

NITROGEN OXIDES ANALYSIS: INRIM ACTIVITY

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Abstract – The monitoring of nitrogen oxides (NO_x) is prescribed by European directives by means of chemiluminescence. This paper presents the activity carried out at INRiM for the preparation and analysis of NO_x mixtures, with the aim of establishing metrological traceability. Together with the use of chemiluminescence, the application of Fourier Transform Infrared (FTIR) spectroscopy is also under investigation as it can allow the identification of some impurities occurring in the gas mixtures which cannot be discriminated by chemiluminescence.

Keywords: nitrogen oxides, chemiluminescence, FTIR, metrological traceability.

1. INTRODUCTION

Nitrogen oxides (NO_x) are a class of highly reactive gases: most of them are emitted in the form of nitric oxide (NO) and nitrogen dioxide (NO₂). Nitrogen oxides are formed in fuel combustion processes at high temperatures, as occurs in automobile engine and they are atmospheric pollutants having health and environmental impact. One of the most important pollution problems is the photochemical smog [1]: nitrogen oxides act like catalysts in photochemical reaction cycles which generate ozone (O₃) in urban areas at tropospheric level. The European legislation [2] prescribes chemiluminescence as the reference method for the analysis of NO_x monitoring as described also in [3]. Other methods are allowed if the equivalence of the results can be proved. Chemiluminescence analysers must be calibrated with gaseous reference materials in order to establish metrological traceability. Primary gas standards can be prepared by means of gravimetry, which is a primary method [4].

This paper describes the activity under development at Istituto Nazionale di Ricerca Metrologica (INRiM) concerning the preparation of NO_x gravimetric mixtures and their analysis by means of Fourier Transform Infrared spectroscopy (FTIR), as a new method to detect NO_x under metrological conditions.

2. EXPERIMENTAL

INRiM activity concerning NO_x consists in the preparation of primary reference gas mixtures by gravimetry and their subsequent analysis by chemiluminescence in order both to validate the preparation process and to

investigate the stability of the mixtures. Recently, the attention has been devoted to the application of Fourier Transform Infrared spectroscopy (FTIR) for the analysis of NO_x due to its versatility and sensitivity.

2.1. Mixtures preparation

A facility for the gravimetric preparation of reference gas mixtures in cylinders is in place at INRiM [5]. Gravimetry is a primary method and its application for the preparation of gas mixtures is fully described in the ISO International Standard 6142 [4].

The first step of the procedure consists in the conditioning of the cylinder in order to promote the removal of interfering species, even adsorbed on the cylinder internal walls. The conditioning process is based on repeated cycles in which the cylinder is firstly evacuated and heated, then filled with the proper matrix gas and rolled for several hours.

After the conditioning, the cylinder is ready to be filled with the gases to be used for the mixture preparation, which are introduced into the cylinder in subsequent steps, one for each component. Each preparation step is accompanied by a high accuracy weighing to determine the masses of the gases introduced into the cylinder. The weighing process is carried out on a Mettler Toledo PR-10003 mass comparator, following the double substitution scheme. The metrological traceability is guaranteed by the use of calibrated mass standards.

In parallel to gravimetry, another primary method is under development at INRiM, based on calibrated mass flow controllers for the production of gaseous mixtures by dynamic dilution. This is a complementary method, as it can be applied to challenging mixtures either at low concentrations or containing reactive gases.

The preparation of reference gas mixtures of NO₂ by the gravimetric method is carried out starting from parent mixtures of NO in nitrogen. NO is quantitatively oxidised to NO₂ by adding oxygen (O₂). The gravimetrically prepared mixtures were employed to establish a response curve for both the chemiluminescence and the FTIR analysers. Some studies on possible interfering species were carried out by FTIR spectroscopy.

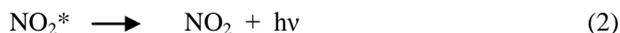
2.2. Chemiluminescence

Chemiluminescence is a technique used for the analysis of NO_x. It is widely used due to its selectivity towards oxygenated nitrogen compounds. The measurement process

consists of two steps: first, the amount of NO is quantified by means of a chemical reaction (1) in which NO reacts with O₃ generating the electronically excited species NO₂*.



Afterwards NO₂* releases a photon (hν), returning to the ground state NO₂, and the generated photons are counted by a photomultiplier as in reaction (2).



In the second step NO_x reacts with a molybdenum-based catalyser, which converts NO_x into NO (as reaction 3), starting again the reaction (1).



The total amount of NO₂ is calculated by difference between NO_x and NO (4).

$$\text{NO}_2 = \text{NO}_x - \text{NO} \quad (4)$$

A Thermo Fisher Scientific 42i chemiluminescence analyser was employed to analyse and validate several NO_x mixtures after their gravimetric preparation and to carry out stability studies over the short and the long term.

Despite of the selectivity of chemiluminescence, the study of the behaviour of these mixtures highlighted a non-linear dependence of the analyser response to the presence of O₂ in the matrix. As a consequence, NO₂ mixtures, which are prepared from NO in a synthetic air matrix, cannot be correctly analysed if the instrument had been previously calibrated with mixtures containing different amounts of O₂ in the matrix. In addition, the chemiluminescence analyser cannot discriminate among different oxygenated species, hence other molecules different from NO₂ and NO might be detected as NO_x.

The occurrence of these phenomena led to investigate in INRiM an alternative techniques as FTIR.

2.3 FTIR

Infrared-based techniques are sensitive to the functional groups of the molecules, as the infrared radiation is absorbed at specific frequencies characteristic of the group. The obtained spectra can be used for the molecule identification by comparison with libraries. A criterion for a IR radiation absorption is a net change in the dipole moment of the molecule as it bonds vibrate or rotate: this means that IR is non-sensitive towards homonuclear species, as O₂ and nitrogen (N₂). In addition, in the case of small molecules having few functional groups, this technique can be used also for the species quantification.

A FTIR instrument is equipped with a Michelson interferometer: a source emits infrared light, the light is collimated and arrives at a beam splitter that reflects half of the beam (and half is transmitted). The reflected beam is sent towards two mirrors: one is fixed and one can move. The mirrors reflect the beam towards the beamsplitter where the two beams give an interference that can be constructive

or destructive depending on the movement of the mirror. The difference in optical path length between the two arms to the interferometer is known as the retardation. An interferogram is obtained by varying the retardation and recording the signal from the detector corresponding to various retardation values.

Half of the beam now passes through the beam splitter arriving at the sample compartment and then at the detector. When a sample is present the background interferogram is modulated by the presence of absorption bands in the sample.

The Fourier Transform is a mathematical function that transforms an interferogram in the time domain into a spectrum in the frequency domain.

The FTIR used at INRiM is a Thermo Fisher Nicolet iS50 which is equipped with two different gas cells: a Gemini Mars gas cell with path length of 6.4 m and a Thermo Fisher Scientific gas cell, having a path length of 10 m.

3. RESULTS AND DISCUSSION

3.1 Comparison between chemiluminescence and FTIR

In order to investigate the behavior of FTIR as a possible substitute of chemiluminescence, some analyses were carried out to assess the linearity of the response in the range between 1 and 15 μmol/mol of NO₂. Reference gas mixtures of NO₂ in synthetic air at different molar fractions (1, 5, 10 and 15 μmol/mol) were analysed in static condition. Each measurement was repeated 3 times and the spectra perfectly overlapped, thus indicating a good repeatability. Fig. 1 shows the peak at 1628 cm⁻¹, which is the maximum of the absorbance of NO₂, at different mass fractions. During the measurements, particular care at the background stability should be taken, due to the absorbance of H₂O that occurs at the same wavelength of NO₂.

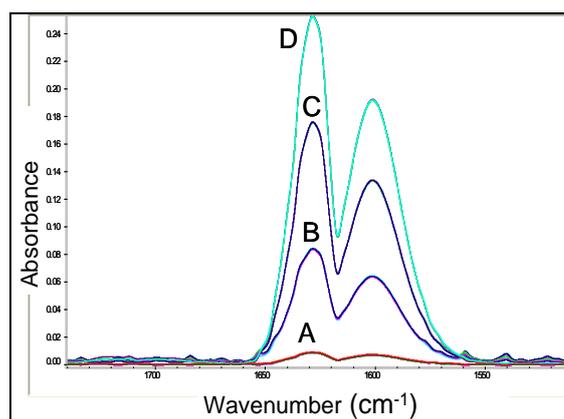


Fig. 1: NO₂ peaks at 1628 cm⁻¹, for increasing molar fractions: A) 1, B) 5, C) 10, and D) 15 μmol/mol.

The same mixtures were then analysed by chemiluminescence. Fig. 2 shows the response curves for the two analysers.

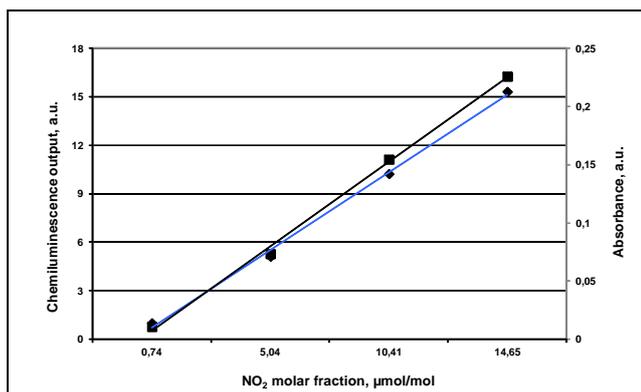


Fig. 2: Response curves of chemiluminescence (\blacklozenge , $R^2 = 0.9975$) and FTIR (\blacksquare , $R^2 = 0.9977$) for NO_2 in synthetic air in the range (1-15) $\mu\text{mol/mol}$.

The results reported in fig. 2 show that the linear model fits to both chemiluminescence and FTIR in the NO_2 molar fraction range between 1 and 15 $\mu\text{mol/mol}$. Due to this linear behaviour there is the possibility, in principle, of doing further extrapolation also at lower concentration values.

The calibration curve was also used to evaluate the instrument response in gas mixtures with different amounts of oxygen in matrix. In comparison with the chemiluminescence analyser, the FTIR spectrometer seems to be non sensitive toward the oxygen composition in matrix.

3.2. Impurity identification by FTIR

As previously said, a drawback of chemiluminescence is the impossibility to distinguish oxygenated nitrogen species, hence other molecules different from NO_2 and NO might be detected as NO_x , thus leading to a potential incorrect value assignment of NO and NO_2 molar fractions.

FTIR, due to its capability of detecting the different molecules, can help in assessing the presence of impurities in the mixtures and also in obtaining information on the ageing of the mixtures contained in cylinders.

A preliminary analysis of some gas mixtures of NO_2 at mass fractions of some $\mu\text{mol/mol}$ in synthetic air was carried out by FTIR, equipped with the Gemini Mars gas cell, and showed the presence of nitric acid (HNO_3), identified by comparison with literature data [6-8]. The HNO_3 peak falls off after flushing the gas mixtures for some minutes as shown in fig. 3, until its complete disappearance. This behaviour could be due to the stratification of HNO_3 close to the cylinder valve, as suggested in [8]. The presence of the nitric acid and the stratification of the gas, means that a particular care must be taken when handling gas cylinders to avoid stratifications that would lead to inconsistent results.

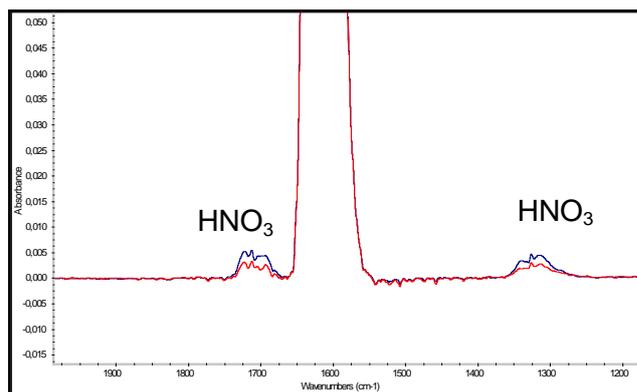


Fig. 3: Evidence of nitric acid presence in gas mixtures of NO_2 in synthetic air: — first spectrum of the day ; — spectrum after some minutes of gas flushing.

A different instrumental set up was employed to carry out further measurements. The FTIR, equipped with the Thermo Fisher Scientific gas cell, was sealed in a glove box filled with N_2 , in order to minimise the interferences due to the external environment and to obtain a stable background. A preliminary set of analyses was carried out aiming at identifying the wavelengths in which typical occurring species may absorb, in order to proceed with the impurities identification. At this purpose, mixtures of NO in N_2 , NH_3 in N_2 and a CO_2 mixture in synthetic air (at about 100 $\mu\text{mol/mol}$) were analysed and the results are shown in fig. 4.

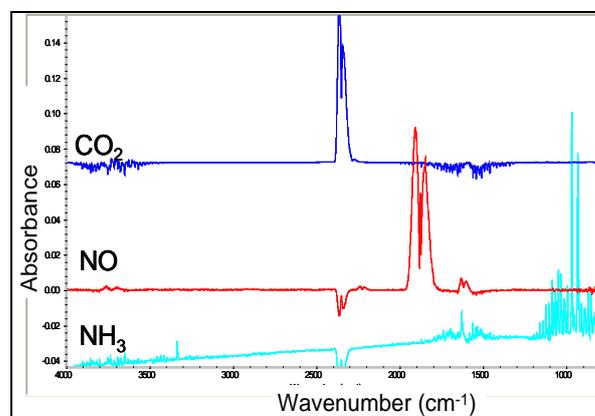


Fig. 4: FTIR spectra for NO in N_2 , NH_3 in N_2 and CO_2 in synthetic air (spectra are not scaled).

Considering that the gravimetric preparation of NO_2 gas mixtures is carried out starting from NO mixtures used as parent mixtures, some investigations were performed in order to assess the presence of possible impurities also in latter mixtures. Two different gas mixtures of NO in N_2 , having similar concentration in the range 5-6 $\mu\text{mol/mol}$ but different ages (a two-year old one and a freshly prepared one) were studied to identify potential ageing phenomena. The analysis of this two gas mixtures with chemiluminescence had previously lead to unexpected inconsistent results. Fig. 5 shows that the older gas mixture contains nitrogen protoxide; the newest one, instead, does not show this impurity. This might explain the

chemiluminescence inconsistency, as the impurity is not discriminated and it is considered as NO_x .

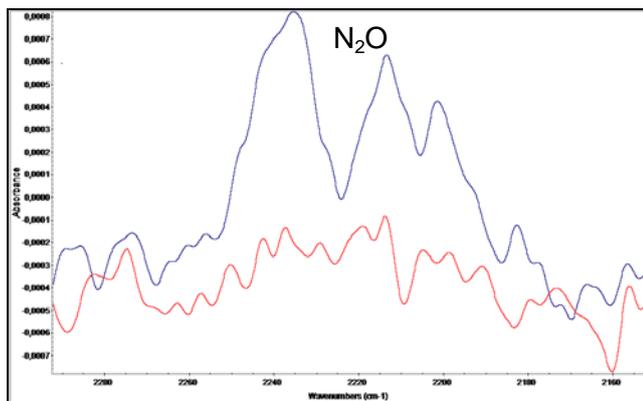


Fig. 5: Peak of nitrogen protoxide in a two-year old mixture of NO in N_2 (blu line) compared with a younger gas mixture (red line).

The occurrence of N_2O was determined also in a more concentrated gas mixture, having NO at a nominal concentration of $100 \mu\text{mol/mol}$, showing N_2O together with some NO_2 impurities; instead no HNO_3 was detected. This gas mixture was used as a parent gas to prepare the oldest of the two gas mixtures investigated. The presence of nitrogen protoxide represents a double problem: if it is formed inside the gas cylinder, it leads to an incorrect response by chemiluminescence [9], but when the formation occurs in the parent gas it leads to an incorrect concentration assignment by gravimetry. In this case, only the verification by FTIR can avoid gross mistakes.

The potentiality of FTIR can be used also to verify the formation of the dimer N_2O_4 from NO_2 , which cannot be detected by chemiluminescence. At this purpose, a gas mixture of NO_2 in synthetic air at $100 \mu\text{mol/mol}$ was stored in the FTIR gas cell for 4 hours at 1 atm. The recorded spectra showed the slow decreasing in the peak of NO_2 and the increasing of a the peak around 1263 cm^{-1} , as shown in fig. 6.

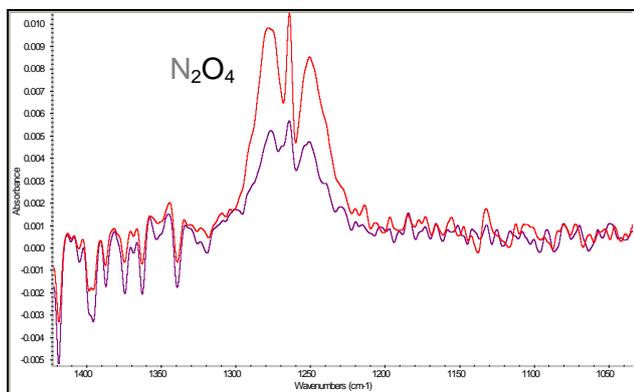


Fig 6: Formation of N_2O_4 peak in a mixture of NO_2 in synthetic air at $100 \mu\text{mol/mol}$, stored in the FTIR gas cell, after 4 hours.

The formation of HNO_3 was excluded by comparing it with a reference HNO_3 spectrum as shown in fig. 7 [7].

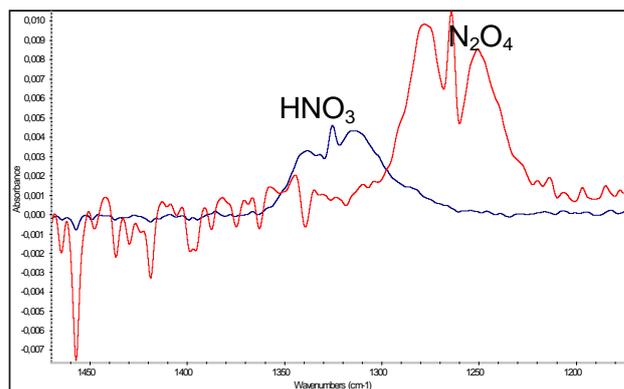


Fig 7: Comparison of N_2O_4 peak with a HNO_3 reference spectrum [7].

Then the wavelength numbers were compared with literature data [10-14] regarding the N_2O_4 peaks of PQR branches around 1263 cm^{-1} ; another branch in our spectra is partially visible at about 1750 cm^{-1} , thus confirming the identification.

4. CONCLUSIONS

This paper describes the metrological approach for the analysis of NO_x developed at INRiM.

NO_x mixtures are prepared by means of the gravimetric method, which is a primary method. Chemiluminescence, being the reference method, is used for the validation and quantification of the mixtures and for stability studies, but the application of FTIR spectroscopy is also under investigation. One of the major advantages of FTIR is the possibility of identifying some impurities occurring in the gas mixtures which cannot be discriminated by chemiluminescence. A particular care was devoted to the identification of impurities in the mixtures an N_2O in NO and HNO_3 and N_2O_4 in NO_2 . Many of these impurities are nitrogen oxygenated compound that can lead to an incorrect calibration and quantification of NO_x by chemiluminescence. Further activities will be devoted to the quantification of these impurities.

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