INTERNATIONAL STANDARD

ISO
15796

Gas analysis — Investigation and treatment of analytical bias

Analyse des gaz — Investigation et traitement des biais analytiques

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Contents

Foreword

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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]).

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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 $\pm$ 1 standard deviation,

c)   the mean $\pm$ 2 standard deviations (warning limits), and

d)   the mean $\pm$ 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 $\pm$ 1, $\pm$ 2 and $\pm$ 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 $\pm$ 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 $\pm$ 1 standard deviation;

—   eight points in a row above and below the mean, but all exceeding $\pm$ 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, …, x_N with mean value $\langle x \rangle$, the mean-square successive difference Δ^2 is determined according to

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

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

$$s^2 = \left[(x_1 - \langle x \rangle)^2 + (x_2 - \langle x \rangle)^2 + ... + (x_N - \langle x \rangle)^2 \right]/(N-1) \tag{2}$$

If successive values in the series are independent (and moreover from a normal distribution), then $\Delta^2 \approx 2\,s^2$. In case of a trend $\Delta^2 < 2\,s^2$ because successive values are closer than to be expected for values drawn at random from a normal distribution.

For a significance test, the test statistic Δ^2/s^2 is compared with the critical value for the specified length N of the series under investigation and the specified significance level. Values of the test statistic below the critical value indicate a significant trend. In this International Standard a significance level of 95 % or 99 % is recommended. Critical values for these significance levels are given in Table A.1, Annex A.

EXAMPLE   Consider a series of drift-control data (carbon monoxide in nitrogen, expressed in mmol/mol): 1,28; 1,30; 1,30; 1,28; 1,26; 1,24; 1,27; 1,27; 1,24; 1,26. For these data the mean-square successive difference Δ^2 is $38 \times 10^{-4}/9$, while the variance s^2 is $40 \times 10^{-4}/9$. Hence the test statistic Δ^2/s^2 takes a value of 0,95. For $N = 10$, the critical value is 0,751 8 for a significance level of 99 % and 1,062 3 for a significance level of 95 %. Therefore, under the assumptions of independence and normality, the drift-control data exhibit a significant trend on the 95 % level, while the trend is not significant at the 99 % level.

Consider now the modified data series generated by interchange of the 3rd and 9th datum: 1,28; 1,30; 1,24; 1,28; 1,26; 1,24; 1,27; 1,27; 1,30; 1,26. For these data, the mean square successive difference Δ^2 is now $98 \times 10^{-4}/9$, while the variance s^2 still is $40 \times 10^{-4}/9$. Hence the test statistic Δ^2/s^2 takes a value of 2,45 which means that the modified data series does not exhibit any indication of drift, under the above assumptions.

For stability monitoring based on regular drift-control measurements, a moving window comprising 10 to 20 data is recommended.

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.

4.3   Drift correction

4.3.1   General considerations

This clause specifies a general method for post-processing analytical data to correct for instrumental drift. For this purpose an analytical system is treated as a "black box". Here the input is the value of the measurand, i.e. the (true) concentration of the analyte under consideration in the analysed sample, and the output is the measured value of this analyte concentration.

This clause is applicable for absolute methods, i.e. analytical methods where analyte concentration is determined directly, or relative methods where the relationship between measured response and analyte concentration is known. It is also applicable for comparison methods, i.e. analytical methods where the relationship between measured response and analyte concentration is determined empirically by calibration.

Two drift-correction mixtures are required which are typical of the gases for which the analytical procedure is used. Each analyte to be determined by the procedure shall be present in both mixtures, at different levels bracketing an appropriate concentration range. The composition of the mixtures shall be stable, and the concentration of the analytes used for drift investigation shall be known with specified uncertainty.

4.3.2 and 4.3.3 specify two complementary approaches, based on additive and multiplicative drift modelling respectively. Usually only one or neither of these procedures will work. If in a particular case both approaches work, the one with the better performance, i.e. with lower correction uncertainty, should be used.

NOTE 1   For an analytical comparison method, drift correction is sometimes better performed using measured responses instead of analyte concentrations.

NOTE 2   Using reference gas mixtures for drift control has the advantage of providing an "absolute" drift correction, i.e. relative to reference values of analyte concentration. As an alternative, less well-characterized gas mixtures could be used for drift correction relative to analyte concentrations measured at a specified time t_0. The latter approach would, in addition, require a proof of stability of the drift-control mixtures. Secondly, the concentrations measured at t_0 would have to be investigated for bias in a later stage.

4.3.2   Additive drift correction

In this subclause, instrumental drift is presented as an additive bias according to Equation (3):

$$x(t) = x + \delta(x,t) \tag{3}$$

where

$x(t)$ is the measured concentration of the analyte under consideration at time t,

x is the true analyte concentration,

$\delta(x,t)$ is the bias at analyte level x, due to drift at time t.

If, for a given analyte, this bias should be the same for different levels of analyte concentration, it can be corrected by determining the bias obtained on a sample with known concentration of the analyte as a function of time, and subtracting the applicable bias from the results obtained on other samples.

To this end, the concentrations of two mixtures (called A and B) as specified above are measured on a regular basis, and the time-series of results are recorded. For the given analyte, these are x_{A1}, x_{A2}, ..., x_{AN} and x_{B1}, x_{B2}, ..., x_{BN}. The two time-series are smoothed by interpolation or regression, yielding two curves (or functions) $x_A(t)$ and $x_B(t)$. Given concentration-invariant additive bias for that analyte, these curves should be parallel, with a distance of $x_A(t) - x_B(t) = x_{A,ref} - x_{B,ref}$ where $x_{A,ref}$ and $x_{B,ref}$ are the reference values given for mixture A and B.

If this is true (within experimental variability) the differences $x_{Ai} - x_{A,ref}$ and $x_{Bi} - x_{B,ref}$ are pooled and the combined time-series is smoothed yielding a curve (or function) $\delta(t)$. This curve is then used to correct the result obtained on another mixture M at any time t within the period covered according to

$$x_M = x_M(t) - \delta(t) \tag{4}$$

The standard uncertainty of the corrected result is determined by

$$u^2(x_M) = u^2\left[x_M(t)\right] + u^2\left[\delta(t)\right] \tag{5}$$

In this uncertainty budget, the first term is obtained from the uncertainty budget of the analytical procedure. The second term is estimated from the residual scattering of the pooled differences used to determine the correction curve $\delta(t)$. In addition, the uncertainty contributions of the drift measurements and the composition of the drift-correction mixtures are included if significant.

If bias corrections should be approximately the same for different analytes, then a joint correction may be derived for a group of such analytes from pooled time-series.

4.3.3   Multiplicative drift correction

In this subclause, instrumental drift is presented as a recovery factor according to Equation (6):

$$x(t) = Q(x,t)x \tag{6}$$

where

$x(t)$ is the measured concentration of the analyte under consideration at time t;

x is the true analyte concentration;

$Q(x,t)$ is the recovery factor at analyte level x, due to drift at time t.