

THE CERTIFICATION OF TEST GASES

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INTRODUCTION

The marked for calibration gases have increased considerably during the last years, partly because of better instrumental analysis methods.

The new methods:

- Have replaced manual methods of chemical analysis.
- Are used for control of the ambient air within and outside the chemical works.
- Will detect components which were not detectable some years ago (for instance sulfur containing components).
- Are more precise and selective.

The limit of uncertainty has been lowered, due to economic demands. It is thus of importance to:

- Obtain maximum production.
- Obtain the optimal efficiency.
- Calculate heat values.

A calibration gas is a homogeneous mixture, consisting of one or more components, qualitatively and quantitatively determined. The accuracy of concentration is given for each component.

A calibration gas mixture may contain as many as 20-25 components, depending on the necessity of accurate analysis.

All information concerning the actual mixture is given in the certificate of analysis. The certificate contains:

- The method of mixture preparation.
- Concentration (mole %, volume % or weight %).
- Relative uncertainty of the value of concentration, for each component $\Delta C/C$.
- The original pressure of the gas in the cylinder.
- Dew point temperature, which means at what temperature liquid is formed.
- Lowest utilization pressure.
- The period of time the mixture is guaranteed.

PRODUCTION OF CALIBRATION GASES

A stable calibration gas mixture in one selected type of cylinder, can be highly unstable if the mixture is filled into another cylinder with different type of material. By choosing unsuitable cylinder-material chemical reactions can occur between a single gas component and the cylinder-material, or the cylinder-material may act as a catalyst and the gas components may react.

Therefore the certification of a calibration gas is started by choosing the correct cylinder and cylinder valve. The cylinder material shall not react with any component, or the reaction shall be so slow that the concentration of the components shall be within the limits $\pm \Delta C$ in the period of guarantee. To achieve good results, it is necessary to passivate or treat the inner surface of the cylinder in special ways, - most important for corrosive components in the low ppm-range.

Note: The stability of a calibration gas mixture must be confirmed through time related stability tests of the calibration gas mixture in question.

CALCULATION OF PRODUCTION PARAMETRES

For mixtures containing condensable components, it is necessary to perform a dew point calculation.

Based on the calculated pressure with for instance dew point + 10 °C, 0 °C and other temperatures a filling procedure can be established.

Depending on requirement to accuracy in concentration, and the composition of the mixture, the filling method has to be defined and selected.

The filling methods are as described in the following ISO-documents.

ISO 6146 Gas Analysis-Calibration gas mixtures- Preparation by manometric methods

ISO 6144 Gas analysis - Preparation of calibration gas mixtures - static volumetric methods.

ISO 6142 Gas analysis - Preparation of calibration gas mixtures - weighing methods.

The weighing-method gives the possibility of preparation of calibration gas-mixtures for which the accuracy of the concentration of each component is better than 1%. The method is applicable only to gaseous components which do not react between themselves or with the cylinder-walls, and to totally vaporized components if they are condensable.

To produce low-concentration mixtures is it possible to make a single or multidilution.

Calibration gas mixtures can be produced by using NBS traceable "S" serie weights.

Gravimetric prepared calibration gas-mixtures are so-called primary calibration gas-mixtures, since it is directly related to the measurement of basic standards (such as mass, length, etc.)

Mixtures prepared by manometric method must be analyzed against a primary standard, and can be certified as a secondary calibration mixtures.

When producing calibration gas mixtures, it is only allowed to use high purity, preanalyzed starting components.

HOMOGENISATION OF A MIXTURE

Prior to use of a calibration gas-mixture, we have to be sure that the mixture is homogeneous. If a gas-cylinder after filling is allowed to be kept stationary and undisturbed, many weeks may expire before the calibration-gas is completely mixed.

The homogenization procedure is accelerated by the use of a mechanical cylinder roller.

Laboratory tests have shown when the gas-mixture is homogeneous, it will remain in the state, unless liquid is formed due to low temperature.

ERROR CALCULATION

The accuracy of the weighing-system is estimated, to calculate the error involved in the weighing operation.

The purity of liquids and gases, and their content of other components is taken into consideration (Example 1).

For the mixture previous shown, it should be possible to prepare accurate concentration better than 0,5% relative for all components (the result is based on use of the weighing system

previous shown:

1. Volland weight and s-series weights.
2. One skilled operator.
3. Preanalysed high purity gases and liquids.
4. Use of clean and polished gas cylinders.

CERTIFICATION

All calibration gas-mixtures are analyzed before certification. For the gravimetric prepared (not reactive) calibration gas mixture, this is done to make valid that the weighing system functions correctly.

For manometric or volumetric prepared blends, or calibration gas containing reactive components, the certificate has to be based on the results of analyses.

References

[1] Paper presented at the North Sea Flow Measurement Workshop, a workshop arranged by NFOGM & TUV-NEL

Note that this reference was not part of the original paper, but has been added subsequently to make the paper searchable in Google Scholar.