DYNAMIC DILUTION AS A TOOL FOR CALIBRATION OF CHEMILUMINESCENCE ANALYSERS

Michela Sega, Francesca Romana Pennecchi, 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

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

1. Introduction

- **Nitrogen oxides** (NO_X) are described by European Directive 2008/50/EC [1] as the sum of nitrogen monoxide (NO) and nitrogen dioxide (NO_2). 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 monitoring 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 a 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 analyser.

2. MFCs calibration

- Three MKS **Mass Flow Controllers** (MFCs), with full scale range of 200, 500 and 2000 SCCM (fig. 1), respectively, are calibrated at the INRIM micro gas station against the primary flow reference standard MICROGAS (fig. 2).
- Characterization of the calibration coefficient *C* as a function of the nominal flow Q_N:

$$C = \alpha / Q_N + \beta + \gamma\, Q_N + \delta\, Q_N^2$$

- **Weighted Least Squares** (WLS) regression by means of the CCC-software [4] is applied to get the MFCs calibration function (fig. 3). Uncertainty contributions to *C* values: measurement repeatability and uncertainty associated with the MICROGAS.

Fig 1: INRIM MKS Mass Flow Controller


Fig 2: INRIM primary flow reference standard (MICROGAS)

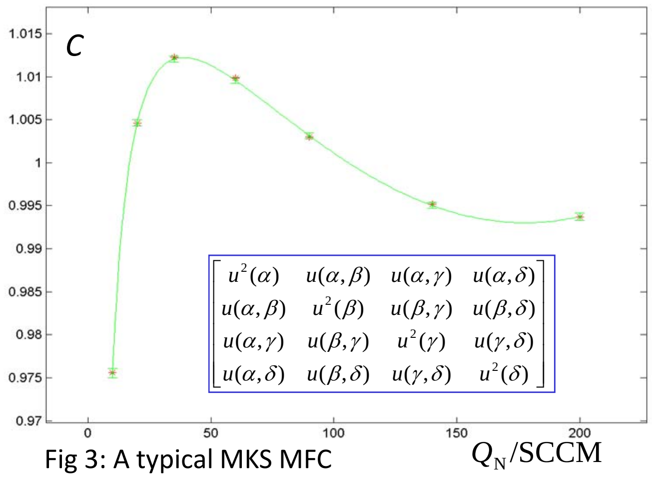

Fig 3: A typical MKS MFC calibration function

3. Calibrated MFCs in use

- The flow provided by the calibrated MCF is a function of *C* and the nominal flow Q_{Na}:

$$Q_a = Q_{Na}\, C_a$$

- Uncertainty $u(Q_{Na})$ and covariance $u(Q_{Na},Q_{Nb})$ 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 *a* 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.

$$X_2 = 0,\ u(X_2) = 0 \;\rightarrow\; X_a = \frac{X_1 \cdot Q_{1a}}{Q_{1a} + Q_{2a}}$$

- Three different mixtures having molar fractions X_a, X_b and X_c are prepared. Uncertainty $u(X_{a,b,c})$ and covariance $u(X_a,X_b)$ 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**.


Fig 4: reference gases


Fig 5: INRIM dynamic dilution system: MFCs and mixing chamber

5. Chemiluminescence analyser calibration

- A Thermo Fisher Scientific 42i **chemiluminescence analyser is calibrated for the analysis of both NO/N_2 and NO_2/SA** (synthetic air) against the reference mixtures prepared by dynamic dilution containing molar fractions X_a, X_b and X_c 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/N_2 and of NO_2/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

[1] European Directive 2008/50/EC On ambient air quality and cleaner air for Europe
[2] EN 14211:2012 Ambient air. Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence
[3] ISO 6145-7:2009 Gas analysis - Preparation of calibration gas mixtures using dynamic volumetric methods - Part 7: Thermal mass-flow controllers
[4] A. Malengo, F. Pennecchi, P. G. Spazzini, Calibration Curves Computing - Software for the evaluation of instrument calibration curves, Version 1.3, (2015), https://www.inrim.eu/research-development/quality-life/ccc-software (accessed on 2019.03.21)
[5] A. Malengo, F. Pennecchi, A weighted total least-squares algorithm for any fitting model with correlated variables, Metrologia 50 (2013) 654-662

ACKNOWLEDGEMENTS

The project 17NRM05 "Examples of Measurement Uncertainty Evaluation" leading to this application has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.