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Gas analysis — Preparation of calibration gas mixtures using dynamic methods —

Part 1: General aspects

Analyse des gaz — Préparation des mélanges de gaz pour étalonnage à l'aide de méthodes dynamiques —

Partie 1: Aspects généraux

Reference number
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Contents

Page

Foreword

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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).

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For an explanation on 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 the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 158, *Gas analysis*.

This third edition cancels and replaces the second edition (ISO 6145-1:2003), which has been technically revised. The main changes compared to the previous edition are as follows.

— The techniques for the preparation of gas mixtures are described in an abbreviated manner since there is no need to repeat the text and formulae from each of the different parts of the ISO 6145 series. However, a summary table (Table 1) presenting the advantages and limitations of each method has been introduced.

— Recommendations regarding the handling of the dynamic mixing systems and quality considerations have been added.

— The methods and instruments to calibrate a dynamic system have changed and are better described.

— The calculations to obtain composition and uncertainties are more detailed, and the different ways of mixing gases (volume flow rates or mass flow rates) have been taken into account.

— Clauses on certificates (7.4) and verification (Clause 10) have been added.

A list of all parts in the ISO 6145 series can be found on the ISO website.

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

This document is one of a series of standards which describes the various dynamic methods for the preparation of calibration gas mixtures.

Several techniques are available and the choice between them is decided based on the desired gas composition range, the consistency of equipment with the application and the required level of uncertainty. This document aids with making an informed choice by listing all the advantages and limitations of the methods.

The main techniques used for the preparation of gas mixtures are:

a) piston pumps;

b) continuous injection;

c) capillary;

d) critical orifices;

e) thermal mass-flow controllers;

f) diffusion;

g) saturation;

h) permeation;

i) electrochemical generation.

In dynamic methods, a gas A is introduced at a known constant volume or mass flow rate into a known constant flow rate of a complementary gas B. Gases A and B can be either pure gases or gas mixtures. The preparation process can be continuous (such as mass flow controllers, permeation tube) or pseudo-continuous (such as piston pump).

The dynamic preparation techniques produce a continuous flow of calibration gas mixtures into the analyser but do not generally allow the build-up of a reserve by storage under pressure.

Gas analysis — Preparation of calibration gas mixtures using dynamic methods —

Part 1:
General aspects

1 Scope

This document gives a brief overview of each of the dynamic techniques which are described in detail in the subsequent parts of ISO 6145. This document provides basic information to support an informed choice for one or another method for the preparation of calibration gas mixtures. It also describes how these methods can be linked to national measurement standards to establish metrological traceability for the composition of the prepared gas mixtures.

Since all techniques are dynamic and rely on flow rates, this document describes the calibration process by measurement of each individual flow rate generated by the device.

Methods are also provided for assessing the composition of the generated gas mixtures by comparison with an already validated calibration gas mixture.

This document provides general requirements for the use and operation of dynamic methods for gas mixture preparation. It also includes the necessary expressions for calculating the calibration gas composition and its associated uncertainty.

Gas mixtures obtained by these dynamic methods can be used to calibrate or control gas analysers.

The storage of dynamically prepared gas mixtures into bags or cylinders is beyond the scope of this document.

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 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*

ISO 19229, *Gas analysis — Purity analysis and the treatment of purity data*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 7504 and the following 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/

3.1
mass flow rate
q_m
mass of gas per unit of time

3.2
volume flow rate
q_v
volume of gas per unit of time

4 Symbols

Symbol	Definition
i, k	Indices for components in a gas or gas mixture
j	Index for a parent gas
K	Conversion factor between two gases
m	Mass of a component
M	Molar mass of a component
p	Pressure
q	Number of components in the gas mixture
q_m	Mass flow rate
q_n	Amount-of-substance flow rate
R	Ideal gas constant
r	Number of parent gases
T	Temperature
V	Volume
q_v	Volume flow rate
$u(x)$	Standard uncertainty of a quantity x
v	Mass fraction of a component in a parent gas
w	Mass fraction of a component in a gas mixture
x	Amount-of-substance fraction of a component in a parent gas
y	Amount-of-substance fraction of a component in a gas mixture
Z	Compressibility factor
φ	Volume fraction of a component in a parent gas
ϕ	Volume fraction of a component in a gas mixture

5 Principle

5.1 General

All preparation techniques described in ISO 6145 (all parts) are based on the combination of gas flows. These flow rates can be measured on a volume or mass basis. The composition is calculated from the flow rate data and the composition of the parent gases.

It is applicable only to

— pure gases,

— gas mixtures, or

— totally vaporized components at ambient pressure,

which do not react with each other or with any surfaces of the mixing device.

For the calculation of the composition, it is essential to appreciate the composition of the parent gases used for preparing the calibration gas mixture. Even if such gases are considered “pure”, their purity shall be verified in accordance with ISO 19229. The corresponding compositional data of these parent gases shall be used in the calculation of the composition, as described in Clause 7.

Practically, all preparation systems are furthermore sensitive to changes or fluctuations in the conditions under which the calibration gas mixture is prepared. These conditions typically include the pressure and temperature of the gases, as well as the dynamic effects of combining flows and homogenization of the calibration gas mixture, among others. In the subsequent parts of ISO 6145, attention is drawn to these effects, and care shall be taken to follow these instructions.

Several techniques are available and the choice between them should be decided based on the desired composition range, the availability of equipment and the required uncertainty.

The principles of gas mixing systems are described in each part of ISO 6145.

Depending on its principle, each dynamic method will generate gas mixtures of composition based on either volume fraction, mass fraction, amount-of-substance fraction or mass concentration. The calibration procedure will also affect the expression of gas mixture composition (mass, volume or amount-of-substance fraction). The final fraction and its associated uncertainty depend both on the calibration method and on the preparation technique.

5.2 Suitability of the method to the application

Before preparing a gas mixture, it is necessary to consider the suitability of the dynamic system to the application. Pressure and flow rates should be consistent with the analyser to which the dynamic system will be linked.

Users shall comply with the manufacturers' recommendations. Check if the dynamic method is sensitive to external parameters, such as temperature or atmospheric pressure, and follow the recommendations given in each part of ISO 6145.

Depending on the principle used by the dynamic system, the achievable range of concentration in the final mixture will differ. In order to compare the capabilities of each method, a dilution ratio is estimated as follows:

— use of pure components as parent components (for example: in cylinders, or permeation tubes or by syringe injection);

— only one step dilution is considered.

This dilution ratio could be extended for some dynamic systems by two step dilution.

When choosing the type of the dynamic method, the user shall take into consideration the advantages and limitations of each method.

5.3 Piston pumps

ISO 6145-2 specifies a volumetric method for the dynamic preparation of calibration gas mixture using piston pumps. Two or more piston pumps, combined in a gas-mixing pump, are driven with a defined ratio of strokes. The stroke volume of each piston pump is individually determined by the geometry (cross-section) of the cylinder and the height of stroke of the piston. The composition is rapidly changed by the mechanical changing of the ratio of strokes. Suitable peripherals for gas feeding and homogenization of the final mixture are recommended.

The calibration of the stroke volume is made by dimensional measurements in the SI base unit of length. Uncertainty evaluation of the gas mixture composition and an assessment of potential sources with quantification of significant sources of uncertainty are out lined in detail in ISO 6145-2.

The merits of the method are that the composition and the associated uncertainty of the calibration gas mixture are calculated from the geometric stroke volume and the ratio of strokes of the piston pumps. The content of each component is directly expressed in volume fractions and in amount-of-substance fractions.

Final mixture flow rates from 5 l/h to 500 l/h can be prepared depending on the equipment used.

Using this method, dilution ratios from 1:1 up to $1:10^4$ can be prepared from initial amount-of-substance fraction. Higher dilution ratios can be prepared by a two-stage dilution.

5.4 Continuous (syringe) injection

ISO 6145-4 specifies a method for preparation of calibration gas mixtures using continuous injection.

The calibration component, either in the gaseous or liquid phase, is displaced from a reservoir through a capillary into a complementary inert gas stream. The system may contain a syringe, whose plunger is continuously driven by a suitable variable-speed motor. Alternatively, the component may be forced through the capillary by controlled pressurization of the reservoir.

This method applies also to multi-component mixtures of known composition. In the case of liquids, the calibration component is vaporized while mixing with the complementary gas.

The flow rate of the calibration component is determined by the geometry (cross-section) of the syringe and the linear velocity of the plunger or by the continuous weighing of the reservoir.

Using this method, dilution ratios from $1:10^4$ up to $1:10^7$ can be prepared from initial amount-of-substance fraction.

5.5 Capillary

ISO 6145-5 specifies a method for the continuous preparation of calibration gas mixtures from pure gases or gas mixtures using capillary tubes in single or multiple combinations.

A constant flow of gas from a capillary tube under conditions of constant pressure drop is added to a controlled flow of complementary gas. The complementary gas may be derived from another capillary tube.

This application is used in industrial gas mixing panels for the production of specific gas atmospheres. Gas dividers can be used to divide gas mixtures prepared from pure gases or gas mixtures into controlled proportions by volume.

Using this method, dilution ratios from 1:1 up to $1:10^4$ can be prepared from initial amount-of-substance fraction.

5.6 Critical flow orifices

ISO 6145-6 specifies a method for the continuous preparation of calibration gas mixtures by use of critical flow orifice systems.

When passed through a critical orifice at increasing upstream pressure P_{in}, the volume flow rate of gas passing through the orifice will increase. When the ratio of the gas pressure downstream P_{out} and the gas pressure upstream P_{in} of the orifice has reached the critical value, the volume flow rate of the gas becomes independent with respect to P_{out} and is proportional to P_{in}.

To prepare calibration gas mixtures, the gas blender mixes the complementary gas flowing at a known rate out of one or several critical flow orifice(s) and the gas to be diluted flowing out of one or several critical flow orifice(s). The resulting mixture is generally homogenized in a mixing chamber.

Although it is more particularly applicable to the preparation of gas mixtures at atmospheric pressure, the method also offers the possibility of preparing calibration gas mixtures at pressures greater than atmospheric. The upstream pressure should be at least two times higher than the downstream pressure. The range of flow rates covered by this document extends from 1 ml/min to 10 l/min.

It has the merit of allowing multi-component mixtures to be prepared as readily as binary mixtures if an appropriate number of critical flow orifices are used.

Using this method, dilution ratios from 1:1 up to $1:10^4$ can be prepared from initial amount-of-substance fraction. Higher dilution ratios can be prepared by a two-stage dilution.

5.7 Thermal mass flow controller

ISO 6145-7 specifies a method for continuous preparation of calibration gas mixtures using thermal mass flow controllers. By adjustment of the set-points on the flow controllers, it is possible to change the composition of the gas mixture rapidly and in a continuously variable manner.

The range of flow rates covered by this document extends from 1 ml/min to 10 l/min.

The advantages of the method are that a large quantity of the gas mixture can be prepared on a continuous basis and that multi-component mixtures can be prepared as readily as binary mixtures if the appropriate number of thermal mass-flow controllers is utilized.

Using this method, dilution ratios from 1:1 up to $1:10^4$ can be prepared from initial amount-of-substance fraction. Higher dilution ratio can be prepared by two stage dilution.

5.8 Diffusion

ISO 6145-8 describes a method, which applies to components that are liquids or solids that can produce a vapour. The vapour of the pure component migrates by diffusion through a diffusion cell of suitable dimensions (length, diameter) into a flow of a complementary gas. The rate of diffusion should remain constant, if the system is kept at constant temperature and the pure component is still present as liquid or solid.

The substance, of a known high purity, is contained in a reservoir that acts as the source of the component vapour. The reservoir is provided with a vertically placed diffusion cell. This assembly (the diffusion cell) is placed in a temperature-controlled enclosure that is purged at a constant flow rate by a high-purity and inert complementary gas. The diffusion rate is measured by periodic weighing of the diffusion cell.

Using this method, dilution ratios from 1:10 up to $1:10^3$ can be prepared from initial amount-of-substance fraction.

5.9 Saturation

ISO 6145-9 specifies a method for the dynamic preparation of calibration gas mixture based upon the vapour saturation pressure of liquid and solid substances. The complementary gas flow is passed through a temperature-controlled saturator in which the vapour of the calibration component is maintained in equilibrium with their liquid or solid phases.

The amount-of-substance fraction of the calibration component in the gas flow is approximately equal to the ratio of the vapour pressure of the component and the total pressure of the mixture at that temperature. The saturation pressure values for very many components as a function of temperature are given in reference books.

This method applies to all pure components that are in a stable equilibrium with their vaporized and liquid phase. The vapour pressure in equilibrium with its condensate phase depends only on temperature. Variation of volume fraction is achieved by variation of temperature and pressure in the saturator.

Two procedures are described for the application of this method. Calculation of composition and uncertainty evaluation are given based on vapour pressure data.

The merits of the method are that calibration gases with condensable components can be dynamically prepared and used at ambient conditions near the individual component condensation point. In combination with other volumetric dynamic methods a small flow of saturated calibration gas can be easily diluted by a large flow of complementary gas to very small volume fractions.

Using this method, dilution ratios from $1:10^3$ up to $1:10^6$ can be prepared from initial amount-of-substance fraction .

5.10 Permeation method

ISO 6145-10 describes a method in which the calibration component is contained in a sealed tube or container, which consists either wholly or partly of a polymer through which the component can permeate. The component is usually contained as a liquid or solid in equilibrium with its own vapour but can be contained as a gas. In the former case, the rate of permeation should remain constant while the liquid is still present. In the latter case, the rate decays with the pressure of the gas. In either case, the rate of permeation is dependent on temperature.

The vessel containing the calibration component is put into an enclosure. The diluent gas is passed through the enclosure at a fixed flow rate. The entire housing is placed in a temperature-controlled chamber.

The permeation rate can be measured by weighing the tube periodically. This procedure is described in ISO 6145-10.

Using this method, gas mixtures of dilution ratios from 1:10 up to $1:10^3$ can be prepared from the permeation rate.

5.11 Electrochemical generation

ISO 6145-11 describes a method based on electrochemical generation of one pure component which is diluted in a complementary gas. The composition of the gas mixture is controlled by the magnitude of the electrical charge passed through the electrolyte in the cell and by the flowrate of the complementary gas and is dependent on the efficiency of the cell.

An advantage of the method is that a stable gas mixture can be established rapidly within a few minutes. However, in ISO 6145-11, a list indicates that the number of different gases that can be produced by electrochemical generation is limited to those which follow: oxygen, nitrogen, hydrogen, hydrogen cyanide, hydrogen sulphide, chlorine, bromine, chlorine dioxide, ammonia, phosphine, arsine, nitric oxide, carbon dioxide and ozone.

Using this method, dilution ratios from $1:10^4$ up to $1:10^7$ can be prepared from initial amount-of-substance fraction.

5.12 Summary

Table 1 gives a summary of the preparation techniques.

