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RECOMMENDATION

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# Requirements concerning pure gases CO, $CO_2$, $CH_4$, $H_2$, $O_2$, $N_2$ and Ar intended for the preparation of reference gas mixture

Prescriptions pour les gaz purs CO, $CO_2$, $CH_4$, $H_2$, $O_2$, $N_2$ et Ar destinés à la préparation des mélanges de gaz de référence

OIML R 73 Edition 1985 (E)

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OF LEGAL METROLOGY

# Contents

*Foreword* ..... 3

1 Technical requirements for pure gases ..... 4

2 Appendix ..... 5

# Foreword

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# REQUIREMENTS CONCERNING PURE GASES $CO$, $CO_2$, $CH_4$, $H_2$, $O_2$, $N_2$ and Ar INTENDED for the PREPARATION of REFERENCE GAS MIXTURES

This Recommendation sets out the requirements for pure gases ($CO$, $CO_2$, $CH_4$, $H_2$, $O_2$, $N_2$ and Ar) used as components for the preparation of reference gas mixtures, in the 0.01 - 0.99 mole ratio range(*).

The purpose of this Recommendation is to establish a harmonized method for the elaboration of specifications for those pure gases, which are intended for metro-logical purposes.

**Technical requirements for pure gases**

1. Industrially produced pure gases, supplied under pressure in cylinders, shall be used as reference gases.
2. The mole ratio of the pure gas shall be not less than 0.999 9.
3. The error limit on the evaluation of the mole ratio of the pure gas shall not exceed $1 \cdot 10^{-4}$.
4. The mole ratio of any impurity (He, Ne, $H_2$, Ar, $O_2$, $N_2$, Kr, $CO$, $CO_2$, $N_2O$, Xe) shall not exceed $1 \cdot 10^{-5}$ (**).
5. The mole ratio of any corrosive gas ($NH_3$, $N_mO_n$, $SO_2$, $H_2S$, $COS$ and others) shall not exceed $1 \cdot 10^{-6}$.
6. The mole ratio of the sum of hydrocarbons shall not exceed $1 \cdot 10^{-6}$.
7. The mole ratio of water vapour shall not exceed $2 \cdot 10^{-6}$.

(*) It is accepted to express the concentrations in a mixture in terms of volume ratio.

(**) BIML note : see however the Appendix, 7th paragraph.

## APPENDIX

The majority of gas analysers in laboratories of industry and government is used for measuring the mole ratio of industrially important gases (CO, $CO_2$, $CH_4$, $H_2$, $O_2$, $N_2$ and Ar) in the 0.01 to 0.99 mole ratio range. The fiducial error (in relation to the scale range) of the most accurate gas analysers is in the range from 0.5 to 1 %. To achieve harmonization and to improve accuracy of analytical measurement of gases, it would be appropriate to use the mole ratio expressed in a dimensionless unit or as a percentage.

Compositions of gas mixtures, expressed in terms of mole ratio do not depend on the conditions of their use (temperature and pressure) and can be achieved with proper accuracy to ensure harmonization of analytical measurement of gases, carried out in different countries.

However, most of the scales of ordinary gas analysers are graduated in terms of volume ratio. These gas analysers are calibrated by means of reference gas mixtures, the composition of which is expressed in terms of mole ratio, which leads to a systematic error. For accurate measurement this systematic error can be taken into account using equations of gas state for real gases. But, in most cases of verification, these errors may be ignored when compared with the errors introduced by ordinary gas analysers.

Reference gas mixtures, prepared from pure gases by a gravimetric method, are used for the verification and calibration of the most accurate gas analysers.

The International Standard ISO 6142-1981 « Gas analysis - Preparation of calibration gas mixtures - Weighing methods » describes in detail the gravimetric method for the preparation of reference gas mixtures.

The accuracy of preparation of reference gas mixtures is greatly influenced by the concentration of impurities in the pure gases, used for the preparation of mixtures. That is why the technical requirements for pure gases as given in this Recommendation are necessary. The composition of pure gases is determined on the basis of the preparation process, the purification methods and the measurement of the concentration of impurities.

All the impurities mentioned in points 4, 5, 6 and 7 of this Recommendation may not be present in the pure gases at the same time. Some impurities are removed from the pure gas with considerable difficulties and some of the impurities have no influence on the calibration of a gas analyser. This means that in some cases the concentration of impurities in the pure gas may be higher than stated in the Recommendation if the calibration of the gas analyser, by means of a reference gas mixture, is not affected by these impurities. For example, even a high concentration of helium in a gas mixture containing CO and $N_2$ has no influence on the calibration of a non-dispersive infrared CO gas analyser.

The gas mixtures used for metrological purposes comprise both, active and ballast gases.

When preparing gas mixtures produced by the gravimetric method the limit of the relative error range on the evaluation of the mole ratio of the active gas may vary from 0.1 to 0.2 %.

If the systematic errors are the predominant component of the calibration errors of the reference gas mixture and assuming uniform (rectangular) distribution for the evaluation of the standard deviation, one can write :

$$S_u = \frac{0.1 \text{ to } 0.2 \ \%}{\sqrt{3}} \simeq 0.06 \text{ to } 0.12 \ \%$$

If the random errors are the predominant component, we have for the law of normal distribution :

$$S_u = \frac{0.1 \text{ to } 0.2 \ \%}{\sqrt{3}} \simeq 0.03 \text{ to } 0.07 \ \%$$

Since the ratio between $s_u$ and $s_n$ differs in each particular case, the most severe conditions for the standard deviation of the total error must be taken :

$$s_t = 0.03 \ \%$$

If the error of measurement of the mole ratio of the basic components in the gas mixtures is to have no influence on $s_t$, an error value of about 0.01 % must be assumed.

In this case, ordinary technical gases may be used as reference gases, provided that the mole ratio of their basic component is at least 0.999 9, with a mole ratio of corrosive gases ($NH_3$, $N_mO_n$, $SO_2$, $H_2S$, COS and others) at the most $1 \cdot 10^{-6}$ and a mole ratio of water vapour at the most $2 \cdot 10^{-6}$

Two methods may be used for the preparation of pure gases :

1) determination of the mole ratio of the basic component,

2) determination of the mole ratio of specified impurities or of their sum, with subsequent calculation of the mole ratio of the basic component.

The first method involves the measurement of the physical properties of the gases, for example density, phase transformation temperatures, etc., which are linked, by a strict relationship, with the physical property to be measured.

For the second method, it is reasonable to use an instrumental analytical method (gas chromatography, mass spectrometry, chromato-mass-spectrometry), for which the detection limit is of the order of $1 \cdot 10^{-5}$ to $1 \cdot 10^{-7}$ in terms of mole ratio.

Since instrumental analytical methods are most commonly used in the field of analytical measurement of gases throughout the world, it is logical to recommend them for the measurement of impurities, in connection with the evaluation of concentrations of the basic component.

In order to harmonize the requirements for pure gases and the equipment intended for their calibration, it is logical to apply these requirements also to the mole ratio below 1 %, although in this case the error limit on the evaluation of the mole ratio of the basic component may reach 0.1 %. Furthermore, for the indicated mole ratio range it is also necessary to introduce requirements for the impurity contents in the ballast gas which acts as the active gas in the preparation of gas mixtures.