INTERNATIONAL
STANDARD

ISO
19229

Second edition
2019-07

Gas analysis — Purity analysis and the treatment of purity data

Analyse des gaz — Analyse de pureté et traitement des données de pureté

Reference number
ISO 19229:2019(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

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

This second edition cancels and replaces the first edition (ISO 19229:2015), which has been technically revised.

The main changes compared to the previous edition are as follows:

- the methods for traceable purity analysis have been elaborated;
- Clauses 8 and 9 have been added describing how to calculate coverage intervals and set up certificates, respectively;
- Annex A has been added with worked examples.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The use of purity data in the calculation of the composition of calibration gas mixtures is an essential element in establishing metrological traceability of the certified gas composition. Purity analysis is usually challenging as, normally, trace levels of various components should be determined in a matrix for which limited or no measurement standards are readily available.

In many practical situations, purity data in some form are available. For the preparation of calibration gas mixtures, it is important that this information is interpreted in a consistent fashion and taken into account in the calculation of the composition of the mixture.

Gas analysis — Purity analysis and the treatment of purity data

1 Scope

This document establishes the requirements for the purity analysis of materials used in the preparation of calibration gas mixtures and the use of these purity data in calculating the composition of the mixture thus prepared.

2 Normative references

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

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO 6141, *Gas analysis — Contents of certificates for calibration gas mixtures*

ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 7504, *Gas analysis — Vocabulary*

ISO 12963, *Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration*

ISO 14912, *Gas analysis — Conversion of gas mixture composition data*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 7504 apply.

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

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 Symbols

In this document, the following symbols are used.

i	running index over the components in a mixture
j	index of the parent gas
k	index of a specific component in a mixture
L_{ij}	limit of detection of component i in parent gas j
u	standard uncertainty (of the quantity between brackets)

w_{ij} mass fraction of component *i* in parent gas *j*

x_{ij} amount–of–substance fraction of component *i* in parent gas *j*

ϕ_{ij} volume fraction of component *i* in parent gas *j*

5 Principles

5.1 General

The determination of the impurities contained in each material (gas or liquid) used in the preparation has an impact on the uncertainty associated with the content of the component.

Assess and list all of the impurities that might be present in the material. These can be identified by different means, including

- open literature,
- information provided with the material,
- previous experience of using the same or similar materials, and
- knowledge of the process used to produce the material.

In order to decide the extent of purity analysis required, it is necessary to specify which of the potential impurities are "critical" and which are "significant" to the final composition of the mixture.

5.2 Assessment of critical and significant impurities

5.2.1 Critical impurities

A critical impurity is an impurity that meets one or more of the following criteria:

- an impurity in the parent gas of a binary or multi-component mixture that is also present as a minor component in the same mixture at low concentrations;

  EXAMPLE 1 If preparing a low-concentration oxygen in nitrogen mixture, oxygen might also be present as an impurity in the nitrogen.

  EXAMPLE 2 For natural gas mixtures, i-pentane is often found as an impurity in n-pentane and neo-pentane, as well as being added as a minor component in its own right.

- an impurity that has the potential to influence the result of an analytical verification of the mixture composition;

  EXAMPLE 3 The presence of argon in nitrogen or oxygen will influence the analytical verification of the oxygen content when using gas chromatography with a non-selective detector.

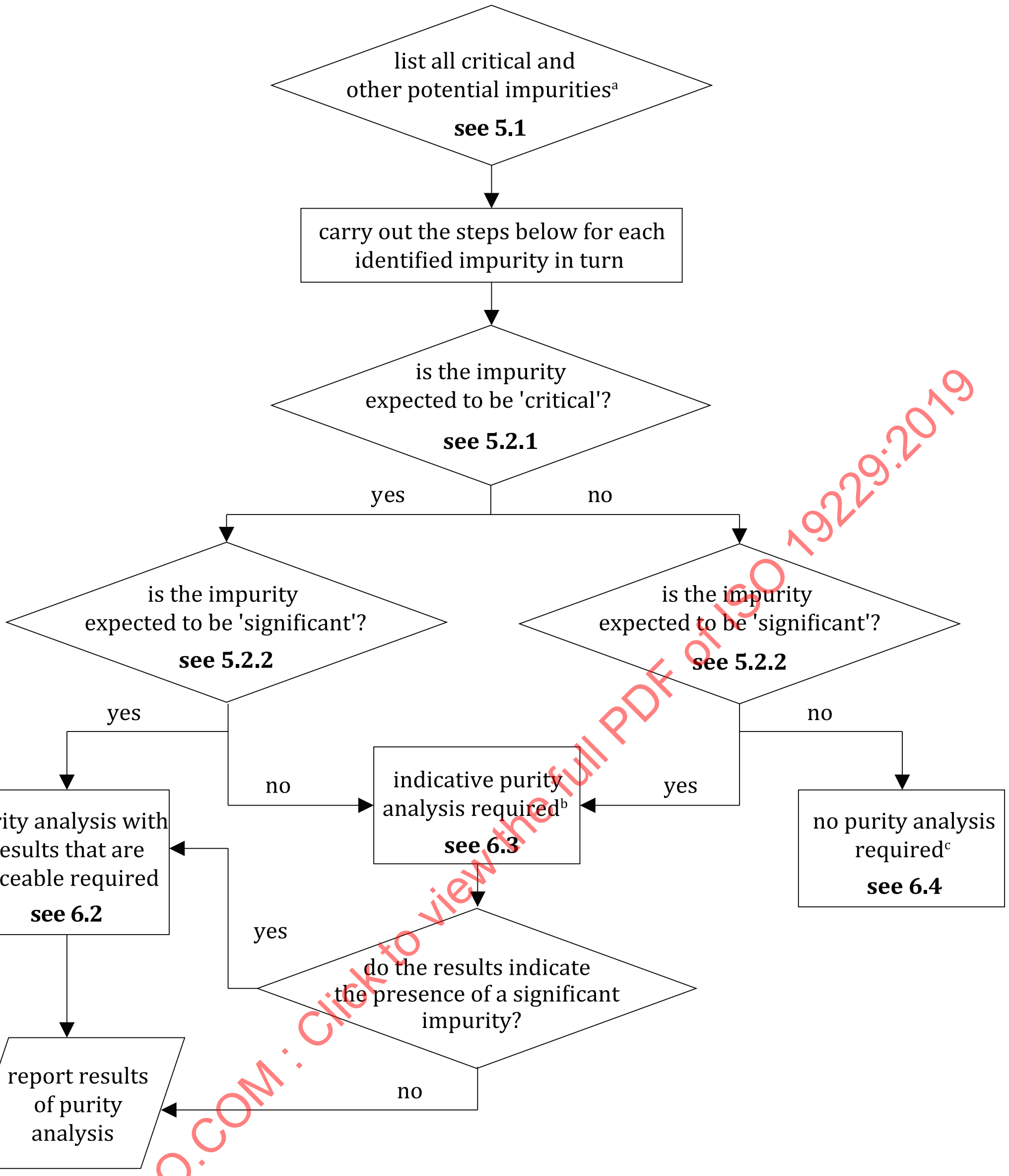
- an impurity that might be reactive with respect to any other component in the mixture.

  EXAMPLE 4 If preparing a mixture of nitric oxide in nitrogen, any oxygen present as an impurity in the nitrogen might react with the nitric oxide to form nitrogen dioxide.

5.2.2 Significant impurities

A significant impurity is an impurity that is predicted to contribute more than 10 % to the target uncertainty of the content of any of the components in the calibration gas mixture. The application of this criterion requires knowledge of the preparation method used (gravimetric, volumetric, static, or dynamic) and the uncertainties associated with the various steps involved.

The above described steps are summarized as a flowchart in Figure 1.



[a] If an unpredicted or unknown impurity is identified during the course of a purity analysis, return to the start of the flowchart.

[b] If preferred, a purity analysis with results that are traceable can be carried out instead of an indicative purity analysis.

[c] If preferred, a traceable or indicative purity analysis can be carried out.

Figure 1 — Purity analysis flowchart

6 Analysis of impurities

6.1 General

The extent of purity analysis required shall be determined by the outcome of the flowchart in Figure 1. Each of these levels is discussed in 6.2 to 6.4.

The process shown in the flowchart in Figure 1 shall be undertaken for each of the listed potential impurities. Purity analysis can be carried out by one or more appropriate analytical techniques. In some instances, more than one technique might be needed.

EXAMPLE When determining the purity of methane, hydrocarbon impurities can most accurately be determined by gas chromatography with flame ionization detection (GC-FID), while other impurities can be determined by GC with thermal conductivity detection (GC-TCD) or discharge ionization detection (GC-DID).

For some materials (such as liquids and corrosive gases), it might not be practicable to analyse the material in its "pure" state. In these cases, an alternative approach can be taken such as the preparation of a gravimetric mixture with a lower amount-of-substance fraction for purity analysis (using a carefully chosen matrix gas of known high purity). This approach has, however, a detrimental effect on the achievable limits of detection and that care should be taken to account for the purity of the matrix gas when calculating the purity of the component of interest.

When using liquids or liquefied gases in gas mixture preparation, this phase shall be subjected to a purity analysis rather than the vapour phase. If the vapour phase is used, this phase shall be analysed. As the compositions of the vapour and liquid phase differ, these compositions might change during use of the liquid/vapour. Appropriate measures shall be taken to ensure that the purity data remain valid within their stated uncertainties.

When carrying out a purity analysis, care should be taken to check for any unexpected impurities (i.e. any observed impurities that were not identified as a potential impurity when following the assessment procedure in 5.2). For example, when using gas chromatography, unexpected impurities can be observed as unexpected peaks in the chromatogram. If one or more unexpected impurities are observed, each should be assessed as to whether it is "critical" and/or "significant", and the appropriate impurity analysis then carried out, as determined by the flowchart in Figure 1.

6.2 Purity analysis with results that are traceable

To carry out a purity analysis with results that are traceable, calibrate the analyser(s) using calibration gas mixtures with defined uncertainties and quantify the impurity by direct comparison with these calibration mixtures by use of methods described in ISO 6143 and ISO 12963.

For the purity analysis of high-purity matrix gases, a direct measurement of the impurities can be obtained with analysers of suitable limit of detection, typically 10 times lower than the targeted impurity fraction[5].

Laser spectroscopy and gas chromatography are typical methods used in case of analysers with a defined zero. The measurement procedure to assign amount fractions of trace impurities to high-purity matrix gas with this type of analysers shall be carried out by direct comparison with calibration gas mixtures. In the case of laser spectroscopy, using the impurity's optical line strength or cross-section with established metrological traceability is a valid alternative. In the case of gas chromatography, relative response factors (RRF) can be used in case they are validated for the specific measurement on the specific instrument. The uncertainty of the RRF shall be evaluated in accordance with ISO/IEC Guide 98-3 (GUM).

In case the analyser has no defined zero, the standard addition method in combination with well-characterized purification systems shall be used. The manufacturer's specification stating the purifier removal efficiency shall be taken into account when calculating the amount fraction of the impurity and its associated uncertainty. The measurement procedure to assign amount fractions of trace impurities to high-purity matrix gas with this type of analysers shall be carried out according to the following steps.

— Calibrate the analyser at the higher end of the measurement range (so called "span gas").

— Analyse the sample matrix gas passing through the purifier and calibrate the analyser as zero.

— Analyse the sample matrix gas without passing through the purifier.

- Prepare at least one calibration gas mixture of a trace impurity that needs quantification in the matrix gas by, for example, dynamic dilution using a certified reference material and flow controllers (see ISO 6145).
- Analyse the calibration gas mixture(s) with and without passing through the purifier.
- Verify that the gas analysed after passing through the purifier contains the same (zero) amount (or response) regardless of the amount fraction of the gas entering the purifier. It can then be assumed that the purifier removes the specific trace impurity under investigation from the sample matrix gas.
- Calculate the amount fraction of the trace impurity in the sample matrix gas from the analyser response when the matrix gas enters the analyser without passing through the purifier.

NOTE 1 This recipe can also be used for other quantities than amount fractions, such as mass fractions, volume fractions, or mass concentrations. Annex A gives examples in the use of analysers for traceable purity analysis with and without a defined zero.

If metrologically traceable purity data from another source (for example, on a certificate of analysis) are available, these data can be used for this purpose. The metrological traceability of the data shall be assessed, if not explicitly stated on the certificate or in the report provided. Such assessment shall include, but is not limited to, checking whether appropriate certified reference materials or other measurement standards have been used and a rigorous uncertainty evaluation of all steps leading to the measurement result has been performed.

NOTE 2 A reference gas mixture is a mixture of appropriate metrological quality that has composition data that are traceable to a national or international measurement standard through an unbroken chain of comparisons with stated uncertainties. An example is a gas mixture certified by a calibration laboratory, fulfilling the conditions stipulated in ISO/IEC 17025 and/or ISO 17034.

NOTE 3 Where traceable gaseous measurement standards are not available, certified reference materials can be available in liquid form with certified purity.

NOTE 4 Where appropriate measurement standards or certified reference materials are not available, it can be necessary to redesign the proposed preparation in a way that traceable purity analysis is not required, by using for example materials with better purity.

NOTE 5 Where traceable measurement standards or certified reference materials are not available, it is sometimes possible to estimate the purity of starting materials by use of a kind of standard addition method. A series of standards containing the "pure" material at different concentrations is prepared and the analysed values are extrapolated back to zero.

6.3 Indicative purity analysis

In the field of gas analysis, an indicative purity analysis is one that provides data of which the metrological traceability is not established. Such a situation might arise from, for example:

- an analysis that uses gas mixtures with a composition for which the metrological traceability has not been established;
- the determination of at least part of the results using theoretical response factors;
- the use of optical line strength from databases from which the metrological traceability has not been established;
- data from a “certificate of analysis” without stated metrological traceability.

All data for which the metrological traceability has not been established shall be regarded as “indicative”. Such data can be used for indicative purity analysis.

When expressing the result(s) of an indicative purity analysis, any possible bias in the data shall be dealt with by either including an appropriate uncertainty component to account for the possible bias or applying a correction for the bias.

Gas manufacturers often quantify the purity of their pure gases using a specification (see Table 1 for an example of high-purity nitrogen). Such specifications might stem from the analytical capabilities used for the purity analysis or from monitoring the production process.

Table 1 — Example of manufacturers' purity specification for nitrogen

Impurity	Specification µmol mol⁻¹
CO	≤1,0
CO_2	≤1,0
C_xH_y	≤0,5
NO	≤0,1
NO_2	≤0,1
SO_2	≤0,1
Ar	≤50
H_2O	≤1,0

If an impurity, likely to be present in the "pure" parent gas, is below the limit of detection of the analytical method used for the purity analysis, then the limit of detection is usually quoted in the gas manufacturer's specification.

In this case, the amount-of-substance fraction of the expected impurity, x_{ij}, shall be set equal to half of the value of the detection limit of the analytical method, L_{ij}, as shown by Formula (1):

$$x_{ij} = \frac{L_{ij}}{2} \qquad (1)$$

The uncertainty associated with x_{ij} is evaluated assuming a rectangular distribution with L_{ij} being the upper limit of the rectangle, and zero the lower limit. The standard uncertainty associated with the amount-of-substance fraction x_{ij} is calculated using Formula (2).

$$u(x_{ij}) = \frac{L_{ij}}{2 \times \sqrt{3}} \qquad (2)$$

Table 2 — Amount-of-substance fractions and associated standard uncertainty from the purity specifications from Table 1 using Formula (2)

Impurity	x_{ij} µmol mol⁻¹	$u(x_{ij})$ µmol mol⁻¹
CO	0,5	0,3
CO_2	0,5	0,3
C_xH_y	0,25	0,15
NO	0,05	0,03
NO_2	0,05	0,03
SO_2	0,05	0,03
Ar	25	15
H_2O	0,5	0,3

6.4 No purity analysis

A purity analysis is not required for impurities that are both non-critical and insignificant.

6.5 Estimation of the amount-of-substance fractions of unmeasured (but expected) impurities

When carrying out a purity analysis with results that are traceable or an indicative purity analysis, an impurity might sometimes be expected to be present in a material (through either prior knowledge or information provided by a third party, such as the manufacturer of the material), but cannot be detected by, or is below the limit of detection of the analytical method used.

In these instances, if a more suitable and/or sensitive analytical method is not available, the amount-of-substance fraction of the expected impurity shall be set equal to half of the value of the limit of detection of the analytical method used.

The uncertainty of an amount-of-substance fraction calculated in this manner is based upon a rectangular distribution between zero and the value of the detection limit of the analytical method, thus, assuming that there is an equal probability that the impurity might be present in the material at a level from zero up to the detection limit. An undetected impurity therefore forms a rectangular probability distribution from which its standard uncertainty is given by Formula (2).

7 Use of purity data

7.1 Calculation of the amount-of-substance fraction of the most abundant component

The amount-of-substance fraction of the most abundant component in the material being analysed is determined by Formula (3):

$$x_{kj} = 1 - \sum_{i=1;i\neq k}^{n} x_{ij} \tag{3}$$

The standard uncertainty in the amount-of-substance fraction of the ‘pure’ component is determined using the law for the propagation of uncertainty described in ISO/IEC Guide 98-3 (GUM) and shown in Formula (4):

$$u^2(x_{kj}) = \sum_{i=1;i\neq k}^{n} u^2(x_{ij}) \tag{4}$$

The uncertainty in the amount-of-substance fraction of each impurity shall be determined by combination of all relevant factors. These might include, but are not limited to, the uncertainties in calibration standards, analytical repeatability and reproducibility, and the use of relative response factors.

7.2 Calculation of the mass fraction of the most abundant component

Depending on the measurement standards or certified reference materials used during purity analysis, the purity data might be available in the form of mass fractions. The mass fraction of the most abundant component w_{kj} is calculated by Formula (5):

$$w_{kj} = 1 - \sum_{i=1;i\neq k}^{n} w_{ij} \tag{5}$$

and its associated standard uncertainty by Formula (6):

$$u^2(w_{kj}) = \sum_{i=1;i\neq k}^{n} u^2(w_{ij}) \tag{6}$$

If purity data on a molar basis (as amount-of-substance fractions) are required, the mass fractions of all critical and significant impurities and their associated standard uncertainties shall be known. The conversion of the data, including the uncertainty evaluation, shall be carried out in accordance with ISO 14912.

7.3 Calculation of the volume fraction of the most abundant component

For gases, the purity data are often given in volume fractions (ϕ). In those cases, where for a component the content is specified to be less than a given value, the approach of 6.3 shall be used for obtaining an estimate for the volume fraction and its associated standard uncertainty. In this case, L_{ij} denotes the upper value specified for the component of interest.

The volume fraction of the most abundant component ϕ_{kj} is calculated by Formula (7):

$$\phi_{kj} = 1 - \sum_{i=1;i\neq k}^{n} \phi_{ij} \tag{7}$$

and its associated standard uncertainty by Formula (8):

$$u^2(\phi_{kj}) = \sum_{i=1;i\neq k}^{n} u^2(\phi_{ij}) \tag{8}$$

If purity data are needed in the form of as mass fractions, amount-of-substance fractions, or another quantity, the conversion of the data, including the uncertainty evaluation, shall be carried out in accordance with ISO 14912.

7.4 Other forms of purity data

If purity data are available of which the quantity is unspecified, such data are unusable for calculating the content of the abundant component.

NOTE Such data are often stated in percentages (%), parts per million (ppm), or parts per billion (ppb), without specifying the corresponding quantity.

If the quantities in which the purity data are specified differ from the desired quantity, ISO 14912 shall be used for converting these data and performing the evaluation of measurement uncertainty in any subsequent calculation.

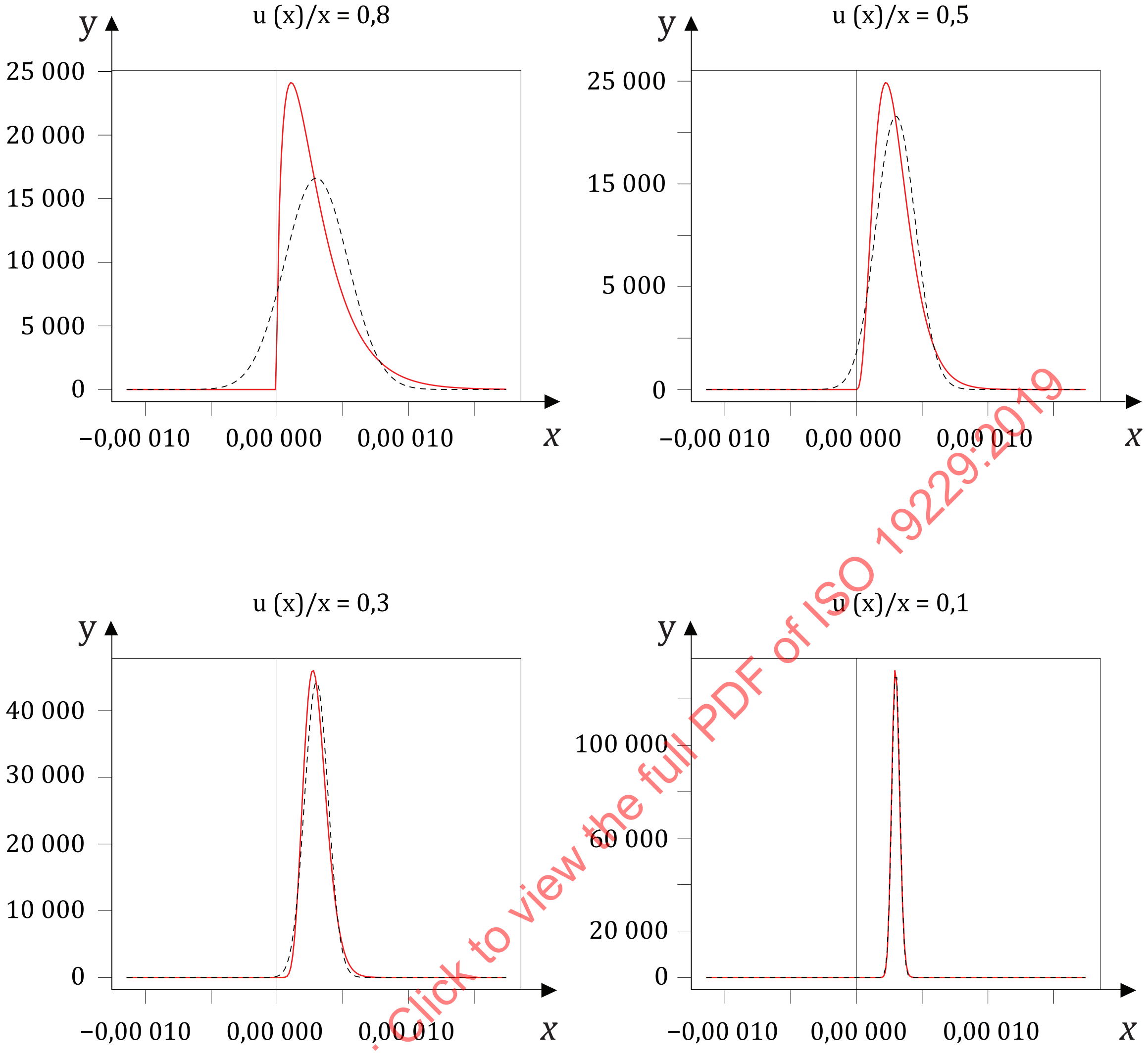
8 Coverage intervals

8.1 General

Fractions of impurities can be close to zero, which potentially leads to problems when calculating a coverage interval with a normal distribution or *t*-distribution. By “close to zero”, it is meant that the difference between the fraction and zero is less than 4 times the standard uncertainty calculated for the fraction, assuming a 95 % probability level. For higher probability levels, a higher multiple should be used. Similarly, the fraction of the most abundant component is considered to be close to one when this fraction is less than 4 times the standard uncertainty away from one.

Coverage intervals shall be expressed in such a fashion, that the lower and upper bounds are within the valid domain for fractions ($0 \leq x_i \leq 1$, and similarly for other fractions). In other words, lower bounds below zero and upper bounds exceeding one shall be avoided at all times (see also Figure 2). Such coverage intervals are invalid. For high relative standard uncertainties, the normal distribution has a significant part of the probability below zero. Other distributions, such as the beta distribution do not have this problem, because of their definition (see Figure 2).

Valid coverage interval for fractions close to 0 or 1 are usually not symmetric. So, the notation $x_i \pm U(x_i)$ is inappropriate for such intervals.



Key

x amount-of-substance fraction

y probability density

Figure 2 — Beta (solid line) and normal (dashed line) distribution for relative standard uncertainties of 80 %, 50 %, 30 %, and 10 % for a measured value close to zero

8.2 Fractions close to 0 or 1

For fractions close to zero or 1, use the beta distribution as approximation of the probability density function of the fraction of the component of interest. A Monte Carlo simulation of the gravimetric preparation of gas mixtures has indicated that this model is a reasonable approximation for the probability density function. The beta distribution is developed for modelling probabilities and proportions[4]. Hence, it is only defined for $0 \leq x \leq 1$. Other probability density functions with similar properties may be used as well.

To calculate a coverage interval using the beta distribution, its parameters are needed. These can be computed from the first and second moments (mean and standard deviation) of the probability distribution. For this purpose, the assigned value of the fraction x_i and the associated standard uncertainty $u(x_i)$ can be taken.

The beta distribution is given by Formula (9)[6]:

$$f(x;\alpha,\beta)=\frac{\Gamma(\alpha+\beta)}{\Gamma(\alpha)\Gamma(\beta)}x^{\alpha-1}(1-x)^{\beta-1} \tag{9}$$

where α and β denote the parameters of the beta distribution and Γ is a symbol of a gamma function. These can be calculated as follows from the mean μ and standard deviation σ. The mean μ is related to the parameters as shown in Formula (10)[6]:

$$\mu=\frac{\alpha}{\alpha+\beta} \tag{10}$$

and the variance σ^2 as shown in Formula (11):

$$\sigma^2=\frac{\alpha\beta}{(\alpha+\beta)^2(\alpha+\beta+1)} \tag{11}$$

From these expressions, it follows Formulae (12) and (13) follows.

$$\alpha=\left(\frac{1-\mu}{\sigma^2}-\frac{1}{\mu}\right)\mu^2 \tag{12}$$

$$\beta=\alpha\left(\frac{1}{\mu}-1\right) \tag{13}$$

Once the values for α and β have been computed, the inverse of the cumulative distribution function (cdf) is needed. This function takes, as arguments, the parameters of the distribution and the probability of the quantile. For a probabilistically symmetric coverage interval and 95 % coverage probability, the probabilities for the quantiles are 0,025 (=2,5 %) and 0,975 (=97,5 %) respectively. As the beta distribution is non-symmetric, such an interval is not the shortest one. It is a “safe” coverage interval, in that the actual coverage probability will exceed the desired one.

Not all implementations of the cumulative distribution function of the beta distribution are numerically stable. It is therefore recommended to perform the calculation with a value and standard deviation in the parts-per-million (ppm) range, and to convert the results of the calculation to the actual situation. The following example shows the entire process.

EXAMPLE

Suppose, from a purity determination, the following results are obtained: $x = 100 \cdot 10^{-9}$ mol mol^{-1} with $u(x) = 30 \cdot 10^{-9}$ mol mol^{-1}.

The distance with respect to zero is 100/30 = 3,3 times the standard uncertainty, so the result is considered to be close to zero.

For the computation of the parameters α and β, the rescaled values $\mu = 100 \cdot 10^{-6}$ mol mol^{-1} and $\sigma = 30 \cdot 10^{-6}$ mol mol^{-1} are used. There is factor of 1 000 between x and μ, and between the respective standard uncertainties, because of rescaling to avoid numerical problems with some spreadsheet calculations.

The values for the parameters of the rescaled probability distribution are

- $\alpha = 11{,}11$ from Formula (12);
- $\beta = 111\ 088$ from Formula (13).

Using the inverse of the cumulative beta probability distribution function to calculate (such as BETAINV() in mainstream spreadsheet software), the following quantiles for $P = 0{,}025$ and $P = 0{,}975$ are obtained

$$q_{0,025} = 50{,}12 \cdot 10^{-6}$$

$q_{0,975} = 166,81 \cdot 10^{-6}$

After dividing both quantiles by the factor 1 000 used for the rescaling, the lower and upper bounds of the 95 % coverage interval are obtained. This interval is given by [50,12 nmol mol^{-1}; 166,81 nmol mol^{-1}].

When rounding the lower and upper bounds of the coverage interval, the width of the coverage interval after rounding shall not be meaningfully smaller than the unrounded interval. This can be ascertained by rounding down the lower limit and rounding up the upper limit.

See Reference [6] for more information on coverage intervals.

9 Certificates

Certificates shall be set up in accordance with ISO 6141.

If the probability distribution used for calculating the coverage interval (see Clause 8) is symmetric, it is sufficient to follow the instructions of ISO 6141. If the probability distribution is not symmetric, then for each component, the following shall be provided on the certificate:

- the fraction;
- the standard uncertainty;
- the lower and upper bound of the coverage interval and the probability level;
- the probability distribution used, if it is a known distribution.

NOTE The information listed here is consistent with the requirements of ISO 6141, but interpreted for non-symmetric probability density functions. In that case, an expanded uncertainty cannot be used (in conjunction with the fraction) to obtain a coverage interval, so this interval can only be given in another form, for example by specifying its bounds. In the non-symmetric case, it is generally impossible to derive the standard uncertainty from the coverage interval. As the standard uncertainty can be required in subsequent calculations, this parameter is also part of the reporting requirements.

EXAMPLE

From the example in Clause 8, the 95 % coverage interval was calculated as [50,12 nmol mol^{-1}; 166,81 nmol mol^{-1}].

The fraction (after rounding) is reported as 100 nmol mol^{-1}, the associated standard uncertainty as 30 nmol mol^{-1}. The (rounded) lower bound of the coverage interval is 50 nmol mo^{-1}, and the (rounded) upper bound is 167 nmol mol^{-1}.

The assumed probability density function is the beta distribution. If desired, the parameters and the scaling factor can be given as a convenience to the reader in case an interval is needed with a different coverage probability.

Annex A
(informative)

Examples

A.1 Purity analysis for nitrogen monoxide (NO) in nitrogen using a method without a defined zero

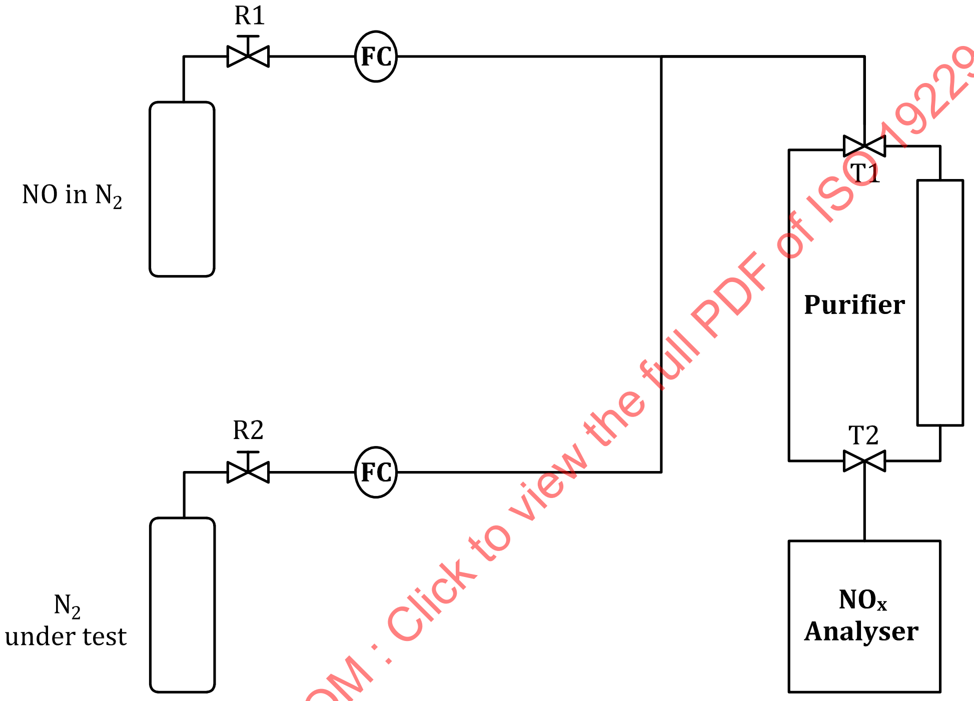


Figure A.1 — Measurement set-up for the purity analysis using the standard addition method

This procedure makes use of a well-characterized purification system. The set-up contains two flow controllers (FC), two open-close valves (R1 and R2) and two “three-way” valves (T1 and T2). It will be assumed that the purifier removes the significant impurities that need to be quantified to a level according to the manufacturer’s specification, or to a level as validated by the laboratory. For this example, the specification of the purifier used for nitrogen monoxide (NO) is < 1 nmol mol^{-1}. From this specification, using a rectangular distribution, an estimate for the residual NO amount fraction of 0,50 nmol mol^{-1} is obtained, with a standard deviation of 0,29 nmol mol^{-1}. This residual NO amount fraction with the associated standard deviation will be added to the analysed NO amount fraction.

The measurement set-up is shown in Figure A.1.

The measurement procedure to assign amount fractions of trace impurities to high-purity matrix gas is carried out according to the following steps.

1) Calibrating the analyser with the “span gas”.

2) Analysing the sample matrix gas passing through the purifier.

3) Calibrating the analyser to zero.

4) Analysing the sample matrix gas without passing through the purifier.

5) Generating at least one reference gas mixture of a trace impurity that needs quantification in the matrix gas by dynamic dilution using a certified reference material and flow controllers (e.g. ISO 6145), for example, with the set-up as indicated in Figure A.1.

6) Analysing the reference gas mixture(s) with and without passing through the purifier.

7) Verifying that the gas analysed after passing through the purifier contains the same (zero) amount (or response) regardless of the amount fraction of the gas entering the purifier. It will then be assumed that the purifier removes the specific trace impurity under investigation from the sample matrix gas.

8) Calculating the amount fraction of the trace impurity in the sample matrix gas from the analyser response when the matrix gas enters the analyser without passing through the purifier. This can be performed by plotting the gravimetric amount fraction of the generated standards against their analytical response. If the sample matrix gas used had no trace impurity, the calibration line obtained would cross the origin. If the sample matrix gas contains an impurity of the target component, the calibration line will cross the y-axis above zero. For a linear function of the model $y = ax + b$, the line crosses the x-axis at the x-coordinate $-b/a$. The impurity content equals the difference in x-coordinate between the origin and $-b/a$ and thus this equals b/a.

The amount fraction of NO in a 50 L nitrogen cylinder under test is determined with an NO-NO_2-NOx chemiluminescence analyser. The selected measurement range of the analyser is 10 nmol/mol NO_2.

The measurement set-up and procedure as described above are applied. The standard addition method was applied using a primary standard gas mixture (PSM) containing nominally 100 nmol mol^{-1} NO. Three calibration points are created by diluting the PSM in a ratio of 1:100, 3:100 and 10:100 respectively.

The amount fraction for the calibration points and the associated standard uncertainty is calculated using Formula (A.1):

$$x_{\mathrm{dil},i} = \frac{x_i V_1}{V_1 + V_2} \tag{A.1}$$

NOTE 1 Formula (A.1) is based on the approximation that the amount fraction is approximately equal to the volume fraction. This assumption is appropriate if the matrix of the gas under test and the calibration gas mixture is the same, pressures and temperatures are the same, and the amount fraction x_i is low (ppm-level or below).

Defining the dilution factor $f = V_1/(V_1 + V_2)$, the standard uncertainty for f is computed with Formula (A.2):

$$u(f) = \sqrt{\frac{V_2^2}{(V_1 + V_2)^4} u^2(V_1) + \frac{V_1^2}{(V_1 + V_2)^4} u^2(V_2)} \tag{A.2}$$

Table A.1 — Volume flow rates and dilution factor for the three-point standard addition method

V_1 mL min^{-1}	$u(V_1)$ mL min^{-1}	V_2 mL min^{-1}	$u(V_2)$ mL min^{-1}	f	$u(f)$
10,607	0,011	994,530	0,995	0,010 553	0,000 015
30,729	0,031	974,380	0,974	0,030 573	0,000 042
101,058	0,101	904,160	0,904	0,100 533	0,000 128
NOTE The amount fraction NO of the PSM is 99,85 nmol mol^{-1} with a standard uncertainty of 0,25 nmol mol^{-1}.					

After a flushing time of 20 min, with a flow of 1 L min^{-1}, 30 responses are collected by the analyser with a 10-second interval. The responses of the analyser (R_{raw}) are corrected for a “zero” reading (involving the purifier) R_0. The corrected response is calculated as $R = R_{\mathrm{raw}} - R_0$. The squared standard uncertainty is obtained from $u^2(R) = u^2(R_{\mathrm{raw}}) + u^2(R_0)$. The responses and the associated uncertainties are given in Table A.2.

Table A.2 — Data set obtained for the purity assessment for nitrogen monoxide in nitrogen

x_1 nmol mol^{-1}	$u(x_1)$ nmol mol^{-1}	R_0 mV	$u(R_0)$ mV	R_{raw} mV	$u(R_{raw})$ mV	R mV	$u(R)$ mV
0		−5,11	14,38	2,01	7,43	7,12	16,18
1,053 7	0,003 0	−8,80	7,50	29,50	6,78	38,30	10,10
3,052 6	0,008 7	0,44	4,45	89,32	6,85	88,88	8,17
10,038 1	0,028 2	5,07	4,68	283,51	8,48	278,45	9,69

Fitting the data using a straight line as calibration function and the procedure of ISO 6143 gives the following results. The intercept a = (8,30 ± 8,55) mV and the slope b = (26,87 ± 1,46) mV mol nmol^{-1}. The covariance $u(a,b) = -9{,}74$ mV^2 mol nmol^{-1}. The stated uncertainties are standard uncertainties.

The result is calculated with Formulae (A.3) and (A.4):

$$\delta_1 = \frac{a}{b} \tag{A.3}$$

$$u^2(\delta_1) = \left(\frac{u^2(a)}{b^2} + \frac{a^2 u^2(b)}{b^4} + \frac{-2a}{b^2} u(a,b) \right) \tag{A.4}$$

The result from the standard addition method for the impurity of nitrogen monoxide is (0,31 ± 0,33) nmol mol^{-1}.

As stated in the introduction of this example, the specification of the purifier shall be added to this value and the uncertainty shall be summed up quadratically. This leads to the final result of:

amount fraction NO = (0,81 ± 0,44) nmol mol^{-1}

NOTE 2 This example is performed under the assumption that the nitrogen under test is not significantly diluted by the added calibration gas. In case of either a 100 nmol mol^{-1} or a 500 nmol mol^{-1} NO in N_2 as a diluent gas, the calculated impurity remains the same within 1 % relative.

A.2 Purity analysis using a method with a defined zero

A.2.1 General

Impurities in zero gas mixtures can also be quantified using measurement methods with a defined zero. These methods include gas chromatography and optical absorption techniques. Here, two examples will be provided for optical absorption techniques to determine the amount of substance in zero gas.

In the first case, the analysis is based on the use of fundamental physical constants and/or universal quantities such as cross-section (σ) or line strength (S). In the second case, a reference gas standard is used.

NOTE 1 The absorption cross-section is typically used for large molecules. Absorption cross-sections are available from various sources including National Institute of Standards and Technology (NIST), Pacific Northwest National Laboratory (PNNL) and High Resolution Transmission database (Hitran). The NIST Infrared Database provides absorption coefficients α from which the cross-section can be calculated as $\sigma = \alpha / N$ with N the number density. Note that only a small part of the available absorption cross-section data is traceable.

NOTE 2 Line strength data are available for small molecules (for larger molecules spectra are so dense that individual lines cannot be measured) in databases such as Hitran or Geisa. The unit of line strength is cm/molecule. Note that only a small part of the available line strength data is traceable.