DYNAMIC DILUTION AS A TOOL FOR CALIBRATION OF CHEMILUMINESCENCE ANALYSERS

Michela Sega, Francesca Romana Penneccchi, Enrica Pessana, Francesca Rolle, Pier Giorgio Spazzini
Istituto Nazionale di Ricerca Metrologica - Strada delle Cacce 91 – 10135 Torino, Italy
E-mail: m.sega@inrim.it

1. Introduction

- Nitrogen oxides (NOx) are described by European Directive 2008/50/EC [1] as the sum of nitrogen monoxide (NO) and nitrogen dioxide (NO2). They are highly reactive gases due to their radical electronic configuration and can be involved in different atmospheric cycles as photochemical smog or acid rains. They have an important impact on human health as they can cause respiratory diseases. European legislation [2] requires continuous monitoring stations and prescribes the chemiluminescence as the reference measurement method.

- Chemiluminescence analysers must be calibrated with reference standards in order to assure metrological traceability. The use of dynamic dilution for preparing reference gas standards is valid alternative to gravimetry when dealing with gases either reactive or present at low mass fractions.

- At the INRIM, dynamic dilution, performed according to [3], is applied to the calibration of chemiluminescence analysers and an associated uncertainty budget is developed for all the process steps, from the calibration of the Mass Flow Controllers (MFCs) involved in the gas dilution to the calibration of the analysers.

3. Calibrated MFCs in use

- The flow provided by the calibrated MFC is a function of C and the nominal flow Q0:

  \[ Q_a = Q_{0\text{a}} C \]

- Uncertainty \(u(Q_0)\) and covariance \(u(Q_{0\text{a}}, Q_0)\) are calculated by the law of propagation of uncertainty (LPU).

4. Dynamic dilution

- Dynamic dilution: two gases are mixed together in order to reach any concentration \(\alpha\) starting from a concentrated gas mixture and a matrix gas. The obtained reference mixtures can be used for instrumental calibration. Another application is validation of a calibration curve with an independent mixture.

  \[ X_a = \frac{X_1 \cdot Q_{1a} + X_2 \cdot Q_{2a}}{Q_{1a} + Q_{2a}} \]

- \(X_a\): molar fraction of the analyte in the mixture.

- \(X_{1a}\): molar fraction of the analyte in the parent mixture.

- \(X_{2a}\): molar fraction of the analyte (impurity) in the diluent gas.

- \(Q_{1a}\): flow of the parent mixture supplied by MFC1.

- \(Q_{2a}\): flow of the diluent gas supplied by MFC2.

- Three different mixtures having molar fractions \(X_1, X_2\), and \(X_a\) are prepared. Uncertainty \(u(X_{0\text{a}})\) and covariance \(u(X_{0\text{a}}, X_a)\) are calculated by the LPU, taking into account uncertainty of the reference parent mixture, uncertainty of the flows provided by the MFCs in use and covariances between flows generated by the same MFC at different levels.

5. Chemiluminescence analyser calibration

- A Thermo Fisher Scientific 42i chemiluminescence analyser is calibrated for the analysis of both NO/N2 and NO2/SA (synthetic air) against the reference mixtures prepared by dynamic dilution containing molar fractions \(X_a\), \(X_1\), and \(X_2\) of the analyte, respectively.

- Weighted Total Least Squares (WTLS) regression [5] by means of the CCC-software: a straight line is fitted as analysis curve (reference molar fractions on the y axis and repeated readings on the x axis), taking into account the covariance matrices of both the input and the output. The analysis curve allows to easily employ the calibration output when the analyser is subsequently used in field: for each new reading, the instrument analysis curve provides a direct estimate of the molar fraction of an unknown sample under analysis, with an associated uncertainty.

- The analysis curves are validated by using independent gas mixtures of NO/N2 and of NO2/SA, respectively. Validation is successful when values of a known gas mixture and corresponding estimate provided by the calibrated analyser are consistent within the expanded uncertainties.

REFERENCES

[2] EN 14211:2012 Ambient air. Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence

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