International Standard 6143

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods

Analyse des gaz — Détermination de la composition de mélanges de gaz pour étalonnage — Méthodes par comparaison

First edition — 1981-06-01

UDC 543.27 : 53.089.68 **Ref. No. ISO 6143-1981 (E)**

Descriptors : gas analysis, determination, calibrating, gas mixtures, comparison analysis.

Price based on 4 pages

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 6143 was developed by Technical Committee ISO/TC 158, *Analysis of gases*, and was circulated to the member bodies in October 1979.

It has been approved by the member bodies of the following countries :

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United Kingdom

Printed in Switzerland

Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods

0 Introduction

Comparison methods are generally used when large quantities of gas are available, for example gas mixtures under pressure. Such mixtures are prepared by methods which are not always conducive to high accuracy, but, from the practical point of view, it is convenient to use them for calibration when they have been accurately analysed for the concentrations of the components.

1 Scope and field of application

This International Standard provides means for determining the composition of calibration gas mixtures by comparison methods. The concentration of each component in the mixture has to be determined, but it should be noted that the accuracy of the value of each concentration may vary over a fairly large range, depending on the type of apparatus used to make the comparison.

The principal application of comparison methods is the preparation of large quantities of gas for frequent calibration of analysers in routine use.

2 Principle

The preparation of a gas mixture can be achieved in several ways. In general, a rapid but imprecise method is used employing large quantities of gas.

Determinations of the composition of mixtures thus prepared, suitably stabilized and homogeneized, is performed with an analyser, by comparison with one or more calibration gas mixtures of closely similar composition.

The accuracy depends on the care taken in performing the analysis, on the analyser used, and on the quality of the calibration gas mixtures.

To minimize uncertainties due to the analyser, it is desirable to carry out several determinations and to analyse the results statistically.

3 Procedure

3.1 Use of a single calibration gas mixture for comparison

A calibration gas mixture E is used, composed of the same components and having a concentration similar to that of the mixture X to be analysed. Mixture E is prepared by one of the methods specified in other appropriate International Standards. Let C_E be the concentration of one component of mixture E and C_X be the concentration of the same component in the mixture X for analysis. Test portions of X and E are introduced successively into the analyser and the ratio r of the respective signals Y_X and Y_E, read from the analyser, is calculated.

For each component, as a function of r,

$$C_\mathrm{X} = C_\mathrm{E} \frac{Y_\mathrm{X}}{Y_\mathrm{E}} = C_\mathrm{E} r$$

Practical limitations require that the maximum error is obtained by the calculation of errors; thus $\Delta C_\mathrm{X}/C_\mathrm{X}$, as defined in the sense of error calculation, is retained for primary calibration mixtures, and ΔY is assigned as the confidence interval at the 95 % confidence level for Y estimated as the mean value of a series of n measurements.

With the reservation that the sample quantities are introduced under identical conditions (temperature, pressure and, if appropriate, flow rate), the maximum relative error of the concentration C_X is given by the formula

$$\frac{\Delta C_\mathrm{X}}{C_\mathrm{X}} < \frac{\Delta C_\mathrm{E}}{C_\mathrm{E}} + 2\frac{\Delta Y}{Y} \;; \quad Y_\mathrm{X} \approx Y_\mathrm{E} \equiv Y$$

NOTES

1 This method of calculation assumes that the response curve of the analyser is linear and passes through the origin. If the analyser does not have a linear response, it is necessary to employ several calibration gas mixtures for the comparison.

2 Random errors due to uncertainty of the analyser are evaluated by statistical analysis of the results.

Assuming a gaussian distribution of results :

$$\Delta y = s_y \frac{t}{\sqrt{n}}$$

where

Δy is, for example, the 95 % confidence level of the measurement for y, estimated as the mean value for a series of n measurements;

s_y is the variation measured;

t is the Student-Fischer coefficient.

The true value will be more closely approached as the number of measurements is increased; the effect of errors will thus be minimized.

3.2 Use of two calibration gas mixtures for comparison

The use of two calibration gas mixtures permits the form of the analyser response curve to be neglected.

The mixtures must be composed of the same components as the mixture to be analysed.

Let Y_i be the value of the signal obtained for concentration C_i.

Given that $C_1 < C_X < C_2$, it can be considered that C_1 and C_2 are very close to C_X, so that section AB coincides with the part of the analyser curve in this measuring region (see figure 1).

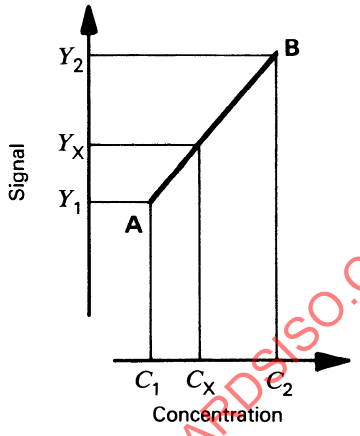


Figure 1 — Graph of signal obtained as a function of concentration

Under these conditions, the concentration C_X is calculated by means of one of the formulae

$$C_X = \frac{1}{S}(Y_S - Y_1) + C_1$$

with $S = \dfrac{Y_2 - Y_1}{C_2 - C_1}$, i.e. S is the slope of the response curve in the region under consideration,

or

$$C_X = C_1 + m(C_2 - C_1)$$

with $m = \dfrac{Y_X - Y_1}{Y_2 - Y_1}$, $0 < m < 1$.

The maximum absolute error of the concentration C_X is given by the formula

$$\Delta C_X \leqslant (1 - m)\Delta C_1 + m\Delta C_2 +$$

$$+ \frac{1}{S}\left[(1 - m)\Delta Y_1 + m\Delta Y_2 + \Delta Y_X\right]$$

where ΔC_1, ΔC_2, ΔY_1, ΔY_2 and ΔY_X are the absolute errors of the concentrations and the responses considered respectively.

It may be considered that

$$\frac{\Delta C_1}{C_1} = \frac{\Delta C_2}{C_2} = \frac{\Delta C}{C}$$

and

$$\frac{\Delta Y_1}{Y_1} = \frac{\Delta Y_2}{Y_2} = \frac{\Delta Y_X}{Y_X} = \frac{\Delta Y}{Y}$$

Furthermore

$$Y_X \approx Y_1 \approx Y_2$$

Thus, the expression for relative error becomes

$$\frac{\Delta C_X}{C_X} < \frac{\Delta C}{C} + \frac{2Y_X \Delta Y}{SC_X Y}$$

where $\Delta Y/Y$ is the repeatability of the analytical unit for the measurement in question.

3.3 Multipoint calibration for use with the comparison method

The use of multiple calibration gas mixtures allows an analyser response curve (linear or non-linear) to be determined. This method of calibration allows an analyser to be used for comparison over the entire useful response range. To eliminate possible analyser response interferences, the calibration gas mixtures, as well as those to be compared, must be composed of identical components unless it is known that these components will not contribute to the analyser response.

Using as many gas mixtures for calibration as is necessary, statistically determine a response curve by measuring the analyser response for each of the known gas mixtures. The number of calibration gas mixtures to be used depends upon the type of analyser response, but should consist of a minimum of three mixtures. After calibration, the mixtures to be compared can be analysed knowing the analyser response as long as the unknown mixture does not exceed or fall below the response obtained for the highest or lowest known concentration respectively. The frequency with which the multipoint calibration must be repeated will depend on the operational history of the specific analyser being used. The number of measurements required to obtain a truly representative analyser response has to be determined by statistical treatment, after considering the analyser precision and the accuracy required.

An example of multipoint calibration is given in the annex.

Annex

Example of multipoint calibration

This example consists of the determination of the concentration of a series of calibration gas mixtures having carbon dioxide concentrations in the range of 0 to 14 % by the use of the comparison method and multipoint calibration. The method of comparison used is based on a non-dispersive infrared analyser and a series of known and verified carbon dioxide calibration gas mixtures to determine the instrument response.

The accuracy of the known carbon dioxide calibration mixtures is ± 1 %, and it is desired that the total uncertainty of the unknown mixtures be determined within ± 5 % of the carbon dioxide component.

The response of the non-dispersive infrared analyser is determined using calibration gas mixtures at approximately 0—10—30—50—75 and 95 % of the useful analyser range. This number of points was selected to define accurately the analyser response to yield the ± 5 % total uncertainty required. The analyser response is plotted after regression calculation as shown in figure 2. The instrument response is subject to small variations, and these are compensated by reference to the calibration gas mixture having a concentration most similar to that of the unknown mixture. The level of these variations can only be determined through experience with a particular instrument. In this example, the analyser response at any point must not vary by more than ± 2 % relative; if it does, or if the constancy of response is not known, the entire calibration curve must be redefined for each use.

The analyser response is measured in triplicate for both the calibration gas mixture and the unknown sample.

The true value of the carbon dioxide concentration in the calibration gas mixture in this example is 7,20 %. The corrected value for the unknown sample is given by the formula

$$\text{Unknown, corrected value} = \text{Unknown, first concentration reading} \times \frac{\text{True value for calibration gas mixture}}{\text{First concentration reading for calibration gas mixture}}$$

i.e.

$$\text{Corrected value} = \text{First concentration reading} \times \text{Correction factor}$$

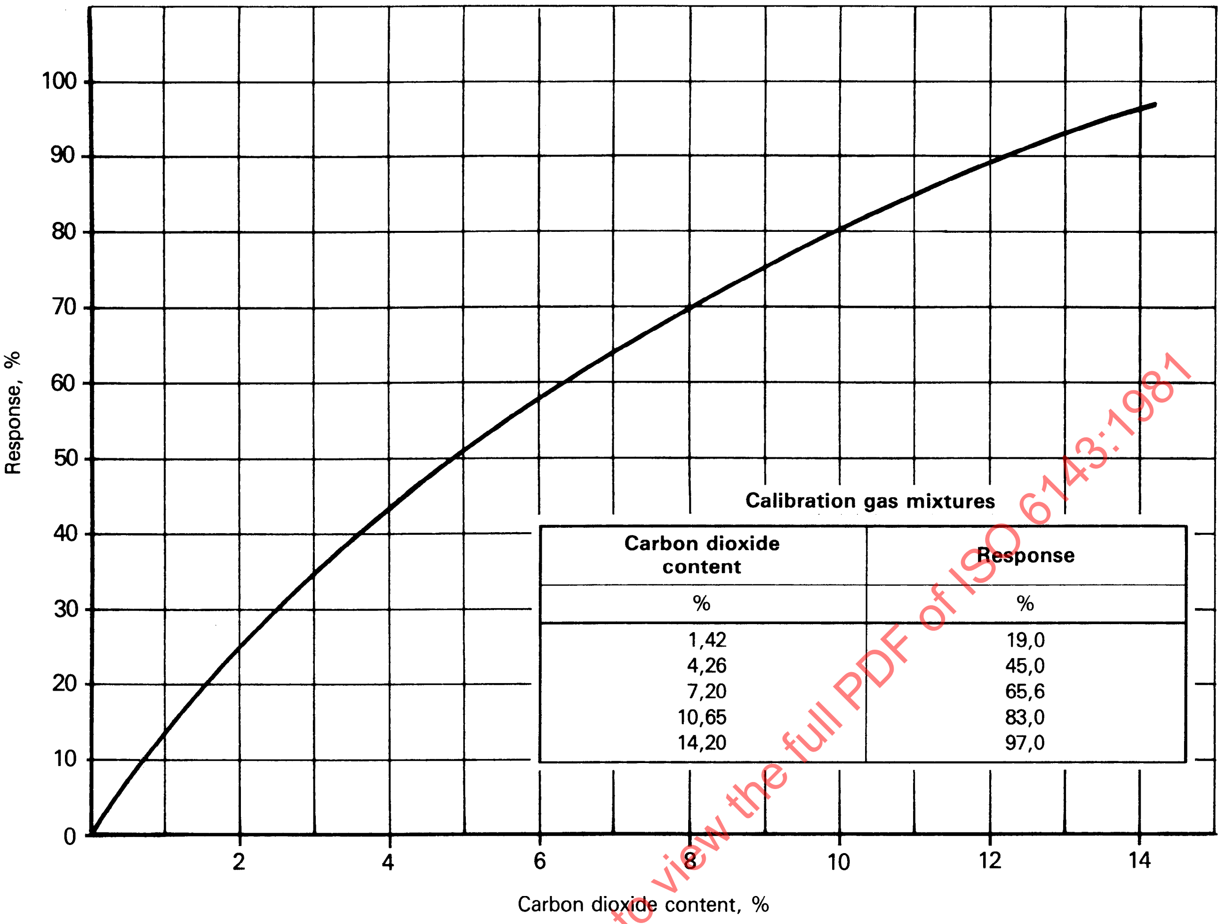
Test No.	Calibration mixture			Correction factor	Unknown mixture		
	True value %	Response %	First concentration reading %		Response %	First concentration reading %	Corrected value %
1	7,20	65,6	7,20	1,000	74,7	8,86	8,86
2	7,20	65,3	7,17	1,004	74,2	8,81	8,85
3	7,20	65,0	7,13	1,010	74,8	8,88	8,97
						Mean	8,89

Since the mean calculated unknown concentration is 8,89 %, the maximum deviation from the mean is

$$\frac{8{,}97 - 8{,}89}{8{,}89} \times 100 = 0{,}9\ \%$$

This procedure is repeated for each mixture to be determined. The number of determinations required will depend on the repeatability and reproducibility obtained.

In this example, it was required that the total uncertainty be not more than ± 5 %, so that three determinations were satisfactory.



Calibration gas mixtures

Carbon dioxide content	Response
%	%
1,42	19,0
4,26	45,0
7,20	65,6
10,65	83,0
14,20	97,0

Figure 2 — Response curve of the analyser to the calibration gas mixtures