SLOVENSKI STANDARD

SIST ISO 6711:1995

01-avgust-1995

Analiza plinov - Preverjanje kalibrirnih plinskih zmesi s primerjalno metodo

Gas analysis -- Checking of calibration gas mixtures by a comparison method

Analyse des gaz -- Vérification des mélanges de gaz pour étalonnage par une méthode de comparaison

Ta slovenski standard je istoveten z: ISO 6711:1981

ICS:

71.040.40	Kemijska analiza	Chemical analysis

SIST ISO 6711:1995 en

International Standard ISO 6711

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

Gas analysis — Checking of calibration gas mixtures by a comparison method

Analyse des gaz — Vérification des mélanges de gaz pour étalonnage par une méthode de comparaison

First edition — 1981-06-01

UDC 543.27 : 53.089.68 **Ref. No. ISO 6711-1981 (E)**

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

Price based on 2 pages

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

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 6711 was developed by Technical Committee ISO/TC 158, *Analysis of gases*, and was circulated to the member bodies in February 1980.

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

Australia
Belgium
Bulgaria
Czechoslovakia
France
Germany, F.R.
India
Ireland
Italy
Mexico
Netherlands
Poland
South Africa, Rep. of
Spain
United Kingdom
USSR

No member body expressed disapproval of the document.

Printed in Switzerland

Gas analysis — Checking of calibration gas mixtures by a comparison method

1 Scope and field of application

This International Standard describes a method for checking calibration gas mixtures using a comparison method.

It is applicable for all calibration gas mixtures stored in cylinders and permits the checking, at any time, of the stated concentrations of the gaseous calibration constituents.

2 References

ISO 6143, *Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods.*[1]

ISO 6144, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric methods.*[1]

3 Principle

The method is based on a series of measurements by repeated preparation of mixtures having the concentration being checked, followed by a repeatability study of the analytical results at the last stage of the repetition.

The method of checking is based on

a) a sufficiently fast method (method A) of preparing calibration gas mixtures E :

- the concentration of which, C, can be adjusted to closer than 0,5 % relative to the value X of the concentration to be checked,
- with a known degree of uncertainty $\frac{\Delta C}{C}$ (in the sense of conventional calculation of errors),
- the principle of which does not allow causes of systematic errors;

NOTE — Methods of this type are the static volumetric methods described in ISO 6144.

b) a method of analysis (method B) of the constituent in question, known as the comparison method (see ISO 6143). This is used to compare the response of a suitable analyser to the constituent in the mixture M to be checked and from calibration gas mixtures E obtained using method A. The analyser response shall not be subject to any interference from other gases, including the complementary gases, in mixtures M and E.

A comparison of the responses R_M and R_E using the two methods gives

$$\frac{R_M}{R_E} = \frac{X}{C} = k$$

4 Procedure

This method comprises three stages:

a) The mixture M to be checked is compared, by means of the analytical method B, with a mixture E_1 having a concentration C_1 close to the stated value of X. A first approximation of the concentration X_1 is thus obtained.

b) A mixture E_2 having a concentration $C_2 \approx X_1$ is then prepared.

This mixture E_2 is compared with the mixture M to be checked. From this, a second approximation X_2 of the concentration X in mixture M is obtained. Generally, $X_2 \approx X_1$ with an accuracy of better than 0,5 % as a relative value. If this is not the case, a mixture E_3 having a concentration $C_3 \approx X_2$ is prepared, and a new analytical comparison is carried out giving $X_3 \approx X_2$ with an accuracy of better than 0,5 % as a relative value. Usually, two comparisons are sufficient.

The mixtures E_p shall be used immediately after preparation to rule out the effect of variations with time of the concentration C of the calibration gas mixture.

c) The repeatability of the analytical method is evaluated.

---

[1] At present at the stage of draft.

After the last stage of repetition, the comparison of mixture M with mixture E_p (i.e. E_2 or E_3) is repeated ten times; the following values are obtained for the normal distribution

$$\frac{X_p}{C_p} = \bar{k} \pm \frac{S_k\, t_9}{\sqrt{10}} \qquad \ldots(1)$$

where

$\bar{k}$ is the mean of the 10 measurements for k [$\bar{k}$ very close to 1; $\bar{k} - 1 < 0{,}005$];

S_k is the estimated standard deviation of X_p/C_p under the actual conditions of measurement;

t_9 is the Student-Fischer coefficient for nine degrees of freedom and a 95 % probability ($t_9 = 2{,}262$) :

$$t_9/\sqrt{10} \approx 0{,}72$$

If the statistical uncertainty of $\bar{k}$ at a 95 % probability $S_k t_9/\sqrt{10}$ is designated by I, then equation (1) reduces to :

$$\frac{X_p}{C_p} = \bar{k} \pm I \qquad \ldots(2)$$

5 Evaluation of the uncertainty of X_p

The concentration X_p is derived from equations (1) and (2) and is given by

$$X_p = C_p\,(\bar{k} \pm I)$$

from which the approximation of the uncertainty of X is

$$\frac{\Delta X}{X} = \frac{\Delta X_p}{X_p} \approx \frac{\Delta C_p}{C_p} + I$$

6 Notes

6.1 The evaluation used is not purely statistical (at 95 % probability). This would be difficult to achieve in this case as it would imply a larger number of preparations of the mixtures E. The evaluation used probably constitutes an evaluation in excess of this statistical uncertainty. This is derived from the term $\Delta C_p/C_p$, which is obtained from classical calculations of error, which defines C_p to the nearest $\pm\ \Delta C_p/C_p$, outside a specified probability. The value $\Delta C_p/C_p$ can be related to the possible deviation (at 95 % probability) between any two measurements taken within a normal distribution of measurements of standard deviation σ; this deviation is 2,77 σ, compared with $\pm\ 0{,}72\ S_k$, of the confidence interval of the analytical comparison.

6.2 Even if the statistical variability of the method of preparation is known, at least two measurements (X_1 and X_2), are made on different mixtures (E_1 and E_2) in order to rule out the possibility of any large errors associated with the preparation of a single mixture E.

To reinforce this precaution, the different mixtures E_p should be prepared using different conditions (for example volumes and final pressures for the static volumetric method).

6.3 The confidence interval, $\pm\ I = 2 \times 0{,}72\ S_k$, thus estimated, is characteristic of the analytical method at the moment when measurement is carried out; this shows up any accidental defect in a component of the apparatus by comparison of the dispersion obtained with that which would be obtained under ideal conditions.

6.4 The possible error of proportionality in the comparison method is reduced by the repetition which results in $\bar{k} - 1 < 0{,}005$.

These conditions, with an agreement of better than 0,5 % as a relative value of repetition, can only be fulfilled by means of an analytical method of adequate and measurable repeatability, the responses being, in particular, sufficiently large. Numerical response with three significant figures, or an analogue response, on a potentiometric recorder, with offsetting in the measuring scale giving responses of more than 250 mm should be obtained.

In certain cases, particularly with mixtures of low concentration associated with analytical methods which are not very sensitive and, generally, of low repeatability, it is possible that repetition with an accuracy of better than 0,5 % will be unobtainable; nevertheless, the method provides a means of calculating the repeatability in this case and a less favourable result for the uncertainty is obtained.

6.5 The effects of the purity of gases used for preparing mixtures E for calibration can be shown in the following way.

Generally, the gases used are guaranteed to be at a concentration higher than a specific value :

a) for the complementary gas, it is necessary to check the absence of, or measure the level of, the constituent to be checked in order to deduce any corrections to the concentration of the mixtures E;

b) for the constituent which is to be checked, the concentration, which is merely guaranteed to be greater than $1 - y$, is in fact between $1 - y$ and 1. In order to take account of this, a total range of uncertainty must be established, wherein :

- the lower limit is $\bar{k}C_p\ [1 - (\Delta X/X)]$;
- the upper limit is $X = \bar{k}C_p\ [1 + (\Delta X/X) + y]$;
- the value of C_p is calculated to within $1 - y$ of the constituent concentration;

y being the maximum guaranteed quantity of impurities.

A more convenient form of presentation consists in calculating C_p from the concentration $1 - (y/2)$ and introducing $\pm\ y/2$ into the relative error $\Delta C_p/C_p$.

6.6 As a consequence of 6.2 and 6.3, the method contains elements for its own verification and is not based solely on studies of dispersions carried out on measurements which are separate from the operation in question.