BS ISO 19229:2015

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Gas analysis — Purity analysis and the treatment of purity data

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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.

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ISBN 978 0 580 85348 7

ICS 71.040.40

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 July 2015.

Amendments issued since publication

Date	Text affected

BS ISO 19229:2015

INTERNATIONAL STANDARD

ISO 19229

First edition
2015-02-15

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 19229:2015(E)

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Published in Switzerland

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Foreword

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The committee responsible for this document is ISO/TC 158, *Analysis of gases.*

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 need to 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.

INTERNATIONAL STANDARD ISO 19229:2015(E)

Gas analysis — Purity analysis and the treatment of purity data

1 Scope

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

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO 7504, *Gas analysis — Vocabulary*

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

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

3 Terms and definitions

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

4 Symbols

In this International Standard, 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 or liquid of a mixture that is also present as a minor component in the same mixture at low concentrations;

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

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

EXAMPLE 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 in a parent gas or liquid of a multi-component mixture that is also present as a minor component in the same mixture;

EXAMPLE 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.

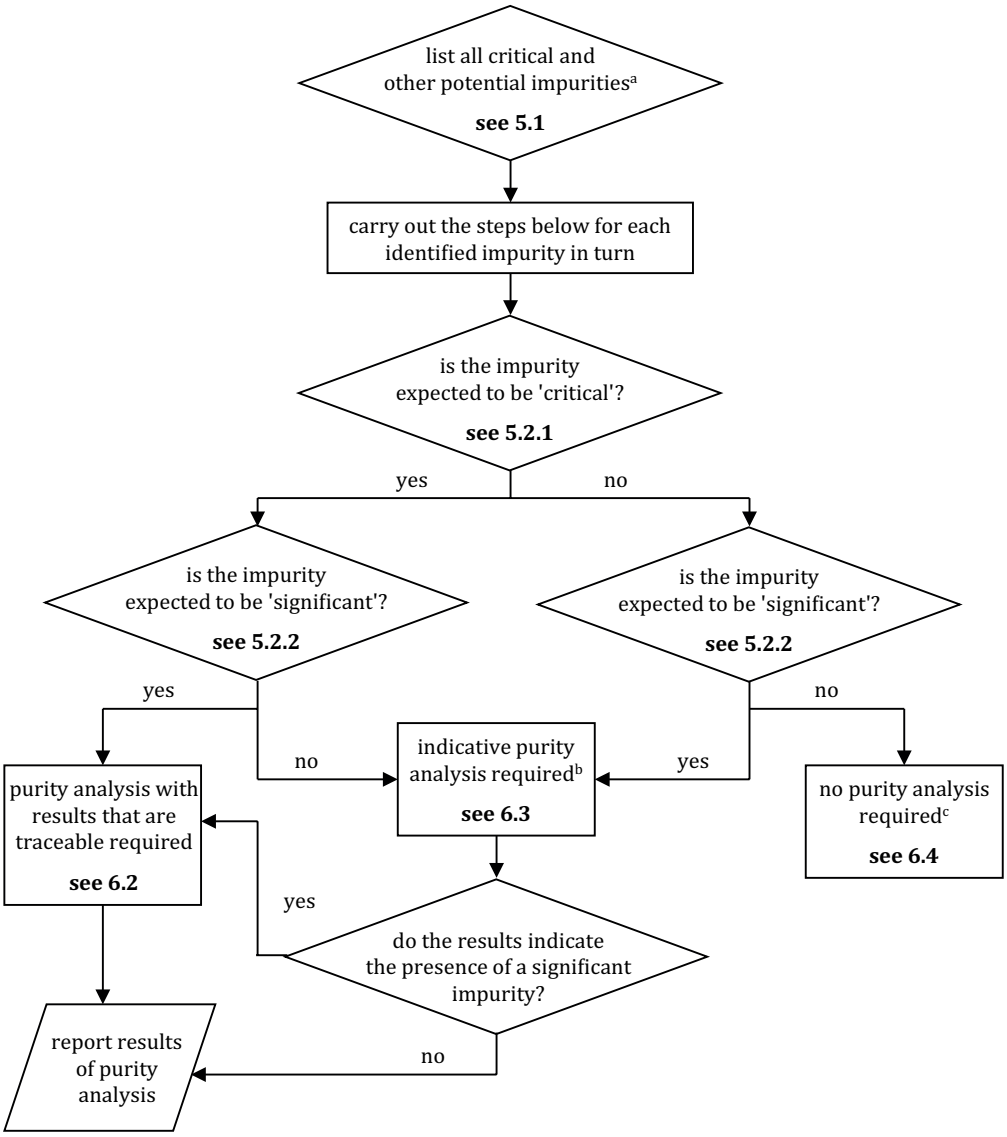
— an impurity that might be reactive with respect to any other component in the mixture.

EXAMPLE 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 (e.g. 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. The use of the flowchart is explained in the following subclauses.



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 (e.g. 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 reference gas mixtures with defined uncertainties and quantify the impurity by direct comparison with these reference mixtures by use of methods described in, e.g. ISO 6143.

If metrologically traceable purity data from another source (e.g. 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/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 1 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.

NOTE 2 Where traceable gaseous measurement standards are not available, certified reference materials can be available in liquid form with certified purity.

NOTE 3 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 4 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. Prepare a series of standards containing the 'pure' material at different concentrations and extrapolate the analysed values 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):

$$x_{ij} = \frac{L_{ij}}{2} \tag{1}$$

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).

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

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

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

and its associated standard uncertainty by

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

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, often the purity data are 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

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

and its associated standard uncertainty by

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

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), "ppm" (parts per million), or "ppb" (parts per billion), 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.

Bibliography

[1] ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ICS 71.040.40

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