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

Page

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.

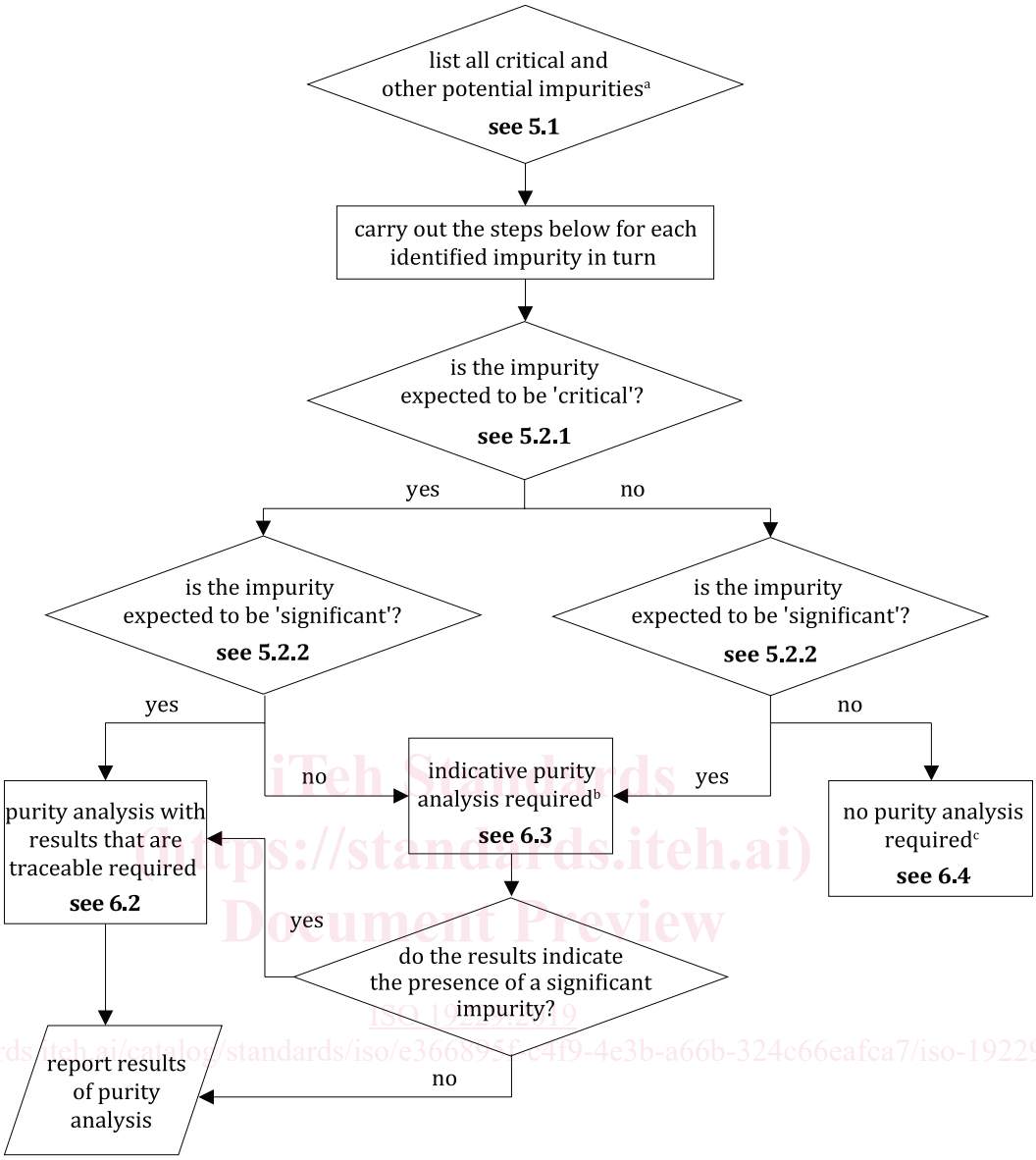
— an impurity that might be reactive with respect to any other component in the mixture.

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.

