

Gas analysis — Investigation and treatment of analytical bias

ICS 71.040.40

National foreword

This British Standard is the UK implementation of EN ISO 15796:2008. It is identical with ISO 15796:2005. It supersedes BS ISO 15796:2005, which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/15, Natural gas and gas analysis.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard cannot confer immunity from legal obligations.

Amendments corrigenda issued since publication

Date	Comments
30 June 2009	This corrigendum renumbers BS ISO 15796:2005 as BS EN ISO 15796:2008

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 5 September 2005

© BSI 2009

ISBN 978 0 580 65014 7

English Version

Gas analysis - Investigation and treatment of analytical bias
(ISO 15796:2005)

Analyse des gaz - Investigation et traitement des biais
analytiques (ISO 15796:2005)

Gasanalyse - Untersuchung und Behandlung von
systematischen Abweichungen (ISO 15796:2005)

This European Standard was approved by CEN on 30 July 2008.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Foreword

The text of ISO 15796:2005 has been prepared by Technical Committee ISO/TC 158 “Analysis of gases” of the International Organization for Standardization (ISO) and has been taken over as EN ISO 15796:2008 by Technical Committee CEN/SS N21 “Gaseous fuels and combustible gas” the secretariat of which is held by CMC.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2009, and conflicting national standards shall be withdrawn at the latest by February 2009.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

Endorsement notice

The text of ISO 15796:2005 has been approved by CEN as a EN ISO 15796:2008 without any modification.

Contents

Page

Foreword	iv
Introduction	v
1 Scope	1
2 Terms and definitions	1
3 Symbols	3
4 Bias related to instrumental drift	4
4.1 Principle	4
4.2 Stability monitoring	4
4.3 Drift correction	6
5 Bias related to effects of sample composition	10
5.1 Principles	10
5.2 Local bias handling	11
5.3 Bias handling for an extended measuring range	23
6 Treatment of matrix interferences	27
Annex A (normative) Critical values for the trend test	29
Annex B (informative) Uncertainty issues	30
Bibliography	33

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15796 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

Introduction

Traceability is considered as one of the key items of quality assurance in gas analysis. In general, it is defined by the existence of unbroken chains of comparisons, relating the analytical result to acknowledged standards of measurement. More specifically, an analytical result is considered traceable if, by way of these comparisons, it has been demonstrated to be free of significant bias, significance referring to the specified uncertainty of the result.

As a rule, traceability is not demonstrated individually for a single analytical result but for a defined analytical procedure with specified ranges of analyte concentration and matrix composition. An analytical procedure is considered traceable if it has been demonstrated to be free of significant bias, or if significant bias has been corrected, by measurement on representative samples of known traceable composition. These may be samples of appropriate reference gas mixtures. Alternatively, other representative samples may be analysed in parallel using an accepted reference procedure.

This International Standard provides generic methods for demonstrating, or establishing, traceability of analytical procedures using reference gas mixtures or reference analytical procedures, implementing principles laid out in ISO 14111 ^[1] and ISO/TS 14167 ^[2], and respecting the principles of the *Guide to the Expression of Uncertainty in Measurement* (GUM) ^[3].

In this International Standard, the term “concentration” is used for two different purposes:

- as a general term for quantities measured in gas composition analysis, replacing the term “content” (see ISO 7504 ^[4]);
- as a generic substitute for any of the specific quantities measured in gas composition analysis such as the mass concentration or the mole fraction of a specified analyte (see ISO 7504 ^[4]).

blank

Gas analysis — Investigation and treatment of analytical bias

1 Scope

This International Standard specifies generic methods for detecting and correcting bias (systematic errors) of analytical procedures for the analysis of gases, using reference gas mixtures or reference analytical procedures, as well as for estimating the correction uncertainty.

The main sources of (and parameters affecting) bias of analytical procedures are instrumental drift (time) and matrix interferences (matrix composition). Moreover, bias normally varies with analyte concentration. This International Standard therefore establishes protocols for

- detecting and correcting drift for an analytical system of limited stability,
- investigating and handling bias of a stable analytical system for a specified range of sample composition,

which are intended to be used in method development and method validation studies, either separately or sequentially.

This International Standard specifies procedures for two options, applicable to systematic effects, as follows:

- a) tracing the observed pattern of deviations and correcting for their effect,
- b) averaging over their effects and increasing the uncertainty,

where normally the first option entails lower uncertainty at the expense of higher effort.

For the convenience of the user, the methods specified in this International Standard are described for procedures of composition analysis, i.e. procedures for measuring the concentration of a specified analyte in a gas mixture. However, they are equally applicable to measurements of physico-chemical properties of a gas or gas mixture relevant to gas analysis, and translation into this subject field is straightforward.

2 Terms and definitions

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

2.1

bias

estimate of systematic error

NOTE Since the true value of a measurand cannot be known exactly, systematic errors cannot be determined exactly but have to be estimated using reference values.

2.2

correction

procedure by which the uncorrected result of a measurement is adjusted to compensate for systematic error

NOTE 1 Since systematic errors cannot be determined exactly, a correction can never be complete.

NOTE 2 In the VIM [5], the term correction is used with a different meaning.

2.3

uncertainty

parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

[GUM:1993 ^[3], definition 2.3.2]

2.4

traceability

property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons

[VIM:1993 ^[5], definition 6.10]

NOTE In ISO 14111 ^[1], the term traceability is defined as the ability to provide evidence of the overall accuracy attributed to measurement results through documented calibrations, using measurement standards of known accuracy and comparison measurements of known performance.

2.5

reference value

estimate of a quantity, with sufficiently well established traceability and specified uncertainty, used as a reference for a specified purpose

NOTE In gas analysis, reference values of composition or physico-chemical properties are most often provided by reference gas mixtures and reference analytical procedures.

2.6

reference gas mixture

calibration gas mixture whose composition is sufficiently well established and stable to be used as a reference standard of composition from which other composition data are derived

[ISO 7504:2001 ^[4], definition 4.1.1]

2.7

reference analytical procedure

analytical procedure which is capable of providing traceable results with sufficiently well established uncertainty for use as reference values

2.8

drift

slow change of output, at constant input, of a measuring system

2.9

stability

(of a measuring system) absence of significant drift

2.10

matrix interference

change in analytical response for a specified analyte, caused by variations in matrix composition

3 Symbols

A, B	specified drift-control mixtures
b_i	parameters of a bias correction model
δ	deviation (from a reference value)
I	interferent under consideration
M	gas mixture under consideration
m, n, N	number of data in a data series
p	number of correction parameters
Q	recovery (with respect to a reference value)
r	number of reference gas mixtures used for bias investigation
R_i	reference gas mixtures used for bias investigation
s	standard deviation of a data series
s_r	relative standard deviation of a data series (coefficient of variation)
s^2	variance of a data series
t	time
$u(x)$	standard uncertainty of an estimated quantity x
$u^2(x)$	variance of an estimated quantity x
$u_r(x)$	relative standard uncertainty of an estimated quantity x
$u(x, y)$	covariance between two estimated quantities x and y
x, y	quantity under consideration
$\langle x \rangle$	mean value of several quantities x_i
X	analyte under consideration
Δ^2	mean-square successive difference of a data series

4 Bias related to instrumental drift

4.1 Principle

This clause specifies procedures for investigating potential drift of an analytical system and taking corrective actions, if significant drift is encountered.

If the analytical system is expected to be stable, a “drift-control mixture” is measured on a regular basis. For each specified analyte, the results are recorded on a control chart, and the time series of control data is examined continuously. As long as these data vary at random within established control limits, the analytical system has been demonstrated to be stable. Monotonic decrease or increase in control data indicates drift. As an alternative to visual inspection, a statistical test based on successive differences may be used to detect a significant trend. As soon as drift becomes significant, e.g. when data exceed control limits, or when a significant trend is observed, the analytical system is removed from service. After adjustment and re-calibration, the analytical system is returned to service.

The “drift-control mixture” should contain all analytes currently being measured. Given sufficient information on the response behaviour of the analytical system, a representative subset of analytes may be used.

If the analytical system is known to exhibit significant drift, it can at least be expected that the drift behaviour of the system does not significantly depend upon sample composition, since this would allow for drift correction based on measurements of appropriate “drift-correction mixtures”. This expectation is tested by analysing two mixtures of distinct composition (different concentrations of the analytes under consideration, different matrix compositions) on a regular basis. The results are recorded, and for each analyte the two time-series of drift measurement data are compared in order to investigate whether drift behaviour can be expressed in a concentration-invariant manner. Given this for every analyte under consideration, the two time-series for each analyte are pooled to derive a drift correction. In fortunate cases, a joint drift correction may be used for several or even all analytes.

If the system exhibits significant drift, and if moreover drift characteristics depend upon concentration, drift correction needs to be integrated with calibration. This topic is beyond the scope of this International Standard.

4.2 Stability monitoring

4.2.1 General considerations

A drift-control mixture is required which is typical of the gases for which the analytical procedure is used. The composition of the mixture shall be stable, but the concentration of the specified analytes used for stability monitoring does not have to be established in advance with high accuracy.

An analysis of the drift-control mixture should be carried out with each batch of samples. Its composition is unvarying so the results of this analysis can be used as an indication as to whether the procedure is no longer working satisfactorily or re-calibration of the instrument is necessary, or both.

Stability can be monitored using either concentration data or the corresponding response data.

4.2.2 Use of Shewhart control charts

Before first use, the drift-control mixture is analysed at least 10 times in order for precision data to be calculated. For each specified analyte in the drift-control mixture, the mean concentration (or response) and its standard deviation are calculated. If the within-day standard deviation is less than the between-day standard deviation, then these precision data need to be collected one a day for 10 days.

For each specified analyte in the drift-control mixture, a control chart is constructed with points marked on the Y-axis representing

- a) the mean concentration (or response),

- b) the mean ± 1 standard deviation,
- c) the mean ± 2 standard deviations (warning limits), and
- d) the mean ± 3 standard deviations (action limits).

Lines parallel to the X-axis are drawn from these points. Each time the drift-control mixture is analysed, the value is plotted using the X-axis as a time scale. As more information becomes available the means and standard deviations can be updated. This assumes that the analytical system has remained stable. Data which clearly indicate some fault shall not be used to revise the control limits.

The plotted values from the analysis of the control gas are compared with the mean value and the ± 1 , ± 2 and ± 3 standard deviation lines. It is assumed that the composition of the drift-control mixture is stable and that the analytical results for this follow the normal distribution. If this is true, then while the system is behaving normally, any individual results for the components of the drift-control mixture may fall outside the warning limits on 1 occasion in 20. This means that if individual results fall outside the warning limits more than just occasionally, this can indicate that either there is a systematic tendency for the results to be too high (or too low) or the random error for measurement of that component has increased. Likewise, individual results may fall outside the action limits on 3 occasions out of 1 000.

ISO 8258 ^[6] contains the following tests which can be used for indicating the presence of variation:

- one point exceeding ± 3 standard deviations;
- nine points in a row on one side of the mean;
- six points in a row steadily increasing or decreasing;
- fourteen points in a row alternating up and down;
- two out of three points in a row exceeding $+2$ standard deviations or -2 standard deviations;
- four out of five points in a row exceeding $+1$ standard deviation or -1 standard deviation;
- fifteen points in a row above and below the mean, but not exceeding ± 1 standard deviation;
- eight points in a row above and below the mean, but all exceeding ± 1 standard deviation.

If any of these tests indicates the presence of variation, then that shall be diagnosed and corrected. If this investigation indicates that there is no fault with the measuring procedure, then re-calibration of the instrument is required.

4.2.3 Statistical trend test

As an alternative to monitoring monotonic increase or decrease, drift-control data may be investigated for trends using a statistical test based on successive differences. Given a time-series of drift-control data $x_1, x_2, \dots, x_N$ with mean value $\langle x \rangle$, the mean-square successive difference Δ^2 is determined according to

$$\Delta^2 = \left[(x_1 - x_2)^2 + (x_2 - x_3)^2 + \dots + (x_{N-1} - x_N)^2 \right] / (N - 1) \quad (1)$$

This quantity is compared with the variance s^2 given by

$$s^2 = \left[(x_1 - \langle x \rangle)^2 + (x_2 - \langle x \rangle)^2 + \dots + (x_N - \langle x \rangle)^2 \right] / (N - 1) \quad (2)$$