

INTEGRATE APPROACH TO THE CALIBRATION OF NITROGEN OXIDES ANALYSERS AND TO THE EVALUATION OF THEIR MEASUREMENT UNCERTAINTY

*Elena Amico di Meane*¹, *Davide Baroncini*², *Stefano Crispu*³, *Gian Carlo Piras*⁴, *Michela Segà*⁵

¹ Istituto Nazionale di Ricerca Metrologica, Torino, Italy, e.amicodimeane@inrim.it

² Bi-Lab S.r.l., Civitavecchia, Italy, bi-lab@bi-lab.it

³ Bi-Lab S.r.l., Civitavecchia, Italy, bi-lab@bi-lab.it

⁴ Bi-Lab S.r.l., Civitavecchia, Italy, bi-lab@bi-lab.it

⁵ Istituto Nazionale di Ricerca Metrologica, Torino, Italy, m.sega@inrim.it

Abstract – The present work describes the approach to evaluate in a metrological correct and exhaustive way the contribution of the several sources to the uncertainty related to the calibration of nitrogen oxides (NO_x) analysers, focusing in particular on non dispersive infrared (NDIR) analysers. In order to minimize the contribution due to the uncertainty on the composition of the calibration standards, gas mixtures of NO_x prepared with the gravimetric method are used. The performances of two different techniques, namely NDIR and chemiluminescence, are compared by analysing primary reference gas mixtures prepared at the Istituto Nazionale di Ricerca Metrologica (INRIM), having concentrations within 100 μmol·mol⁻¹ of NO_x.

Keywords: nitrogen oxides, NDIR spectroscopy, chemiluminescence

1. INTRODUCTION

Nitrogen oxides represent an important class of atmospheric pollutants; they derive from all combustion processes in which air is involved and their main emission sources in the ambient are road traffic and thermal plants. In the atmosphere several species of NO_x are present but about air pollution, the only reference term is the sum of the concentration of nitrogen monoxide (NO) and of nitrogen dioxide (NO₂), commonly indicated as NO_x. Recently anthropogenic emissions of NO_x have been increasing remarkably with the consequent enhance of their concentration, especially in urban areas. Because of the associated effect with acid rain, the presence in reaction mechanisms involving ozone and the irritant effect on human beings and on other organisms, NO_x are among the species for which the monitoring, according to the air quality laws in force [1], is foreseen. In particular, NO₂ is monitored in Italy, by the bodies in charge of the environmental monitoring (ISPRA, ARPA, APPA) [2], with chemiluminescence analysers calibrated with NO mixtures according to the European standards [3]. NO_x monitoring is usually carried out by analysers in continuous: the analytical technique commonly used is chemiluminescence but also NDIR spectroscopy is a valid alternative nowadays basically

used to monitor pollutants in chimney emissions. Threshold limits for NO_x emissions and the calibration periodicity for the analysers in continuous are referred in national standards [4]. Metrological traceability of such measurement results can be assured using, to calibrate analysers, traceable certificated gas mixtures i.e. produced by a primary metrological institute or by an accredited laboratory, or through the calibration of instruments performed by a competent body. At the Istituto Nazionale di Ricerca Metrologica (INRIM), a research line to prepare primary gas mixtures of NO_x has been started.

In this paper, the approach to evaluate in a metrological correct and exhaustive way the contribution of the several sources to the uncertainty budget [5] related in particular to the calibration of NO_x NDIR analysers is described. To minimize the contribution due to the uncertainty on the composition of the calibration standards, gravimetrically prepared gas mixtures of NO_x are used. Furthermore performances of such analysers are compared with those typical of chemiluminescence ones analysing primary reference gas mixtures prepared at INRIM, in the concentration range within 100 μmol·mol⁻¹ of NO_x.

2. PRIMARY MIXTURES OF NITROGEN OXIDES: ACTIVITY AT INRIM

INRIM carries on a research activity on the preparation with the gravimetric method of primary gas mixtures in pressurized cylinders. The realization of gas mixtures of carbon dioxide in matrices of synthetic air and of nitrogen (N₂) has been a consolidated activity since a few years [6] and has been validated by the successfully participation to international measurement comparisons [7]. Recently, due to the importance of NO_x among the environmental pollutants and to the national needs of metrological traceability, INRIM has extended the gravimetric preparation to mixtures of NO in matrix of N₂ in concentration of tens of μmol·mol⁻¹. At present, some mixtures are prepared by diluting a certified mixture (parent gas) with N₂; their concentration is determined according to the gravimetric data and the certified value of the parent

gases and then verified by using a chemiluminescence instrument (Thermo 42i). The first goal in time is the stability evaluation of such mixtures by repeating their analysis periodically. The preparation has just been extended also to NO₂ in matrix of synthetic air and the extension of the concentration ranges is foreseen.

3. CALIBRATION OF NDIR ANALYSERS FOR NO_X

The calibration of the instrument (analyser Maihac S710), property of Bi-Lab S.r.l (SIT accredited Centre n. 190), to measure NO_X via NDIR spectroscopy was carried out in laboratory following the procedure accredited by SIT, the Italian accreditation body for calibration laboratories. Metrological traceability of the measurement results was assured using certified reference gas mixtures purchased from an accredited centre which were also used to prepare mixtures at lower concentrations by dynamic dilution under traceable conditions. In Fig. 1, a typical calibration curve of the analyser is shown: the concentration C , in $\mu\text{mol}\cdot\text{mol}^{-1}$, of the calibration mixtures obtained by dynamic dilution is represented on x -axis; the corresponding analyser reading, in mA, is represented on the y -axis.

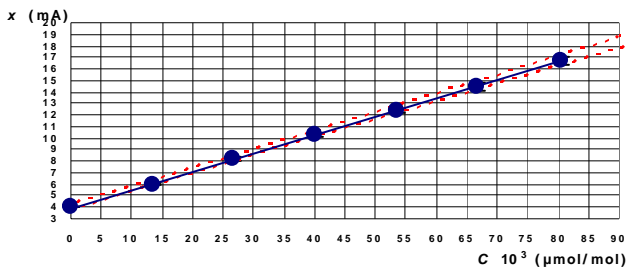


Fig. 1. A typical calibration curve of the NDIR analyser

The uncertainty budget related to the calibration of the analyser is reported in Table 1.

The combined standard uncertainty is calculated, according to (1), combining in a quadratic way each contribute due to standard deviations of calibration, u_{cal} ,

repeatability, u_r , dynamic dilution, u_d , and instrumental uncertainty, u_i , shown in the columns of Table 1.

$$u_c = \sqrt{u_{\text{cal}}^2 + u_r^2 + u_d^2 + u_i^2} \quad (1)$$

The value of the expanded uncertainty U , for a confidence level of about 95%, is calculated multiplying the value of the combined standard uncertainty by a covering factor k equal to 2.

To validate the calibration curve, a not diluted certified mixture was analysed. The results are presented in Fig. 2: the blue point represents the certified concentration, the green point is the concentration analytically determined by Bi-Lab with the calibrated analyser. The expanded uncertainty bands, for a confidence level of about 95%, are indicated. The two values are compatible within the declared uncertainties.

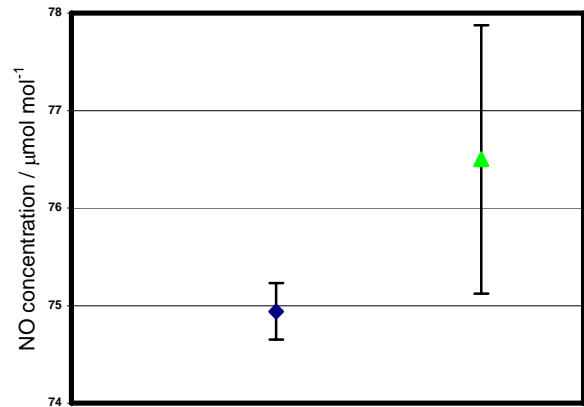


Fig. 2. NDIR analysis of the SIT certified gas mixture with NO concentration of $74,94 \mu\text{mol}\cdot\text{mol}^{-1}$ in N₂

Table 1. Uncertainty budget for the calibration of the NO_X NDIR analyser.

Concentration		Calibration u_{cal}	Repeatability u_r	Dynamic dilution u_d	Instrumental u_i	Expanded uncertainty U ($\mu\text{mol}\cdot\text{mol}^{-1}$)	Relative expanded uncertainty (%)
C_i (%v/v)	C_i ($\mu\text{mol}\cdot\text{mol}^{-1}$)						
0,001	13,354	0,524	0,077	0,071	0,007	1,069	8,0%
0,003	26,732	0,501	0,154	0,142	0,013	1,086	4,1%
0,004	40,103	0,493	0,230	0,213	0,020	1,170	2,9%
0,005	53,481	0,501	0,307	0,283	0,027	1,306	2,4%
0,007	66,834	0,522	0,384	0,354	0,033	1,479	2,2%
0,008	80,421	0,561	0,462	0,426	0,040	1,687	2,1%

4. CALIBRATION OF CHEMILUMINESCENCE ANALYSERS FOR NO_x

The calibration of the chemiluminescence analyser used at INRIM was carried out using three certified mixtures of NO_x. According to the procedure followed, at the beginning the zero and the span (usually a concentration at about the 80% of the measurement range) were forced. Then the analysis of the three calibration mixtures, in order of increasing concentration, was carried out recording for each one three readings, made independent one from the others by ambient air analysis between two subsequent readings. At the end of the sequence of measurements, in order to verify the analyser consistency, the readings of span and zero are checked again. In Fig. 3, a typical correction curve with its bands of expanded uncertainty, corresponding to a confidence level of about 95%, is depicted. In such way correction values, and their respective uncertainties, can be applied in correspondence of an input concentration to the analyser.

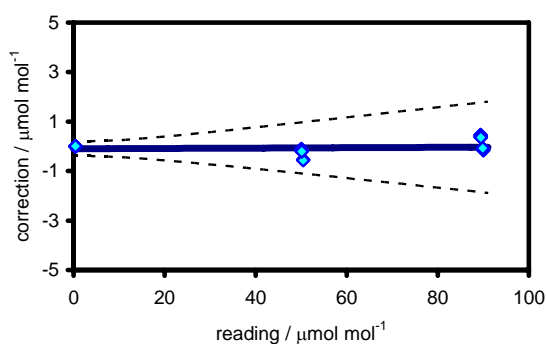


Fig. 3. Correction curve of the INRIM chemiluminescence analyser.

The uncertainty contributions, taken into account in the statistical-mathematic elaboration of the data by means of the Weighed Least Squares, are: the resolution of the instrument, its repeatability, the uncertainty on the composition of the calibration mixtures, the non perfect fitting of the model equation to the experimental data i.e. the model uncertainty.

5. COMPARISONS OF THE PERFORMANCES OF THE TWO TECHNIQUES

Mixtures of NO_x gravimetrically prepared at INRIM were analysed with the above analysers. Whilst Bi-Lab carried out the analysis of the mixtures after having calibrated the analyser, at INRIM to take into account possible drift phenomena of the instrument, the determination of the concentration of the cylinders in study was carried out during the analyser calibration itself. In order to do this, three certified reference mixtures, i.e. the calibration standards, spanned in a concentration range including the concentration of the INRIM mixtures, were used and the analysis of such mixtures was carried out in

between two calibration standards. The results obtained analysing the two gas mixtures are shown in Fig. 4 and 5, where the blue points represent the gravimetric concentration, the pink points indicate the concentration obtained at INRIM via chemiluminescence analysis and green points the concentration determined at Bi-Lab by NDIR spectroscopy. For all the concentration values, the expanded uncertainty bands for a confidence level of about 95% are indicated.

The analysis of the data shows the presence of a bias between the two techniques that however are both compatible, within the declared expanded uncertainties, with the corresponding gravimetric value. A bias in the same direction, still with values compatible within the declared uncertainties, was highlighted also in Fig. 2. In Fig. 4 and 5, the high uncertainty associated to the gravimetric value (the blue one) is due to the contribution of the certified gas mixture, used as parent gas, equal to 2% (as expanded uncertainty with $k=2$).

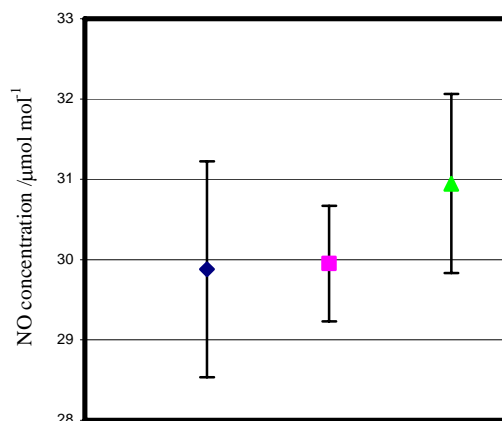


Fig. 4. Analysis of the INRIM primary gas mixture with a NO concentration of 29,88 $\mu\text{mol}\cdot\text{mol}^{-1}$ in N₂.

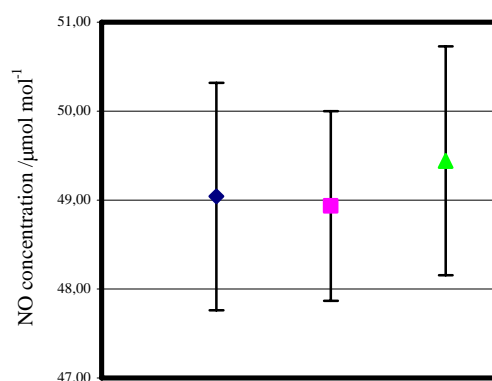


Fig. 5. Analysis of the INRIM primary gas mixture with a NO concentration of 49,04 $\mu\text{mol}\cdot\text{mol}^{-1}$ in N₂.

About the analytical techniques, even though the calibration procedures followed are different, the expanded uncertainties are of the same order of magnitude.

6. CONCLUSIONS

Further studies are needed to investigate the causes of the bias between the two techniques results. The analysis of certified gas mixtures with lower uncertainty, for example, could give more significant information.

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