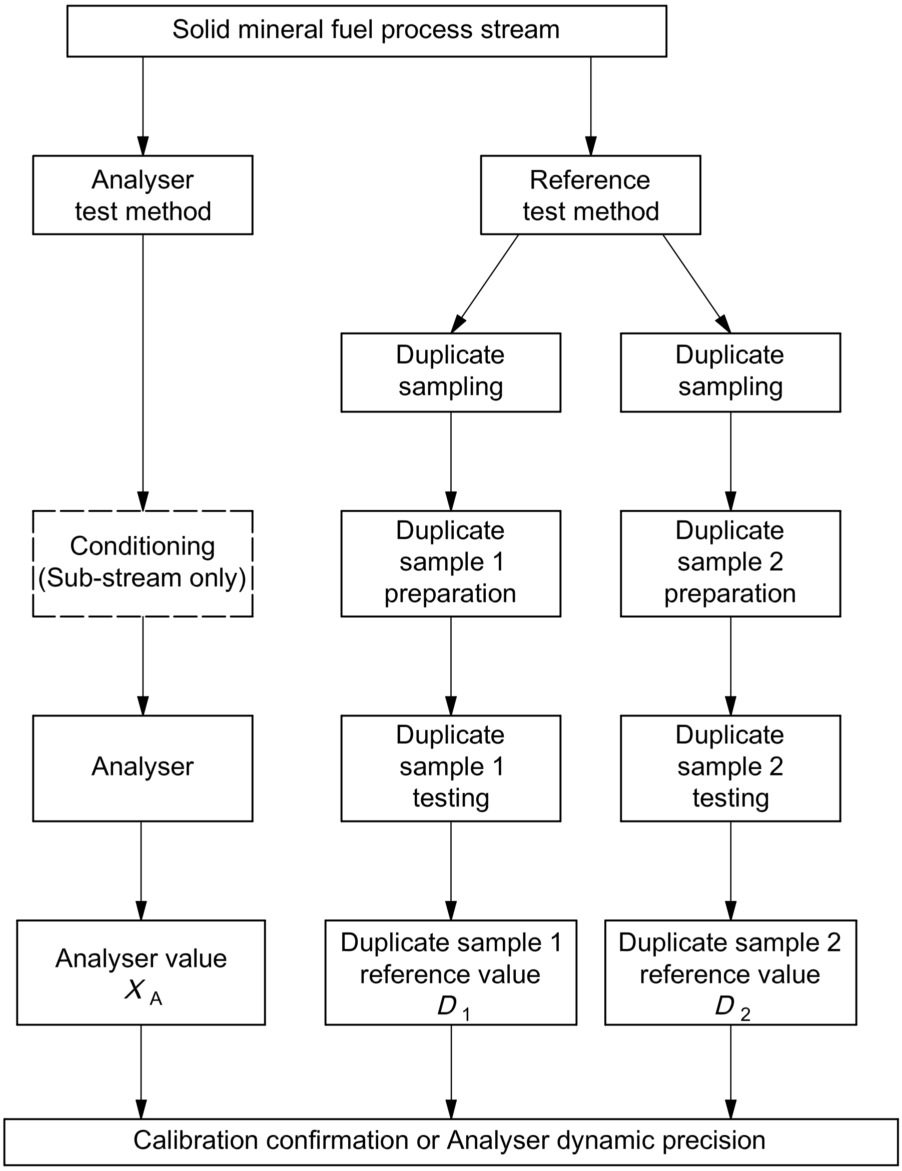


**Figure C.1 — Outline of the two-instrument test procedure for calibration confirmation or analyser dynamic precision**

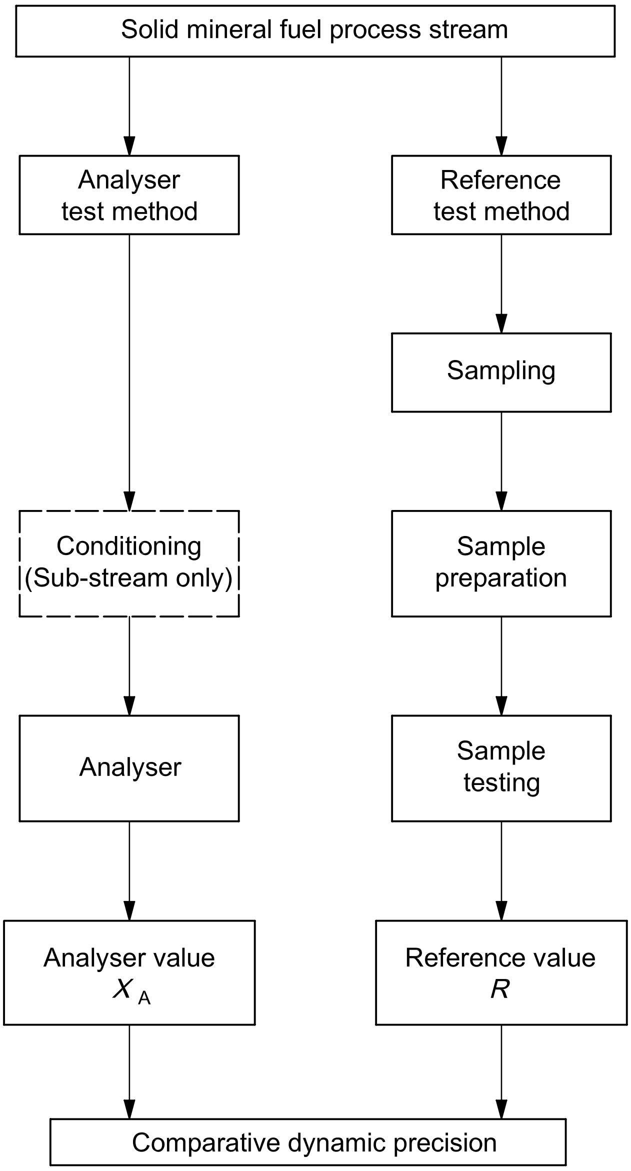


**Figure C.2 — Outline of the two-instrument test procedure for comparative dynamic precision**

### C.2.2 Three-instrument test

A three-instrument test is used to measure analyser dynamic precision (see 10.2). It returns one analyser value and two reference samples, representative of each chosen test unit or sub-lot. The reference samples are prepared and tested to provide single reference values. The data analysis method used in this case (Grubbs' estimators, see D.17) requires the two reference test systems to be independent procedures, that is, carried out by different operators with different equipment. Figure C.3 is an outline of the basic steps required to measure analyser dynamic precision.

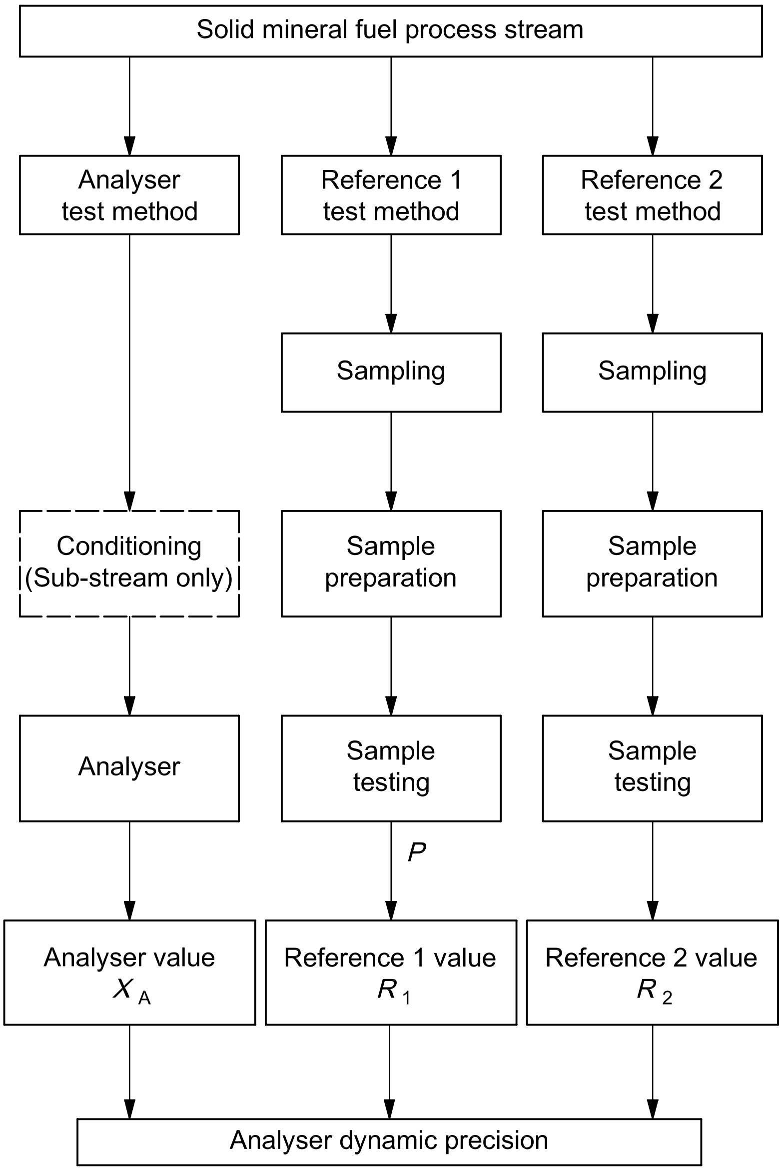


**Figure C.3 — Outline of the three-instrument test procedure for analyser dynamic precision**

### C.2.3 Installation layouts

Details of installation layouts depend on the design of the plant in which the installation is made, the type of analyser and the facilities for taking reference samples that can be made available. It is vital to ensure that the data logged by the analyser, to give an analyser value, represent the same physical mass of solid mineral fuel from which the increments that constitute the sample(s) for the reference value(s) are extracted.

Typical layouts suitable for the evaluation of an analyser in a mainstream (Figure C.4) or sub-stream (Figure C.5) configuration are shown. Other designs are possible. Both figures illustrate layouts for two-instrument and three-instrument tests.

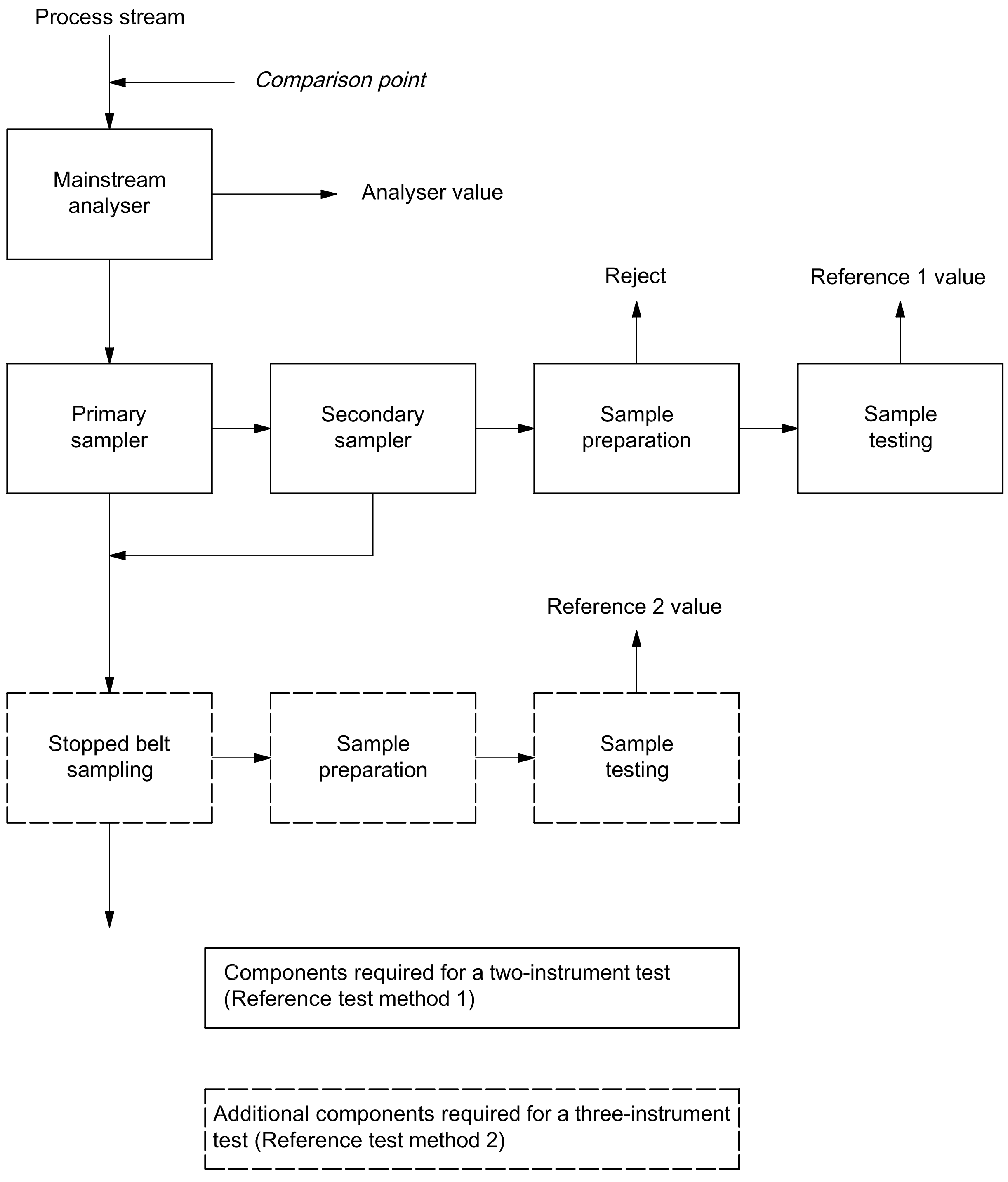


**Figure C.4 — Typical layout for a mainstream configuration**

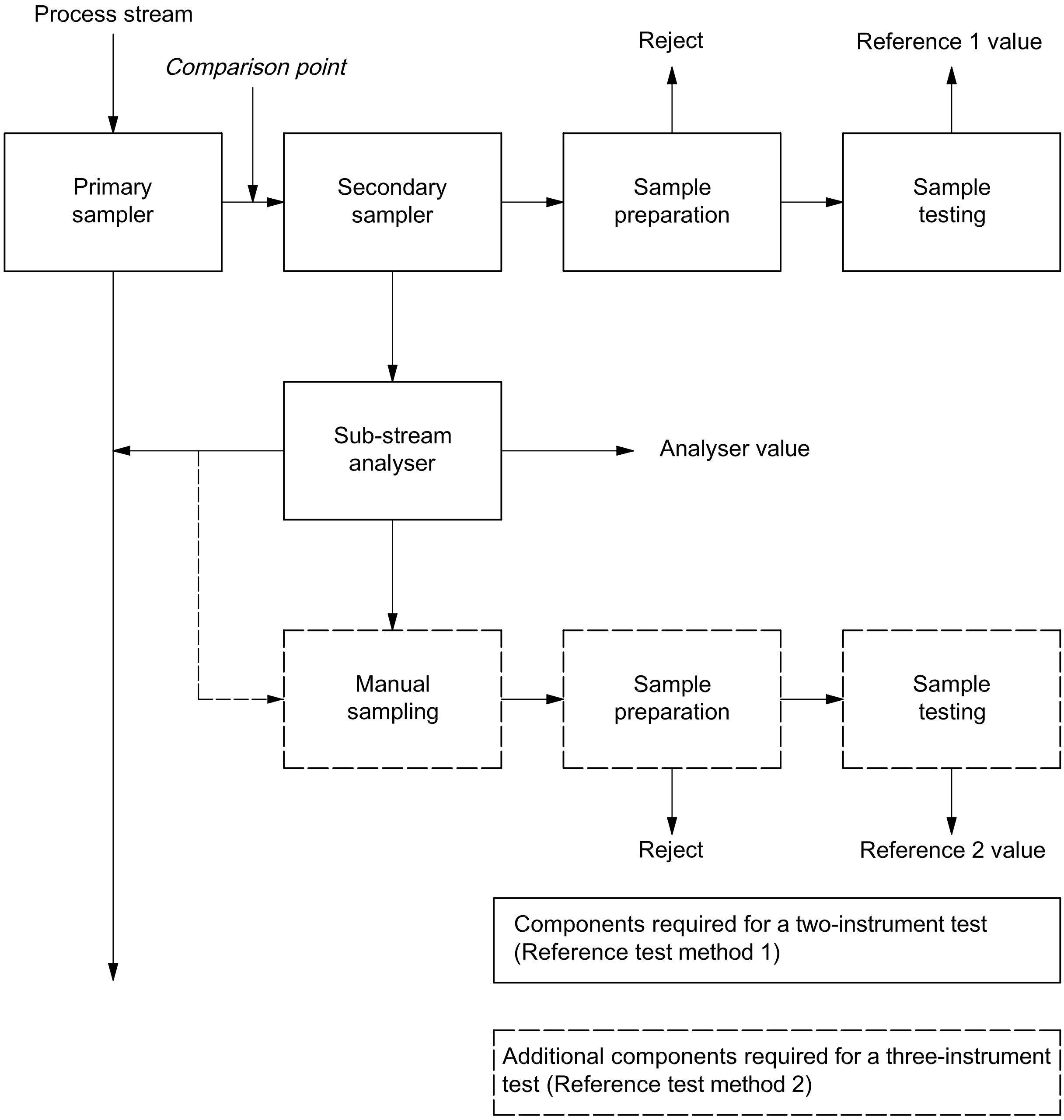


**Figure C.5 — Typical layout for a sub-stream configuration**

## C.3 Comparison point

The point in the solid mineral fuel process stream for which the comparison is made needs to be clearly identified to ensure that valid inferences can be drawn.

The comparison point in a mainstream configuration is located as closely as possible to the point of intervention (see Note 1 and Figure C.4). No significant variations should be induced in the main process stream by the intervention operations (see Note 2). In a typical sub-stream configuration, where the analyser is installed on the secondary sampler reject stream, the secondary “save” sample is often used to provide a reference value and the comparison point is the primary sample (see Figure C.5 and Note 3). In those instances where the “save” sample cannot be obtained, or a second reference value is required, it is possible to construct a test with samples from the analyser discharge (see Note 4).

NOTE 1 The point of intervention refers to either the point at which the analyser interrogates the solid mineral fuel stream, or the point at which primary or stopped belt sample increments are extracted.

NOTE 2 This is the case in most mainstreams, which are usually high-density flow installations. The analyser has little or no physical effect on the solid mineral fuel. Although sampling can result in large variations in the aliquots that are removed (the “save”), there is relatively little effect on the mainstream (the “reject”) by virtue of the large ratio of the mass of the mainstream to the aliquots. Secondary sampling will not cause significant variations in the reject stream, providing the ratio of the reject to the save is about 10 to 1 or higher.

NOTE 3 In this case, the values obtained by the Grubbs test refer to the precision of measurement of the solid mineral fuel quality in the primary sample. It does not indicate the precision with which the test methods measure the solid mineral fuel quality in the main process stream.

NOTE 4 It is possible to construct a three-instrument (Grubbs) test using different comparison points in a sampling system. However, it is important to use the point furthest downstream from which a continuous route to the final determined values can be traced. This will often be a stopped belt or primary sample.

## C.4 Assessment of variances

In a comparative dynamic precision test, the total variance is the sum of the variances that occur at each operational step between the analyser and reference test values.

In a properly designed analyser dynamic precision test, the analyser and reference variances are independent. In each case, the total variance is the sum of the variances that occur at each operational step between the comparison point and the reference test values.

## C.5 Comparison periods

As an indicator of on-line analyser performance, it is necessary that the precision of measurement be associated with a specific period in order to be fully definitive. The optimum duration for a comparison period however, varies with the aspect of analyser operation that is under evaluation. The demands of a number of factors, such as operational needs, reference sample constraints and test method requirements shall be considered when making a choice for a particular test.

A comparison period shall be sufficiently long to allow the collection of an adequate number of increments to

- give a reasonable precision to reference values (see C.6),
- minimize the error of the analyser due to instrumental and presentation variations (see 8.1),
- minimize the impact of any synchronisation error.

A useful period is one that produces a value of consequence for operations e.g. over an hour or a shift, or the time associated with a specific consignment. This period can be considered optimum for tests addressing the evaluation of operational performance but might not be convenient for regular routine monitoring. The final choice must be tailored to meet individual circumstances.

In the case of confirmation of calibration, a fully representative range of coal quality and the best precision of the reference values within the practical constraints of sample size and operations are the dominant considerations.

For a test to measure analyser dynamic precision, consideration shall be given to the need, by the test method, to constrain the precision of the reference test methods to be approximately the same as the expected analyser precision.

Within the duration of a single comparison period, the problem of bias occurring in the analyser value as a result of correlation between data collection and periodic variations in quality does not normally arise since data are usually aggregated continuously. If this is not the case, then the timing of the collection of data increments shall be treated in the same way as is required for physical increments in the reference samples in order to avoid such correlation. See ISO 13909 for the detection of, and dealing with, periodic variations in quality.

As a generalization, the number of periods in a test shall be large enough and the total duration of the test sufficient to cover the whole range of measurand values expected. It is also vital that all variations in perturbing factors (e.g. iron concentration) be represented in the samples.

The number of comparison periods required is governed by the test method and the statistical treatment to be used. For a two-instrument test, a minimum of 15 periods is preferable to improve the resolving power of statistical tests. For a three-instrument test, increase the minimum to 40 periods.

Consideration shall also be paid to the expected precision of measurement; less precise values, such as can arise from short comparison periods, require a larger number of pairs of observations to allow statistically significant conclusions to be drawn.

The frequency of comparison periods depends mainly on practical considerations of operation. It should not correlate with periodic variations in quality; otherwise, an adequate range of measurand values will not be obtained. This can result in a misleading indication of precision in the case of the evaluation of operational measurements and will result in improper calibration information.

## C.6 Reference method

For systems in which a mechanical sampling system is installed, the collection and preparation of samples representing the comparison periods required (see C.5) shall be carried out in accordance with the relevant requirements of ISO 13909. When the solid mineral fuel concerned is brown coal or lignite, due regard shall be made to any particular requirements of ISO 5069. If the procedure is based on manual sampling, then the appropriate requirements of ISO 1988 shall apply for hard coal and ISO 2309 for coke.

In the case of fuel/water slurries, the provisions of these International Standards with respect to reference sampling do not apply and the system normally in use should be employed (see Note). However, once de-watered, prepare the samples for analysis in the manner described in these International Standards for bulk solids.

The time over which each sample is collected shall be noted to ensure that proper synchronisation of the corresponding data collected for the analyser is achieved.

Analysis of the test samples shall be carried out according to the relevant International Standard appropriate to the measurand concerned.

When a three-instrument test (see C.2.2) is being conducted, the two reference sampling systems shall be independent. All operations of sampling, sample preparation and analysis shall be carried out with different equipment by different operators.

Estimate the precision to be expected for a single sample for a period of the chosen size (see ISO 13909-7 for methods for estimating precision of sampling, preparation and analysis). If a reasonable precision is not indicated, adjust the conditions of the reference sampling procedure(s) (see ISO 13909–7 for checking and adjusting sampling precision).

NOTE An Australian National Standard that covers sampling of slurries is in preparation and work on an International Standard has been initiated.

# Annex D
(normative)

## Statistical assessment procedures

### D.1 General

This annex is intended to provide the basic information on the equations used, the mechanics of the mathematical procedures referred to within the subclauses on data analysis (8.5, 9.5, 10.2.5 and 10.3.5) in this International Standard and guidance on the interpretation of the results. The forms of the equations given are intended to illustrate procedures suitable for relatively simple calculators. Other equivalent forms may be used.

In the equations in this annex,

$\sum x$ is an abbreviation for the values of $x$ summed over a certain range of conditions or parameters;

$x$ represents a value in, or derived from, a set of observations.

Wherever the symbol $R$ is used to illustrate an assessment procedure, it indicates any reference value demanded by the test procedure, i.e. individual reference values ($R_1$ and $R_2$), duplicate reference values ($D_1$ and $D_2$), or the mean of duplicate reference values ($\overline{D}$). The appropriate symbol should be substituted as the test procedure demands (see D.9, D.10 and D.11). Where a specific reference value is required (see D.12, D.15 and D.17), it is identified in the assessment procedure.

### D.2 Variance

The variance, $V$, is calculated from Equation (D.1)

$$V = \frac{\sum x^2 - \left(\sum x\right)^2 / n}{n - 1} \tag{D.1}$$

### D.3 Standard deviation

The standard deviation, $s$, is the square root of the variance, as given in Equation (D.2).

$$s = \sqrt{V} \tag{D.2}$$

### D.4 Precision

The precision, $P$, is calculated from the standard deviation, as given in Equation (D.3):

$$P = \pm\, t \cdot s \tag{D.3}$$

where

$t$ is the value appropriate to $n - 1$ degrees of freedom;

$L_C = 95$ % as given in Table D.1

**Table D.1 — Values of Student's $t$ for a two-sided distribution**

| $n$ | $t$ ($L_C$ = 95 %) | $t$ ($L_C$ = 99 %) |
|---|---|---|
| 5 | 2,570 | 4,032 |
| 6 | 2,447 | 3,707 |
| 7 | 2,365 | 3,500 |
| 8 | 2,306 | 3,335 |
| 9 | 2,262 | 3,250 |
| 10 | 2,228 | 3,169 |
| 11 | 2,201 | 3,106 |
| 12 | 2,179 | 3,055 |
| 13 | 2,160 | 3,012 |
| 14 | 2,145 | 2,977 |
| 15 | 2,131 | 2,947 |
| 16 | 2,120 | 2,921 |
| 17 | 2,110 | 2,898 |
| 18 | 2,101 | 2,878 |
| 19 | 2,093 | 2,861 |
| 20 | 2,086 | 2,845 |
| 21 | 2,080 | 2,831 |
| 22 | 2,074 | 2,819 |
| 23 | 2,069 | 2,807 |
| 24 | 2,064 | 2,797 |
| 25 | 2,060 | 2,787 |
| 26 | 2,056 | 2,779 |
| 27 | 2,052 | 2,771 |
| 28 | 2,048 | 2,763 |
| 29 | 2,045 | 2,756 |
| 30 | 2,042 | 2,750 |
| 35 | 2,030 | 2,724 |
| 40 | 2,021 | 2,705 |
| 45 | 2,014 | 2,897 |
| 50 | 2,009 | 2,678 |
| 55 | 2,004 | 2,668 |
| 60 | 2,000 | 2,660 |

## D.5 Comparison of variances ($F$-test)

An $F$-test is used to test whether or not there is a statistically significant difference between two variances belonging to two different sets of data.

Calculate the test statistic, $F$, from Equation (D.4):

$$F = V_1/V_2 \tag{D.4}$$

where

$V_1$ is the variance of the set with the greater variance;

$V_2$ is the variance of the set with the smaller variance.

The value of $F$ is compared with the critical value, $F_c$, read from Table D.2. The number of degrees of freedom is $(n_1 - 1)$ on the horizontal axis and $(n_2 - 1)$ on the vertical axis, where $n_1$ is the number of observations corresponding to $V_1$ and $n_2$ is the number of observations corresponding to $V_2$.

If $F > F_c$, there is a statistically significant difference between the variances.

**Table D.2 — Critical values of the $F$-distribution at the 95 % confidence limits**

| $\nu(n_2 - 1)$[a] | $\nu(n_1 - 1)$[b] | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 25 | 30 | 35 | 40 | 50 | 60 |
| 9 | 3,18 | 3,14 | 3,10 | 3,07 | 3,05 | 3,03 | 3,01 | 2,99 | 2,97 | 2,96 | 2,95 | 2,94 | 2,89 | 2,86 | 2,84 | 2,83 | 2,80 | 2,79 |
| 10 | 3,02 | 2,98 | 2,94 | 2,91 | 2,89 | 2,87 | 2,85 | 2,83 | 2,81 | 2,80 | 2,79 | 2,77 | 2,73 | 2,70 | 2,68 | 2,66 | 2,64 | 2,62 |
| 11 | 2,90 | 2,85 | 2,82 | 2,79 | 2,76 | 2,74 | 2,72 | 2,70 | 2,69 | 2,67 | 2,66 | 2,65 | 2,60 | 2,57 | 2,55 | 2,53 | 2,51 | 2,49 |
| 12 | 2,80 | 2,75 | 2,72 | 2,69 | 2,66 | 2,64 | 2,62 | 2,60 | 2,58 | 2,57 | 2,56 | 2,54 | 2,50 | 2,47 | 2,44 | 2,43 | 2,40 | 2,38 |
| 13 | 2,71 | 2,67 | 2,64 | 2,60 | 2,58 | 2,55 | 2,53 | 2,52 | 2,50 | 2,48 | 2,47 | 2,46 | 2,41 | 2,38 | 2,36 | 2,34 | 2,31 | 2,30 |
| 14 | 2,65 | 2,60 | 2,57 | 2,53 | 2,51 | 2,48 | 2,46 | 2,45 | 2,43 | 2,41 | 2,40 | 2,39 | 2,34 | 2,31 | 2,28 | 2,27 | 2,24 | 2,22 |
| 15 | 2,59 | 2,54 | 2,51 | 2,48 | 2,45 | 2,42 | 2,40 | 2,39 | 2,37 | 2,35 | 2,34 | 2,33 | 2,28 | 2,25 | 2,22 | 2,20 | 2,18 | 2,16 |
| 16 | 2,54 | 2,49 | 2,46 | 2,42 | 2,40 | 2,37 | 2,35 | 2,33 | 2,32 | 2,30 | 2,29 | 2,28 | 2,22 | 2,19 | 2,17 | 2,15 | 2,12 | 2,11 |
| 17 | 2,49 | 2,45 | 2,41 | 2,38 | 2,35 | 2,33 | 2,31 | 2,29 | 2,27 | 2,26 | 2,24 | 2,23 | 2,18 | 2,15 | 2,12 | 2,10 | 2,08 | 2.06 |
| 18 | 2,46 | 2,41 | 2,37 | 2,34 | 2,31 | 2,29 | 2,27 | 2,25 | 2,23 | 2,22 | 2,20 | 2,19 | 2,14 | 2,11 | 2,08 | 2,06 | 2,04 | 2,02 |
| 19 | 2,42 | 2,38 | 2,34 | 2,31 | 2,28 | 2,26 | 2,23 | 2,22 | 2,20 | 2,19 | 2,17 | 2,16 | 2,10 | 2,07 | 2,05 | 2,03 | 2,00 | 1,98 |
| 20 | 2,39 | 2,35 | 2,31 | 2,28 | 2,25 | 2,23 | 2,20 | 2,18 | 2,17 | 2,15 | 2,14 | 2,12 | 2,07 | 2,03 | 2,01 | 1,99 | 1,97 | 1,95 |
| 25 | 2,28 | 2,23 | 2,20 | 2,17 | 2,14 | 2,11 | 2,09 | 2,07 | 2,05 | 2,04 | 2,02 | 2,01 | 2,00 | 1,92 | 1,89 | 1,87 | 1,84 | 1,82 |
| 30 | 2,21 | 2,17 | 2,13 | 2,09 | 2,06 | 2,04 | 2,02 | 2,00 | 1,98 | 1,96 | 1,95 | 1,93 | 1,88 | 1,84 | 1,81 | 1,79 | 1,76 | 1,74 |
| 35 | 2,16 | 2,11 | 2,08 | 2,04 | 2,01 | 1,99 | 1,96 | 1,94 | 1,92 | 1,91 | 1,89 | 1,88 | 1,82 | 1,79 | 1,76 | 1,74 | 1,70 | 1,68 |
| 40 | 2,12 | 2,08 | 2,04 | 2,00 | 1,97 | 1,95 | 1,92 | 1,90 | 1,89 | 1,87 | 1,85 | 1,84 | 1,78 | 1,74 | 1,72 | 1,69 | 1,66 | 1,64 |
| 50 | 2,07 | 2,03 | 1,99 | 1,95 | 1,92 | 1,90 | 1,87 | 1,85 | 1,84 | 1,82 | 1,80 | 1,78 | 1,73 | 1,69 | 1,66 | 1,64 | 1,60 | 1,57 |
| 60 | 2,04 | 1,99 | 1,95 | 1,92 | 1,89 | 1,86 | 1,84 | 1,82 | 1,80 | 1,78 | 1,77 | 1,75 | 1,70 | 1,65 | 1,62 | 1,59 | 1,55 | 1,53 |

[a] Degrees of freedom for the set of observations with the smaller variance.

[b] Degrees of freedom for the set of observations with the greater variance.

## D.6 Mean

The mean, $\bar{x}$ is calculated from Equation (D.5):

$$\bar{x} = \sum x_i / n \tag{D.5}$$

## D.7 Comparison of means ($t$-test)

This test is used to compare two sets of data for significant difference when there is no connection between individual observations of set 1 and set 2.

A test statistic, $t_\mathrm{m}$, is calculated from Equation (D.6):

$$t_\mathrm{m} = \frac{\left|\bar{x}_1 - \bar{x}_2\right|}{S_{1+2} \times \sqrt{1/n_1 + 1/n_2}} \tag{D.6}$$

where

$\bar{x}_1$ and $\bar{x}_2$ are the mean values, and $n_1$ and $n_2$ the numbers of observations at time 0 and time $\tau$, respectively;

$s_{1+2}$ is the pooled standard deviation for the two sets of observations.

The value of $s_{1+2}$ is calculated from Equation (D.7):

$$S_{1+2} = \sqrt{\frac{s_1^2\left(n_1 - 1\right) + s_2^2\left(n_2 - 1\right)}{n_1 + n_2 - 2}} \tag{D.7}$$

The critical value, $t_\mathrm{c}$, is the value of Student's $t$ at $(n_1 + n_2 - 2)$ degrees of freedom and $L_\mathrm{C} = 95\ \%$ (see Table D.1).

If $t_\mathrm{m} > t_\mathrm{c}$, there is a statistically significant difference between the means.

## D.8 Static/dynamic response factor

The static/dynamic response factor, $f_\mathrm{SDR}$, is calculated from Equation (D.8):

$$f_\mathrm{SDR} = \left(\sum X_{\mathrm{ADy},i} - \sum X_{\mathrm{ASt},i}\right) / n \tag{D.8}$$

where

$X_{\mathrm{ADy},i}$ is a set of analyser values obtained under dynamic conditions;

$X_{\mathrm{ASt},i}$ is a set of analyser values obtained under static conditions;

$n$ is the number of pairs of values in the set.

## D.9 Visual assessment

### D.9.1 General

A visual assessment of the data using graphical analysis can be very helpful in rapidly identifying outliers, trends, lack of statistical control and bias.

### D.9.2 Reference versus analyser values (scatter diagram)

Plot the data pairs with the vertical axis as the analyser value, $X_{\mathrm{A}i}$, and the horizontal axis as the reference value, $R_i$ using the same scale for both values. Add the base reference line $X_{\mathrm{A}i} = R_i$. Calculate the standard deviation of the differences (see D.3) and draw additional reference lines at ± 2,6 $s_{\mathrm{d}}$ from the reference line. Points lying outside these additional lines should be considered as possible outliers.

If the points trend away from the line, systematic problems may be present in the reference system or the existing calibration may no longer be suitable due e.g. to changes in instrumental characteristics or solid mineral fuel quality.

A broad scattering of the data indicates a lack of correlation. This may be confirmed by calculating the linear correlation coefficient, $r$, as given in Equation (D.9):

$$r = \frac{\sum R \cdot X_A - \dfrac{\sum R \cdot \sum X_A}{n}}{\sqrt{\left[\sum R^2 - \dfrac{\left(\sum R\right)^2}{n}\right] \cdot \left[\sum X_{\mathrm{A}}{}^2 - \dfrac{\left(\sum X_{\mathrm{A}}\right)^2}{n}\right]}} \tag{D.9}$$

A value of 0,5 or less suggests that the correlation may not be adequate.

### D.9.3 Difference versus reference values

Plot the difference values, $d_i$, on the vertical axis against the corresponding reference values, $R_i$, on the horizontal axis. Add a horizontal reference line at $\overline{d}$ . Calculate the standard deviation of the differences (see D.3) and draw additional reference lines at ± 2,6 $s_{\mathrm{d}}$ ($L_{\mathrm{C}} = 99$ % for a two-sided test) from the reference line. Points lying outside these additional lines should be considered as possible outliers.

A trend in data indicates problems either in the operation of the analyser, the reference system or in the existing calibration.

### D.9.4 Difference versus serial number

Plot the difference values, $d_i$, on the vertical axis against the serial number ($i$ = 1,2, .., $n$) of the data pair on the horizontal axis. Add a horizontal reference line at $\overline{d}$ . Calculate the standard deviation of the differences (see D.3) and draw additional reference lines at ± 2,6 $s_{\mathrm{d}}$ from the reference line. Points lying outside these additional lines should be considered as possible outliers.

A trend in data may indicate a time-related change in the system, the test procedure or the quality of the coal.

### D.9.5 Difference versus flow rate

If the flow rate of the coal stream at the time of measurement is available from a flow rate indicator or can be calculated from the mass of the increments, further visual indications of problems may become manifest.

Plot the difference values, $d_i$, on the vertical axis against the flow rate of the coal on the horizontal axis.

If the data points cluster about a line that is not horizontal, there might be a bias in the reference system or a relationship between instrument response and the mass of sample within the interrogation zone (e.g. varying bed depth), which has not been taken into account by the existing calibration.

## D.10 Outliers

### D.10.1 General

An outlier may be the result of a gross deviation from prescribed experimental practice, an error in calculating or recording, or an extreme manifestation of the random variability inherent in the data.

### D.10.2 Cochran’s criterion

Calculate Cochran's criterion, $C$, from Equation (D.10):

$$C = \frac{d_{\text{max}}^2}{\sum d^2} \qquad \text{(D.10)}$$

Critical values, $C_\text{c}$, for Cochran's criterion at $L_\text{C} = 99\ \%$ , are given in Table D.3. If the calculated value of $C$ is greater than the value of $C_\text{c}$ in Table D.3, $d_{\text{max}}$ may be an outlier. In that case, identify $d_{\text{max}}$ in the list of observations, remove it if required by the criteria in D.10.3 and recalculate $C$. Repeat the process until all outliers have been identified.

**Table D.3 — Critical values, $C_\text{c}$, for Cochran's maximum variance level test**

| $n$[a] | $C_\text{c}$ for $L_\text{C} = 99\ \%$ | $n$[a] | $C_\text{c}$ for $L_\text{C} = 99\ \%$ |
|---|---|---|---|
| 9 | 0,754 | 26 | 0,402 |
| 10 | 0,718 | 27 | 0,391 |
| 11 | 0,684 | 28 | 0,382 |
| 12 | 0,653 | 29 | 0,372 |
| 13 | 0,624 | 30 | 0,363 |
| 14 | 0,599 | 31 | 0,355 |
| 15 | 0,575 | 32 | 0,347 |
| 16 | 0,553 | 33 | 0,339 |
| 17 | 0,532 | 34 | 0,332 |
| 18 | 0,514 | 35 | 0,325 |
| 19 | 0,496 | 36 | 0,318 |
| 20 | 0,480 | 37 | 0,312 |
| 21 | 0,465 | 38 | 0,306 |
| 22 | 0,450 | 39 | 0,300 |
| 23 | 0,437 | 40 | 0,294 |
| 24 | 0,425 | 60 | 0,215 |
| 25 | 0,413 | — | — |

[a] $n$ is the number of differences in the series.

### D.10.3 Criteria for removal of outliers

When it is known that a gross deviation from prescribed procedure has taken place, the resultant observation shall be discarded, whether or not it agrees with the rest of the data.

Otherwise, if an observation is considered suspect, the procedures undertaken to arrive at that value shall be carefully reviewed. If there is an error in the calculation, this shall be corrected. If a deviation from prescribed experimental procedure, or the existence of abnormal conditions at that particular time are discovered, it shall be discarded.

If there is no obvious reason why it should differ from the rest of the data, it shall be retained.

## D.11 Independence of differences

Calculate the differences between analyser and reference values from Equation (D.11):

$$d_i = X_{\mathrm{A}i} - R_i \tag{D.11}$$

Determine the median value as follows.

a) Sort the differences into ascending numerical order.

   If the number, $n$, of differences is odd, the median is the value that occurs at observation $(n + 1)/2$.

   If the number, $n$, of differences is even, the median is the mean of the values that occur at observations $n/2$ and $(n + 2)/2$.

b) Subtract the median from each calculated difference and record whether the result is positive or negative.

c) Ignoring the observations where the difference is zero, determine, in the unsorted differences, the number of runs, $\rho$, i.e. sequences of observations in which the sign remains unchanged and the numbers of positive and negative observations.

d) Assign the symbol $n_1$ to the smallest set of like (positive or negative) observations and the symbol $n_2$ to the other set.

e) If $n_1 \leqslant 10$, from Table D.4 determine the critical value, $\rho_\mathrm{c}$, for the number of runs which corresponds to the values of $n_1$ and $n_2$. If $\rho \geqslant \rho_\mathrm{c}$ then there is no evidence that the runs are not randomly ordered and the data are suitable for use.

f) If $n_1 > 10$, calculate the expected number, $E(\rho)$, of runs from Equation (D.12):

$$E(\rho) = \frac{2 \cdot n_1 \cdot n_2}{n_1 + n_2} + 1 \tag{D.12}$$

   and the standard error, $s(\rho)$, of the number of runs from Equation (D.13):

$$s(\rho) = \sqrt{\frac{2 \cdot n_1 \cdot n_2 (2 \cdot n_1 \cdot n_2 - n_1 - n_2)}{(n_1 + n_2)^2 (n_1 + n_2 - 1)}} \tag{D.13}$$

g) Calculate the normal deviate, $z$, from Equation (D.14):

$$z = \frac{\rho - E(\rho)}{s(\rho)} \tag{D.14}$$

If the value of $z$ is less than 1,96 at $L_C = 95$ %, then there is no evidence that the runs are not randomly ordered and the data are suitable for use.

**Table D.4 — Critical values, $\rho_c$, for the number of runs at $L_C = 95$ % (15 to 25 observations)**

| $n_1$ | $n_2$ | $\rho_c$ | $n_1$ | $n_2$ | $\rho_c$ |
|---|---|---|---|---|---|
| 5 | 10 | 5 | *7 (con't)* | 14 | 7 |
| | 11 | 5 | | 15 | 7 |
| | 12 | 5 | | 16 | 7 |
| | 13 | 5 | | 17 | 8 |
| | 14 | 6 | | 18 | 8 |
| | 15 | 6 | 8 | 8 | 6 |
| | 16 | 6 | | 9 | 6 |
| | 17 | 6 | | 10 | 7 |
| | 18 | 6 | | 11 | 7 |
| | 19 | 6 | | 12 | 7 |
| | 20 | 6 | | 13 | 7 |
| 6 | 9 | 5 | | 14 | 8 |
| | 10 | 6 | | 15 | 8 |
| | 11 | 6 | | 16 | 8 |
| | 12 | 6 | | 17 | 8 |
| | 13 | 6 | 9 | 9 | 7 |
| | 14 | 6 | | 10 | 7 |
| | 15 | 7 | | 11 | 7 |
| | 16 | 7 | | 12 | 8 |
| | 17 | 7 | | 13 | 8 |
| | 18 | 7 | | 14 | 8 |
| | 19 | 7 | | 15 | 9 |
| 7 | 8 | 5 | | 16 | 9 |
| | 9 | 6 | 10 | 10 | 7 |
| | 10 | 6 | | 11 | 8 |
| | 11 | 6 | | 12 | 8 |
| | 12 | 7 | | 13 | 9 |
| | 13 | 7 | | 14 | 9 |
| | | | | 15 | 9 |

## D.12 Linear regression analysis by an EIV method

### D.12.1 Slope of the regression line

The slope, $\beta$, of the regression line of analyser values, $X_{\mathrm{A}i}$, on mean duplicate reference values, $\overline{D}_i$, is given by Equation (D.15):

$$\beta = s_{\mathrm{A},\,\overline{\mathrm{D}}} / \left( s_{\overline{\mathrm{D}}}^2 - s_{\mathrm{dup}}^2 / 4 \right) \tag{D.15}$$

where

$$\overline{D} = \left( D1 + D2 \right) / 2 \tag{D.16}$$

$$\mathrm{dup} = D_1 - D_2 \tag{D.17}$$

$$s_{\mathrm{A},\overline{\mathrm{D}}} = \sum X_{\mathrm{A}i} \overline{D_i} - \left( \sum X_{\mathrm{A}i} \sum \overline{D}_i \right) / n \tag{D.18}$$

$$s_{\overline{\mathrm{D}}}^2 = \sum \overline{D^2_i} - \left( \sum \overline{D_i} \right)^2 / n \tag{D.19}$$

$$s_{\mathrm{dup}}^2 = \sum x_{\mathrm{dup}}{}_1^2 - \left( \sum x_{\mathrm{dup},i} \right)^2 / n \tag{D.20}$$

### D.12.2 Variance of the slope

The variance of the slope, $V_\beta$, of the regression line is given by Equation (D.21):

$$V_\beta = n^{-1} \sigma_\mathrm{c}^{-2} \left\{ \left( s_{\mathrm{dup}}^2 / 4 \right) \beta^2 \left( 0{,}5 + \sigma_\mathrm{c}^{-2} \right) + \left( s_\mathrm{A}^2 - \beta^2 \sigma_\mathrm{c}^2 \right) \times \left[ 1 + \left( s_{\mathrm{dup}}^2 / 4 \right) \sigma_\mathrm{c}^{-2} \right] \right\} \tag{D.21}$$

where

$$\sigma^2 = s_{\overline{\mathrm{D}}}^2 - s_{\mathrm{dup}}^2 / 4 \tag{D.22}$$

Other terms have the meanings assigned in D.12.1

## D.13 Bias of scale

Calculate the test statistic, $t_\mathrm{s}$, from Equation (D.23):

$$t_\mathrm{s} = \frac{\left| \beta - 1 \right|}{\sqrt{V_\beta}} \tag{D.23}$$

Compare $t_\mathrm{s}$ with the critical value, $t_\mathrm{c}$, of Student's $t$ at $(n - 2)$ degrees of freedom and $L_\mathrm{C} = 99$ % (see Table D.1).

If $t_\mathrm{s} \leqslant t_\mathrm{c}$, there is no evidence of scale bias.

If $t_\mathrm{s} > t_\mathrm{c}$, there probably is scale bias.

## D.14 Bias of location

Calculate the test statistic, $t_\text{l}$, from Equation (D.24):

$$t_\text{l} = \frac{\left|\bar{d}\right|}{\sqrt{V_\text{d} / n}} \tag{D.24}$$

Compare $t_\text{l}$ with the critical value, $t_\text{c}$, of Student's $t$ at $(n - 1)$ degrees of freedom and $L_\text{C} = 99$ % (see Table D.1).

If $t_\text{l} \leqslant t_\text{c}$, there is no evidence of location bias.

If $t_\text{l} > t_\text{c}$, there probably is location bias.

## D.15 Variance within duplicates

From the two sets of duplicate reference values, $D_{1i}$ and $D_{2i}$, calculate the variance between duplicates $V_\text{dup}$ as given by Equation (D.25):

$$V_\text{dup} = \frac{\sum x_\text{dup}^{\,2}}{2n_\text{dup}} \tag{D.25}$$

where

$x_\text{dup}$ is the difference between duplicate reference values;

$n_\text{dup}$ is the number of pairs of duplicates in the set.

## D.16 Performance guarantee test

Test the significance of the difference between the value of standard deviation found for the analyser in D.17 and a given expected value (e.g. the manufacturer's guarantee of performance) as follows.

Calculate the values of the statistics $Q$, as given in Equation (D.26), and $Z$, as given in Equation (D.27):

$$Q = V_\text{R1} \cdot V_\text{R2} + V_\text{R1} \cdot V_\text{A} + V_\text{R2} \cdot V_\text{A} , \tag{D.26}$$

$$Z = V_\text{R1} \cdot V_\text{R2} + V_\text{R1} \cdot V_\text{g} + V_\text{R2} \cdot V_\text{g} , \tag{D.27}$$

where $V_\text{g}$ equals $s_\text{g}$, the expected (guaranteed) value of precision of the analyser at one standard deviation.

Calculate the test statistic $\delta$ from Equation (D.28):

$$\delta = n\left[{}^{Q}\!/\!_{Z} - \ln\left({}^{Q}\!/\!_{Z}\right) - 1\right] \tag{D.28}$$

Compare the value for $\delta$ with 6,635 (the critical value of $\chi^2$ at the 1 % significance level for 1 degree of freedom).

If $\delta > 6{,}635$, then the analyser precision is significantly larger (worse) than the expected value.

## D.17 Precision by Grubbs' estimator

From the analyser values, $X_{\mathrm{A}i}$, and the two sets of independent reference values, $R_{1i}$ and $R_{2i}$, calculate the following:

- variance of the differences, $V_{\mathrm{A,R1}}$, $V_{\mathrm{A,R2}}$ and $V_{\mathrm{R1,R2}}$: (see D.2);
- variances, $V_{\mathrm{A}}$, as given in Equation (D.29), $V_{\mathrm{R1}}$, as given in Equation (D.30), and $V_{\mathrm{R2}}$, as given in Equation (D.31):

$$V_{\mathrm{A}} = \frac{V_{\mathrm{A,R1}} + V_{\mathrm{A,R2}} - V_{\mathrm{R1,R2}}}{2} \tag{D.29}$$

$$V_{\mathrm{R1}} = \frac{V_{\mathrm{A,R1}} + V_{\mathrm{R1,R2}} - V_{\mathrm{A,R2}}}{2} \tag{D.30}$$

$$V_{\mathrm{R2}} = \frac{V_{\mathrm{A,R2}} + V_{\mathrm{R1,R2}} - V_{\mathrm{A,R1}}}{2} \tag{D.31}$$

- standard deviations, $s_{\mathrm{A}}$, $s_{\mathrm{R1}}$ and $s_{\mathrm{R2}}$: (see D.3);
- precision of the methods, $P_{\mathrm{A}}$, $P_{\mathrm{R1}}$ and $P_{\mathrm{R2}}$: (see D.4).

# Annex E
(informative)

## Reference standards

In order to achieve its prime function of providing a stable response to interrogation by an analyser, a reference standard should be in a form that prevents any significant physical or chemical changes to its constitution.

A sample of the solid mineral fuel to be analysed would be ideal in terms of the level of response but in practice it is very difficult to fabricate it in a way that resists physical and chemical change. Such standards are used but great care must be taken to avoid problems. Grinding to a small particle size helps to minimize heterogeneity and packing density variations; sealing, for example in a plastics container, reduces the risk of oxidation and moisture content change.

More stable standards have been constructed from suitable solid carbonaceous materials, such as chemically cured resins or thermally moulded plastics. With careful choice of material, these can be produced to be dimensionally stable and reasonably inert. Response to interrogation can be adjusted by the inclusion of materials of suitable composition. Some designs make provision for adjustment of response by allowing the physical removal or insertion of suitable agents.

For natural-gamma ash meters, a suitable reference material is potassium sulfate, which provides a response some 10 times greater than coal and reduces the counting periods to a manageable level.

In some designs of analysers, a suitable response can be obtained from the construction materials of the empty interrogation zone or from the belt used to transport the solid mineral fuel.

In the case of slurry analysers, the reference material used is usually pure water. For the measurement of ash in flotation tailings, the best reference material is a plastic plate, of similar colour to the tailings, immersed in water.

# Annex F
(informative)

# Specimen calculations

## F.1 Data

The data for the calculations in F.2, F.4, F.5, etc., were obtained from operational installations. The remainder are random numbers generated within constraints chosen to simulate expected variations in data for ash in coal. Deliberate perturbations were added to illustrate particular effects.

## F.2 Instrument stability (see Clause 8)

### F.2.1 Test procedure

Fifteen repeat measurements were made for each of two reference standards to give benchmark (time $= 0$) and subsequent (time $= \tau$,) data, which are presented in Table F.1.

**Table F.1 — Data for instrument stability tests — Percent ash**

| Reference standard 1 | | Reference standard 2 | |
|---|---|---|---|
| Time 0 | Time $\tau$ | Time 0 | Time $\tau$ |
| 25,54 | 25,65 | 14,27 | 14,35 |
| 24,91 | 25,79 | 14,39 | 14,70 |
| 25,80 | 25,60 | 14,28 | 15,33 |
| 25,46 | 25,23 | 14,10 | 14,39 |
| 25,55 | 25,64 | 14,34 | 14,52 |
| 25,62 | 26,00 | 14,66 | 14,73 |
| 25,74 | 25,35 | 14,08 | 14,71 |
| 25,45 | 25,73 | 14,38 | 14,63 |
| 25,90 | 25,80 | 14,85 | 14,20 |
| 25,38 | 25,82 | 14,65 | 14,86 |
| 25,48 | 25,26 | 14,42 | 14,24 |
| 26,04 | 25,04 | 14,64 | 14,94 |
| 25,41 | 25,43 | 14,58 | 14,72 |
| 25,48 | 25,60 | 14,09 | 14,49 |
| 26,12 | 25,56 | 14,18 | 14,79 |

## F.2.2 Data analysis (see 8.5)

### F.2.2.1 Measurement precision (see 8.5.2)

### F.2.2.1.1 Calculated values (see 8.5.2.1)

The values of variance, standard deviation and precision, calculated as shown in D.2 to D.4, for each set of reference standard values are given in Table F.2:

**Table F.2 — Calculated values of variance, standard deviation and precision**

| Parameter | Reference standard 1 | | Reference standard 2 | |
|---|---|---|---|---|
| | Time 0 | Time $\tau$ | Time 0 | Time $\tau$ |
| Variance, $V$ | 0,089 | 0,068 | 0,057 | 0,086 |
| Standard deviation, $s$ | 0,299 | 0,261 | 0,238 | 0,292 |
| Precision, $P$ | ± 0,555 % | ± 0,626 % | ± 0,508 % | ± 0,623 % |

### F.2.2.1.2 Tests for significance (see 8.5.2.2)

The variance ratios for values at time 0 and time $\tau$, calculated as shown in D.5, are given in Table F.3:

**Table F.3 — Variance ratios**

| Parameter | Reference standard 1 | Reference standard 2 |
|---|---|---|
| Calculated variance ratio, $F$ | 1,319 | 1,509 |
| Critical value from Table D.2 ($n_1 = 15$, $n_2 = 15$), $F_c$ | 2,48 | 2,48 |
| Conclusion | $F < F_c$ not significant | $F < F_c$ not significant |

### F.2.2.2 Changes in response level (see 8.5.3)

### F.2.2.2.1 Calculated values (see 8.5.3.1)

The mean of each set of reference standard values at time 0 and time $\tau$, are given in Table F.4:

**Table F.4 — Changes in response level**

| Parameter | Reference standard 1 | | Reference standard 2 | |
|---|---|---|---|---|
| | Time 0 | Time $\tau$ | Time 0 | Time $\tau$ |
| Mean, % | 25,592 | 25,567 | 14,394 | 14,640 |

#### F.2.2.2.2 Test for significance (see 8.5.3.2)

The comparison of means at time 0 and time $\tau$, carried out as shown in Annex D.7, results in the values given in Table F.5:

Table F.5 — Test for significance

| Parameter | Reference standard 1 | Reference standard 2 |
|---|---|---|
| Calculated test statistic, $t_m$ | 0,248 | 2,526 |
| Calculated test statistic, $t_m$ | 2,048 | 2,048 |
| Conclusion | $t_m < t$, not significant | $t_m > t$, significant |

### F.2.3 Interpretation (see 8.6)

Comparison of the variances of the measurements made at time $\tau$, with those for time 0 (see F.2.2.1.2), shows that there is no significant difference for either reference standard. This indicates that the precision of measurement has not changed in the intervening time.

Comparison of the means of the measurements made at time $\tau$, with those for time 0 (see F.2.2.2.2), shows that in the case of reference standard 1 there is no significant difference, but in the case of reference standard 2 there is. This indicates that the response of the instrumentation has changed in the intervening time.

## F.3 Calibration (see 9.5)

### F.3.1 Test procedure

Values were generated to represent a set of analyser values and a set of duplicate reference values arising from 20 samples with a true ash value range from approximately 10 % to 20 %. The data obtained are given in Table F.6 together with the means of the duplicate reference values.

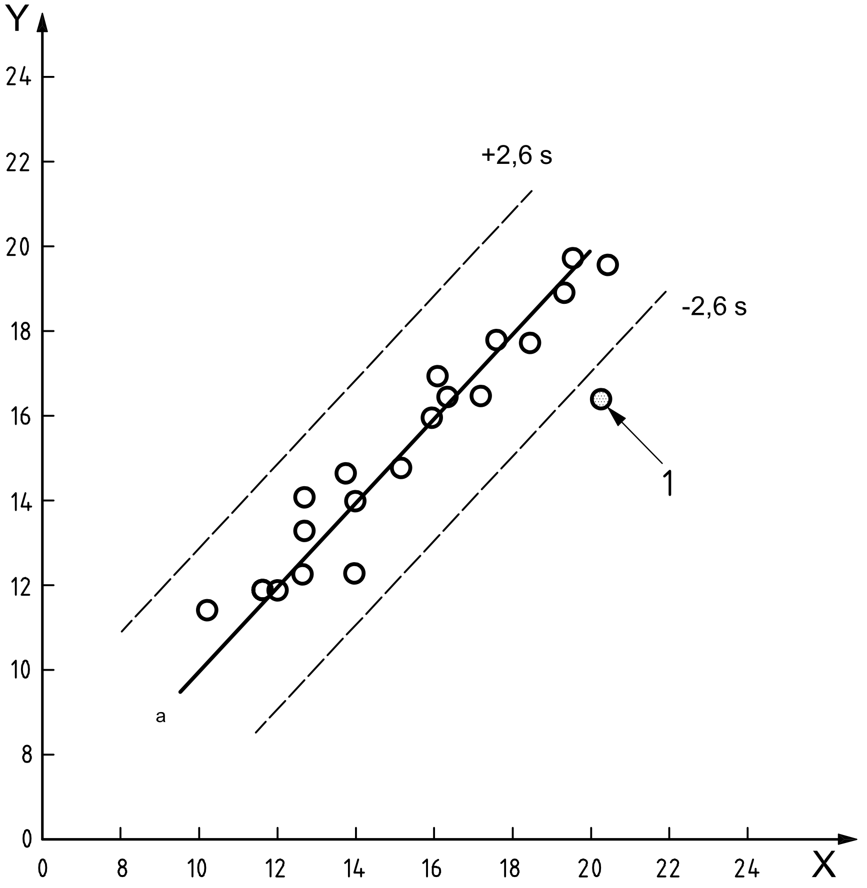
### F.3.2 Data analysis (see 9.5)

#### F.3.2.1 Visual assessment (see 9.5.2)

A graph of the analyser values against the means of the duplicate reference values (see D.9.2) is shown in Figure F.1. Results of other the graphical procedures recommended in 9.5.2 (see D.9.3 to D.9.5) are shown in Figures F.2, F.3 and F.4. It can be seen that one particular sample (No. 4) lies well away from the main plot and outside the ± 2,6 sigma limits. No other particular trends are noticeable.

**Table F.6 — Initial data for calibration confirmation**

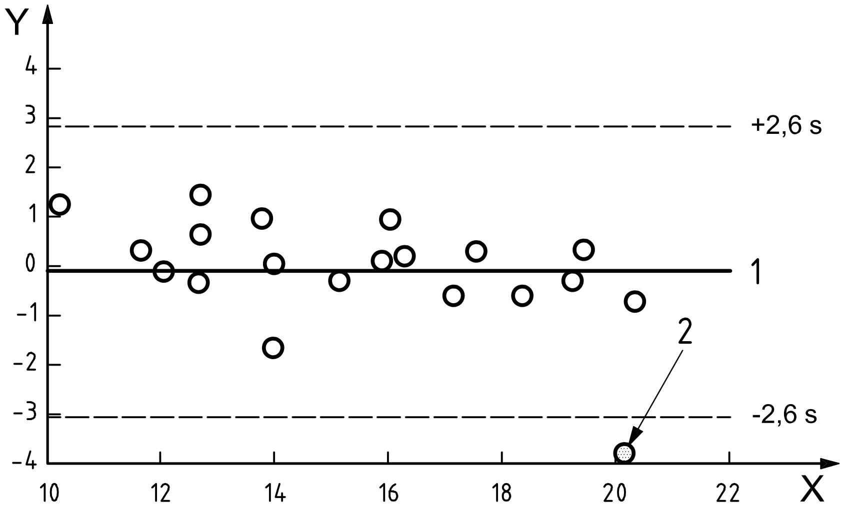
| Number | Ash<br>%, as presented to analyser | | | |
|---|---|---|---|---|
| | Analyser<br>$X_A$ | Reference duplicate 1<br>$D_1$ | Reference duplicate 2<br>$D_2$ | Reference duplicate mean<br>$\overline{D}$ |
| 1 | 16,45 | 16,47 | 16,07 | 16,270 |
| 2 | 19,57 | 19,80 | 20,83 | 20,315 |
| 3 | 12,28 | 12,87 | 12,40 | 12,635 |
| 4 | 16,39 | 16,34 | 15,99 | 20,165 |
| 5 | 17,72 | 18.32 | 18,35 | 18,335 |
| 6 | 15,96 | 15.84 | 15,90 | 15,870 |
| 7 | 16,95 | 15.97 | 16,05 | 16,010 |
| 8 | 9,71 | 9,21 | 9,59 | 9,400 |
| 9 | 16,48 | 17,13 | 17,12 | 17,125 |
| 10 | 14,10 | 12,95 | 12,38 | 12,665 |
| 11 | 13,99 | 14,27 | 13,66 | 13,965 |
| 12 | 11,92 | 11,99 | 11,24 | 11,615 |
| 13 | 18,91 | 18,82 | 19,60 | 19,210 |
| 14 | 11,90 | 12,92 | 11,11 | 12,015 |
| 15 | 14,79 | 15,43 | 14,81 | 15,120 |
| 16 | 17,77 | 17,75 | 17,27 | 17,51 |
| 17 | 11,43 | 10,51 | 9,90 | 10,205 |
| 18 | 14,66 | 13,85 | 13,57 | 13,710 |
| 19 | 13,30 | 12,92 | 12,42 | 12,670 |
| 20 | 12,30 | 14,37 | 13,55 | 13,960 |



**Key**

| | | | |
|---|---|---|---|
| X | reference, ash, % | 1 | sample 4 |
| Y | analyser, ash, % | a | Slope = 1. |

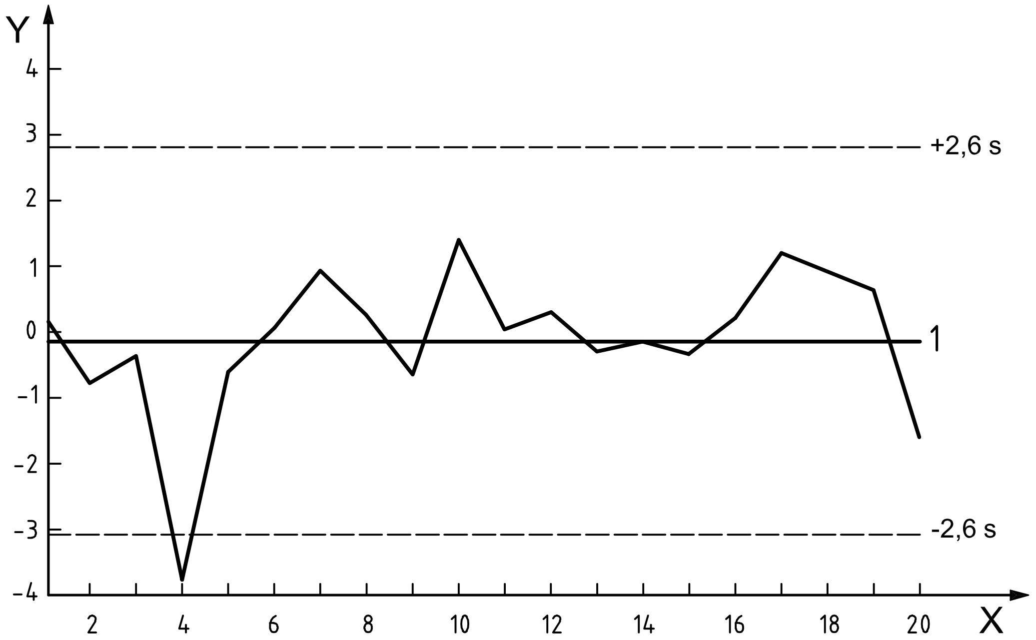
Figure F.1 — Calibration — Analyser values against reference values



**Key**

| | | | |
|---|---|---|---|
| X | reference, ash, % | 1 | mean difference |
| Y | difference, ash, % | 2 | sample 4 |

Figure F.2 — Difference versus reference values



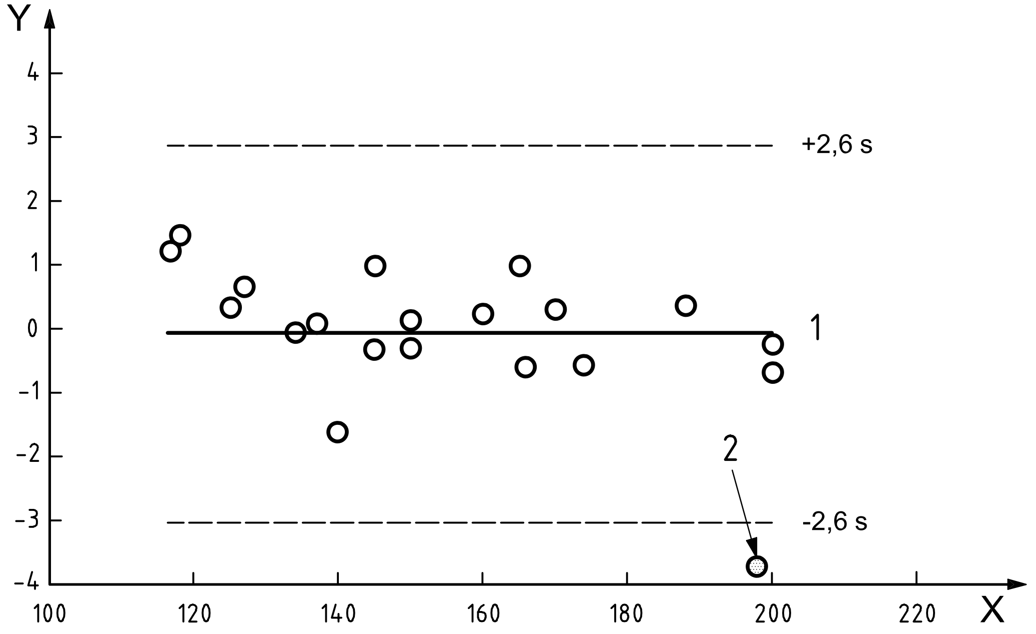
**Key**

X serial number

Y difference, ash, %

1 mean difference

Figure F.3 — Difference against serial number



**Key**

X flow rate, t/h

Y difference, ash, %

1 mean difference

2 sample 4

Figure F.4 — Difference against flow rate

### F.3.2.2 Outliers (see 9.5.3)

**F.3.2.2.1** Cochran's criterion test (see D.10.2), applied to the initial data gives the following values:

| | |
|---|---|
| — maximum difference, analyser values minus mean duplicate reference values, (sample 4): | – 3,78 %; |
| — calculated value of Cochran's criterion, $C$: | 0,576; |
| — critical value, $C_c$, from Table D.3: | 0,480; |
| — conclusion: | $C > C_c$, i.e. sample 4 is an outlier. |

**F.3.2.2.2** Cochran's criterion test (see D.10.2), applied to the data with sample 4 removed gives the following values:

| | |
|---|---|
| — maximum difference, analyser values minus mean duplicate reference values, (sample 20) | – 1,66 %; |
| — calculated value of Cochran's criterion, $C$: | 0,263; |
| — critical value, $C_c$, from Table D.3: | 0,496; |
| — conclusion: | $C < C_c$, i.e. sample 20 is not an outlier. |

For the purposes of this example, it is assumed that sample 4 had suffered a transcription error. The correct value (16,16 %) was entered into the set of results for subsequent calculations.

Visual assessment of the corrected data showed no likely outliers or particular trends.

### F.3.2.3 Independence of differences (see 9.5.4)

The independence of the data and hence its suitability for use in the application of the subsequent bias tests, is assessed by the procedures described in D.11.

The differences between the analyser values and the mean duplicate reference values, sorted into ascending numerical order (see Table F.7) have a median value of 0,135. This value subtracted from the unsorted differences gives results also shown in Table F.7. The numbers of runs and numbers of negative and positive results are the following:

| | |
|---|---|
| — runs, $\rho$: | 12; |
| — negative results, $n_1$: | 10; |
| — positive results, $n_2$: | 10. |

The number of negative results is equal to the number of positive results. Either set may be designated $n_1$. Since $n_1$ is not greater than 10, the critical value for the number of runs is determined from Table D.4.

| | |
|---|---|
| — runs (critical value), $\rho_c$: | 7; |
| — conclusion: | $\rho > \rho_c$, i.e. data are suitable for use. |

For illustration purposes, the test specified in D.11 for $n_1$ greater than 10, applied to these data gives the following values:

| | |
|---|---|
| — expected number of runs, $E_\rho$: | 11; |

— standard error, $s_\rho$: 2,176;

— normal deviate, $z$: 0,459;

— conclusion: $z < 1{,}96$, i.e. data are suitable for use.

**Table F.7 — Independence of differences test (corrected calibration data)**

| Difference (unsorted) | Difference (sorted) | Difference (unsorted) – median (0,135) | Runs |
|---|---|---|---|
| 0,180 | – 1,660 | + 0,045 | 1 |
| – 0,745<br>– 0,355 | – 0,745<br>– 0,645 | – 0,880<br>– 0,490 | 2 |
| 0,225 | – 0,615 | + 0,090 | 3 |
| – 0,615<br>0,090 | – 0,355<br>– 0,330 | – 0,750<br>– 0,045 | 4 |
| 0,940<br>0,310 | – 0,300<br>– 0,115 | + 0,805<br>+ 0,175 | 5 |
| – 0,645 | 0,025 | – 0,780 | 6 |
| 1,435 | 0,090 | + 1,300 | 7 |
| 0,025 | 0,180 | – 0,110 | 8 |
| 0,305 | 0,225 | + 0,170 | 9 |
| – 0,300<br>– 0115<br>– 0,33 | 0,260<br>0,305<br>0,310 | – 0,435<br>– 0,250<br>– 0,465 | 10 |
| 0,260<br>1,225<br>0,950<br>0,630 | 0,630<br>0,940<br>0,950<br>1,225 | + 0,125<br>+ 1,090<br>+ 0,815<br>+ 0,495 | 11 |
| – 1,660 | 1,435 | – 1,795 | 12 |

### F.3.2.4 Tests for bias (see 9.5.5)

The slope of the (EIV method) linear regression of the analyser values on the mean duplicate reference values, and its variance, calculated as described in D.12 are given as follows:

— slope, $\beta$: 0,909;

— variance of slope, $V_\beta$: 0,003.

Calculations to assess the existence of bias of scale, carried out as described in D.13, give the following values:

— calculated test statistic, $t_s$: 1,757;

— critical value, $t_c$, from Table D.1 at $L_C$ = 99 % (= 18) 2,878.

— conclusion: $t_s < t_c$, i.e. there is no bias of scale evident.

Calculations to assess the existence of bias of location, carried out as described in Annex D.14, give:

| | |
|---|---|
| — calculated test statistic, $t_l$: | 0,662; |
| — critical value, $t_c$, from Table D.1 at $L_C$ = 99 % (= 19): | 2,861; |
| — conclusion: | $t_l < t_c$ , i.e. there is no bias of location evident. |

### F.3.3 Interpretation (see 9.6)

There is no evidence of bias of scale or of bias of location and the visual assessment offers no evidence of unwanted correlations or significant problems. The existing calibration may be considered to be satisfactory.

## F.4 Analyser dynamic precision (see 10.2)

### F.4.1 Test procedure

Values were obtained for one set of analyser values and two independent sets of reference values arising from 40 samples with an ash value range from approximately 7 % to 10 %. The data obtained are given in Table F.8.

**Table F.8 — Data for analyser dynamic precision**

| Number | Ash<br>%, as presented to analyser | | | Number | Ash<br>%, as presented to analyser | | |
|---|---|---|---|---|---|---|---|
| | Analyser | Reference 1 | Reference 2 | | Analyser | Reference 1 | Reference 2 |
| 1 | 9,34 | 8,20 | 8,23 | 21 | 8,66 | 7,65 | 7,66 |
| 2 | 9,18 | 8,45 | 8,19 | 22 | 8,72 | 9,05 | 7,41 |
| 3 | 8,93 | 7,98 | 7,86 | 23 | 8,98 | 8,28 | 7,97 |
| 4 | 9,29 | 8,05 | 8,24 | 24 | 8,79 | 7,89 | 8,26 |
| 5 | 9,29 | 8,5 | 8,07 | 25 | 8,74 | 7,71 | 8,05 |
| 6 | 8,97 | 8,02 | 8,78 | 26 | 9,11 | 8,03 | 7,96 |
| 7 | 8,67 | 7,98 | 7,66 | 27 | 8,63 | 7,49 | 7,73 |
| 8 | 8,81 | 7,91 | 7,81 | 28 | 9,07 | 7,94 | 7,75 |
| 9 | 8,83 | 7,84 | 7,85 | 29 | 7,66 | 7,15 | 7,34 |
| 10 | 8,41 | 7,76 | 7,80 | 30 | 7,82 | 7,42 | 7,39 |
| 11 | 8,54 | 7,86 | 8,27 | 31 | 8,27 | 7,29 | 7,27 |
| 12 | 8,81 | 7,80 | 8,49 | 32 | 8,52 | 7,09 | 7,12 |
| 13 | 8,95 | 7,92 | 8,47 | 33 | 8,5 | 7,30 | 7,10 |
| 14 | 8,90 | 8,06 | 8,69 | 34 | 8,42 | 7,57 | 8,04 |
| 15 | 9,10 | 8,57 | 8,22 | 35 | 7,47 | 7,00 | 7,27 |
| 16 | 9,57 | 9,02 | 9,13 | 36 | 7,6 | 7,46 | 7,59 |
| 17 | 10,00 | 9,72 | 9,81 | 37 | 7,93 | 7,77 | 7,33 |
| 18 | 8,12 | 8,13 | 8,05 | 38 | 8,14 | 8,2 | 7,98 |
| 19 | 9,00 | 8,50 | 8,76 | 39 | 8,05 | 8,21 | 7,96 |
| 20 | 9,13 | 8,70 | 9,36 | 40 | 8,02 | 8,26 | 8,22 |

## F.4.2 Data analysis (see 10.2.5)

### F.4.2.1 Visual assessment (see 10.2.5.1)

A graph of the reference 1 values against reference 2 values (see D.9.2) shows that one particular sample (No. 22) lies outside the ± 2,6 sigma limits and may be an outlier. No other trend is obvious. Analyser values against reference 1 values and against reference 2 values show no obvious outliers or trends.

### F.4.2.2 Outliers (see 10.2.5.2)

Cochran's criterion test (see D.10.2), applied to the analyser against reference 1 data gives the following values:

- maximum difference, analyser values minus reference 1 values (sample 32) 1,43 %;
- calculated value of Cochran's criterion, $C$: 0,079;
- critical value, $C_c$, from Table D.3: 0,294;
- conclusion: $C < C_c$ , i.e. sample 32 is not an outlier.

Cochran's criterion test (see D.10.2), applied to the analyser against reference 2 data gives the following values:

- maximum difference, analyser values minus reference 2 values (sample 32) 1,40 %;
- calculated value of Cochran's criterion, $C$: 0,078;
- critical value, $C_c$, from Table D.3: 0,294;
- conclusion: $C < C_c$, i.e. sample 32 is not an outlier.

Cochran's criterion test (see D.10.2), applied to reference 1 against reference 2 data gives the following values:

- maximum difference, reference 1 values minus reference 2 values (sample 22) 1,64 %;
- calculated value of Cochran's criterion, $C$: 0,394;
- critical value, $C_c$, from Table D.3: 0,294;
- conclusion: $C > C_c$, i.e. sample 22 is an outlier.

Cochran's criterion test (see D.10.2), applied to reference 1 against reference 2 data with sample 22 removed gives the following values:

- maximum difference, reference 1 values minus reference 2 values (sample 6) –0,76 %.
- calculated value of Cochran's criterion, $C$: 0,140;
- critical value; $C_c$, from Table D.3: 0,300;
- conclusion: $C < C_c$, i.e. sample 6 is not an outlier.

Re-examination of the data however shows no reason to amend or exclude sample 22 and it is not removed from the data set.

#### F.4.2.3 Precision (see 10.2.5.3)

The standard deviation, variance and precision of each test method, as determined by the Grubbs procedure (see D.17) are given in Table F.9.

**Table F.9 — Calculated values of variance, standard deviation and precision**

| Parameter | Analyser | Reference 1 | Reference 2 |
|---|---|---|---|
| Standard deviation, $s$ | 0,343 | 0,273 | 0,315 |
| Variance, $V$ | 0,118 | 0,075 | 0,099 |
| Precision, $P$, % | ± 0,693 | ± 0,552 | ± 0,636 |

#### F.4.2.4 Performance guarantee (see 10.2.5.4)

It is assumed for the purposes of illustration that the manufacturer has guaranteed the analyser will return a performance indicator at 1 standard deviation of 0,30 % ash or less.

Calculations as described in the procedure given in D.16 give the following values:

— $Q = 0{,}028$;

— $Z = 0{,}023$;

— $\delta = 0{,}769$;

— Conclusion: $\delta < 6{,}635$, i.e. the guarantee has been met.

### F.4.3 Interpretation (see 10.2.5)

Sample 22 is an outlier in the relationship between reference 1 and reference 2 values but there is no evidence to exclude it from the data. Otherwise the visual assessments offer no evidence of unwanted correlations or significant problems. The results indicate a satisfactory precision for the analyser. Although the analyser precision at 1 standard deviation is numerically higher (0,343 %) than the declared performance guarantee (0,30 %), the difference is not significant and the guarantee has been met.

## F.5 Comparative dynamic precision (see 10.3)

### F.5.1 Test procedure

A set of analyser values and reference values arising from 20 samples were obtained from an operational installation. The data are presented in Table F.10.

**Table F.10 — Data for comparative dynamic precision**

| Number | Ash<br>%, as presented to analyser | |
|---|---|---|
| | Analyser | Reference |
| 1 | 8,89 | 8,20 |
| 2 | 8,73 | 7,76 |
| 3 | 8,53 | 7,84 |
| 4 | 8,84 | 8,44 |
| 5 | 8,77 | 8,62 |
| 6 | 8,44 | 7,53 |
| 7 | 7,04 | 6,78 |
| 8 | 8,12 | 7,83 |
| 9 | 7,81 | 7,37 |
| 10 | 8,33 | 7,95 |
| 11 | 8,71 | 8,02 |
| 12 | 8,94 | 8,23 |
| 13 | 8,78 | 8,34 |
| 14 | 9,12 | 8,85 |
| 15 | 9,01 | 8,12 |
| 16 | 8,71 | 8,04 |
| 17 | 8,79 | 8,11 |
| 18 | 8,65 | 8,15 |
| 19 | 8,88 | 8,19 |
| 20 | 8,96 | 8,71 |

### F.5.2 Data analysis (see 10.3.5)

#### F.5.2.1 Visual assessment (see 10.3.5.1)

A graph of the analyser values against the reference values, prepared as described in D.9.2, indicates a good correlation with no outliers. There is a location bias of about 0,5 %. Graphs for the other graphical procedures recommended in 10.3.5.1 (see D.9.3 to D.9.5) show no outliers or trends that would suggest any problems requiring investigation.

### F.5.2.2 Outliers (see 10.3.5.2)

Cochran's criterion test (see D.10.2), applied to the analyser against reference data gives the following values:

| | |
|---|---|
| — maximum difference, analyser values minus reference values (sample 2): | 0,97 %; |
| — calculated value of Cochran's criterion, $C$: | 0,132; |
| — critical value, $C_c$, from Table D.3: | 0,480; |
| — conclusion: | $C < C_c$, i.e. sample 2 is not an outlier. |

### F.5.2.3 Precision (see 10.3.5.3)

The standard deviation, variance and precision, calculated from the differences between analyser values and reference values, as described in D.2 to D.4, are given as follows:

| | |
|---|---|
| — standard deviation, $s$: | 0,242 %; |
| — variance, $V$: | 0,059; |
| — precision, $P$: | ± 0,505 %. |

### F.5.2.4 Comparison with a previous value (see 10.3.5.4)

The variance ratio of the value of variance obtained in F.5.2.3 and variance obtained from a hypothetical standard deviation of 0,283 from a previous set of test data obtained under the same conditions, calculated as shown in D.5 are given as follows:

| | |
|---|---|
| — calculated variance ratio, $F$: | 1,363; |
| — critical value, $F_c$, from Table D.2 ($n_1 = 20$, $n_2 = 20$): | 2,17; |
| — conclusion: | $F < F_c$ , i.e. the difference is not significant. |

## F.5.3 Interpretation (see 10.3.6)

Visual assessment confirms that there is no evidence of unwanted correlations or significant trends and there is no evidence of outliers. The precision obtained compares satisfactorily with a previous (hypothetical) value. The precision of the analyser has not changed significantly.

# Bibliography

[1] JAECH, J L, *Large sample tests of Grubbs' estimators of instrument precision with more than two instruments,* Technometrics, **18**(2), 1976, pp. 127-133

[2] GRUBBS, F E, *An introduction to some precision and accuracy of measurement problems*, J Testing and Evaluation, **10**(4), 1982, pp. 133-143

[3] ROSE, C D, *Methods for assessing the accuracy of on-line analyzers*, J. Coal Quality, **10**(1), 1991, pp.19-28

[4] LOMBARD, F, *Statistical assessment of on-line analyzers, Chemometrics and Intelligent Laboratory Systems*, **37,** 1997, pp. 281-190

[5] Standards Australia, *Guide to the sampling of particulate materials — Part 5: Sampling of slurrie*s. (Draft in preparation), 1998

[6] ISO 20904, *Guide to the sampling of coal slurries*1)

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1) Under preparation.

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BSI
389 Chiswick High Road
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W4 4AL