Analytical Measuring System Using Primary Standards for the Certification of Secondary Reference Gas Mixtures

Key words

Gas chromatography, certification, primary standards, reference gas mixtures

Fields of application

Official certification (legal metrology) of gas mixtures as reference standards of gas composition to assure traceability of calibration gases for vehicle exhaust emission measuring devices as well as for Process Gas Chromatographs or gas calorimeters to national standards of gas composition according to PTB requirements. Certification of secondary reference gas mixtures for the calibration and validation of gas analytical procedures and gas analysers with verified metrological traceability to BAM primary standards (national standards of gas composition).

Methodology and instrumentation

Gas chromatographic determination with thermal conductivity and/or flame ionisation detection.

Primary standards used for calibration are prepared according to static gravimetrical methods (ISO 6142: “Gas analysis – Preparation of calibration gas mixtures – Gravimetric method”).

Items tested

Gas mixtures in pressure vessels fulfilling the “Technical Requirements for the Acceptance of Gas Mixtures as Candidates for Secondary Standards”.

Quantities / characteristics tested

Composition of gas mixtures from 2 up to 17 components
(molar fractions of H_2, He, Ar, N_2, O_2, NO, N_2O, SF_6, CO, CO_2 and hydrocarbons C_1 to C_6 in mol/mol)

Uncertainty / reliability of results

The uncertainty of results depends on the composition of the gas mixture (qualitatively) and upon the magnitude of the molar fraction (quantitatively) and ranges between 0.1 % and 2.0 % rel.

Qualification and quality assurance

The gas analysis laboratory of BAM has widespread experimental experience and theoretical knowledge in the field of gas analysis by gas chromatography as well as in gravimetic preparation of primary reference gas standards (calibration/reference gas mixtures of highest metrological level) and their proper handling. Its qualification is unique in Germany.
Quality assurance is performed by use of analysis control samples and by comparability of the results on the highest international level being demonstrated by successful participation in laboratory intercomparisons of national metrology institutes (CCQM Key Comparisons). (http://www.bipm.fr/)
BAM regularly organises national intercomparisons to enable gas analysis laboratories to demonstrate their competence and in order to link their results to the international traceability chain of metrology.

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Further information

Gas chromatography is a physical separation technique to separate a gas mixture into its individual components by distribution between a stationary and a mobile phase. The gas mixture to be certified (gas sample), the primary standards and the analysis control sample are automatically injected into the stream of carrier gas (mobile phase) of the chromatograph following a given cycle (see diagrams below) via a gas dosing system.

For the separation steps combinations of capillary and packed columns (stationary phase) are used and signals are detected by changes in thermal conductivity and/or ionization characteristics in a flame.

Quantification of components is realised by comparing the peak areas of the sample signal with the peak areas of the signals derived from the corresponding components of the primary standards used.

Certification analysis is either performed

1. by the bracketing technique during which two primary standards with components adjacent (max. ± 10 % rel.) to that of the gas mixture to be certified are used for calibration. Within these narrow boundaries the calibration function takes a quasi linear course and the high accuracy demanded for certification analyses can be met,

   or

2. according to DIN ISO 6143 „Gas analysis – Comparison method to determine the composition of calibration gas mixtures“ (ISO 6143:2001).

To demonstrate correctness of the result a control sample is analysed after each gas sample. The measured value of this control sample has to be found within the single measurement uncertainty of the certified composition.

Testing range

Components	Range of determinable molar fractions in mol / mol	Relative uncertainty in %
Methane (CH_4)	0.00001 - 0.99	0.8 - 0.1
Helium (He)	0.005 - 0.01	0.8 - 0.5
Oxygen (O_2)	0.005 - 0.2	0.8 - 0.5
Argon (Ar)	0.005 - 0,10	0.8 - 0.5
Nitrogen (N_2)	0.001 - 0.20	0,8 - 0.3
Carbon dioxide (CO_2)	0.00001 - 0.50	1.0 - 0.3
Carbon monoxide (CO)	0.00001 - 0.10	1.0 - 0.3
Hydrogen (H_2)	0.01 - 0.20	0.8 - 0.3
Ethene (C_2H_4)	0.005 - 0.01	0.8 - 0.5
Ethane (C_2H_6)	0.00005 - 0,20	1.0 - 0.3
Propene (C_3H_6)	0.005 - 0.01	0.8 - 0.5
Propane (C_3H_8)	0.003 - 0.035	1.0 - 0.3
n-Butane (C_4H_{10})	0.001 - 0.01	0.8 - 0.5
2-Methyl propane (C_4H_{10})	0.001 - 0.01	0.8 - 0.5
n-Pentane (C_5H_{12})	0.0001 - 0.001	1.0 - 0.8
2-Methyl butane (C_5H_{12})	0.0001 - 0.001	1.0 - 0.8
2,2-Dimethyl propane (C_5H_{12})	0.0001 - 0,001	1,0 - 0.8
n-Hexane (C_6H_{14})	0.00001 - 0.001	2.0 - 0.8
Benzene (C_6H_6)	0.0005 - 0.001	1.0 - 0.8
Nitrogen monoxide (NO)	0.0001 - 0.01	2.0 - 1.0
Dinitrogen oxide (N_2O)	0.00001 - 0.01	2.0 - 0.3
Sulfur hexafluoride (SF_6)	0.001 - 0.10	1.0 - 0.5

Instrumentation

Masses up to 20 kg with an uncertainty of ± 6 mg can be determined with this mechanical balance.

It is used to prepare primary gas standards gravimetrically (performed by successive filling of the mixture components and subsequent weighing) with the necessary accuracy.

Two to three of such primary standards of the same type - but with different concentrations of their mixture components - are used to calibrate the gas chromatograph in order to perform certification analysis that may result in a secondary reference gas mixture.

After this analysis has been performed successfully a certificate is issued for the secondary reference gas standard attesting the correctness of its gas composition and its direct traceability to BAM primary standards.

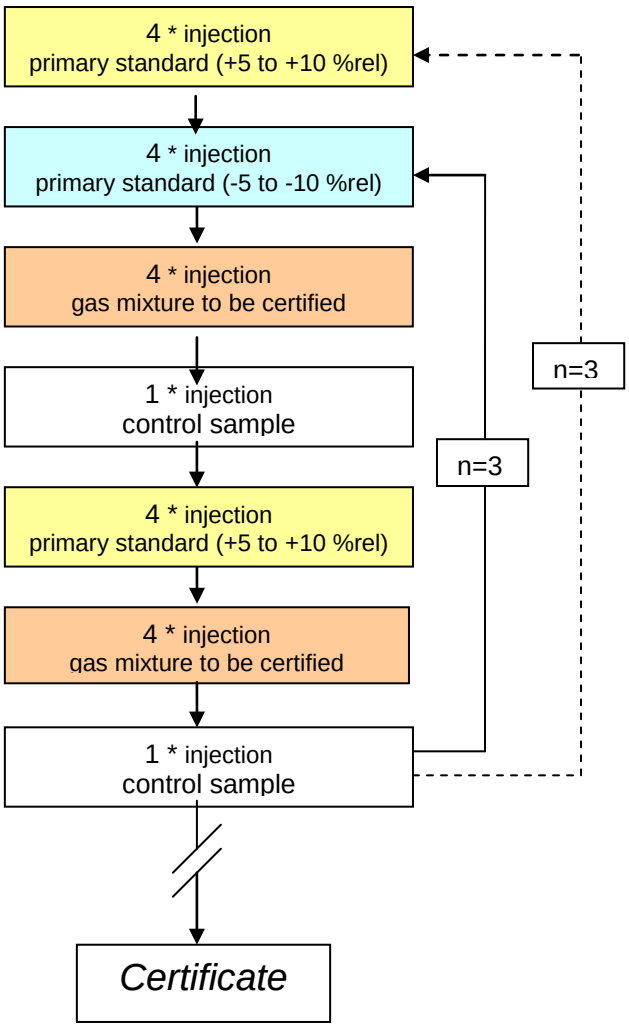
Course of a certification analysis

After the inner cycle (full line) has been performed three times the large circle (dotted line) is driven and is repeated twice, so that the inner cycle has been run nine times before the certification analysis is completed.

This means:

1. using the bracketing technique the gas mixture to be certified is measured 72 times and the primary standards at least 36 times each,
2. using the method according to DIN ISO 6143 the gas mixture to be certified is measured 108 times and the primary standards at least 36 times each.

1. Bracketing technique



2. DIN ISO 6143