



Application Note AN M170

Searching for the needle in the haystack: Quantification of NO, NO₂ and N₂O in exhaust streams

Introduction

Gaseous nitrogen oxides such as NO and NO₂ (NO_x) emerge as common and important reactants, especially in the industrial, chemical, and automotive sector. For process control, quality assurance, or scientific research dedicated analysis methods are required to accurately monitor the concentration of nitrogen oxides continuously and in real-time. Gas analyzers based on Fourier Transform Infrared (FT-IR) spectroscopy fulfill these requirements and are used for the quantification of gaseous compounds in a broad field of application. Spectroscopic quantification limits in the low ppm and often even in the low ppb range are achievable for a huge class of gas compounds.

However, in the case of gas mixtures, the situation might be different and quantification limits might increase significantly due to overlapping IR bands and the associated cross-sensitivity limit. The quantification limits are determined by the environmental conditions and must not be confused with the spectroscopic detection limit. Hence, the quantification limits in IR spectroscopy are determined by a) the instrument noise, b) the cross-sensitivity, or c) a combination of both. This is especially the case for NO and NO₂: in one of the most prominent application, the quantification of nitrous gases within exhaust streams, highly concentrated H₂O acts as a major interferent causing elevated NO_x quantification limits due to spectral interference.

| Keywords | Instrumentation and Software |
|---------------|------------------------------|
| Infrared | OMEGA 5 |
| Gas Analytics | OPUS GA |
| Nitrous Gases | Spectral Databases of Gases |

To demonstrate the feasibility of the quantification of lowly concentrated nitrogen oxides in water vapor and to elucidate the influence of interferents on the quantification limits, FT-IR measurements of nitrogen oxides in highly concentrated water vapor were performed.

Methods and Results

Simulations

Simulations of a gas mixture consisting of NO, NO₂, and N₂O in dry nitrogen gas as well as in nitrogen with additionally 10% H₂O were performed to identify the most suitable spectral regions for quantification and to determine the cross-sensitivity limits.

As shown in Figure 1, the main absorption lines of NO at about 1900 cm⁻¹ and of NO₂ at about 1600 cm⁻¹ are strongly interfering with the absorption lines of H₂O. Hence, quantification of these compounds in a gas mixture with high water concentrations is challenging.

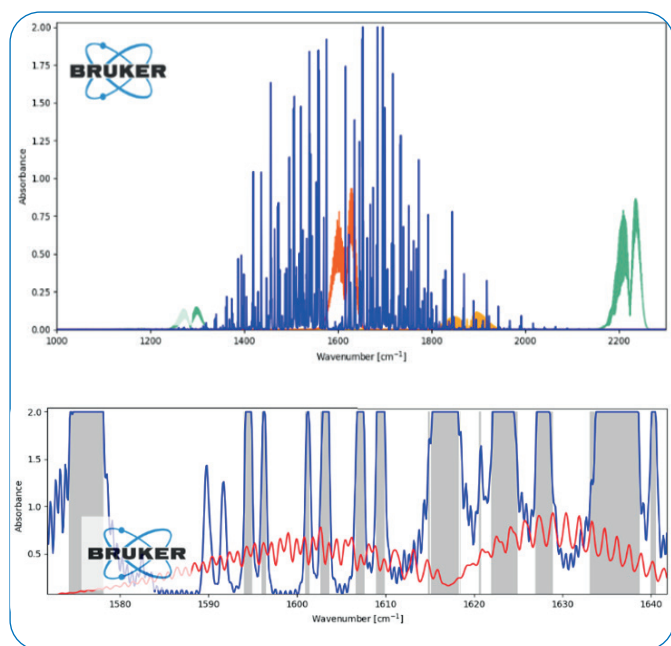


Figure 1: Simulated IR spectra of two gas mixtures. Top: 1000 ppm H₂O (blue) and 100 ppm NO (orange), NO₂ (red), and N₂O (green). Bottom: 10 vol% H₂O and 100 ppm NO₂. The high water concentration limits the applicable spectral windows due to saturation (grey areas).

With 10 vol% H₂O being present, the applicable spectral regions for quantification of NO and NO₂ are strongly limited because the absorptions of the compounds are strongly interfered by the H₂O absorptions in the region from 1350 to 1950 cm⁻¹, as shown in Figure 1. At these high H₂O concentrations, the absorptions of H₂O even lead to total absorption over a large spectral range leaving only a sensible spectral window of about 5 cm⁻¹ for the quantification of NO and NO₂. The simulations suggest that the high cross-sensitivity limits lead to high quantification limits.

Without any H₂O in the gas mixture, NO, NO₂, and N₂O can be quantified in the sup-ppm range with the Gas Analyzer OMEGA 5.

Experiments

FT-IR measurements were conducted using the Bruker Gas Analyzer OMEGA 5 equipped with a thermoelectrically (TE) cooled MCT detector with a spectral resolution of 1.0 cm⁻¹ and a gas cell with an optical pathlength of 5 m. About every four seconds, a time-averaged IR spectrum of four single IR spectra was computed.

Gas mixtures consisting of a constant H₂O and variable NO, NO₂, and N₂O concentrations were guided through the gas cell of the spectrometer. Measurements with 10 vol% gaseous H₂O were performed to verify the simulations. The actual concentrations of the nitrogen oxides were gradually decreased by a mass flow controller to determine the quantification limits empirically. To avoid condensation of H₂O, the transfer lines that were used to guide the gas into the gas cell as well as the gas cell itself were heated to 180° C. Detection and quantification of the gases were achieved using the calibration-free software OPUS GA. For identification and quantification of the single constituents and for considering spectral interferences, reference IR spectra were analyzed using the Bruker spectral library B-GAS-LIBRARY.

Despite the strong absorption of water, quantification limits of below 30 ppm are achievable for nitrogen oxides (Table 1). For N₂O, a quantification limit of about 1 ppm could be reached since the absorption of N₂O is well differentiable from the weak absorption lines of H₂O which also do not lead to total absorption in the spectral range used for quantification (see Figure 1).

| Gas | Limit of Quantification [ppm] |
|------------------|-------------------------------|
| NO | 40 |
| NO ₂ | 30 |
| N ₂ O | 1 |

Table 1: Empirically obtained quantification limits employing the Gas Analyzer OMEGA 5 in the presence of 10 vol% H₂O in the target gas. The high concentration of water leads to elevated NO_x quantification limits due to spectral interference.

Summary and Conclusion

Nitrogen oxides are important reactants whose concentrations need to be monitored in many different applications. However, the determination of the NO_x concentrations is challenging due to spectral interference with strong IR bands of interferents and possible total absorption.

The Gas Analyzer OMEGA 5 enables the quantification of lowly concentrated NO_x of only 30 ppm even in the presence of several percent of H₂O. Even lower concentrations of NO_x below 20 ppm can be quantified using the high-performance gas analyzer MATRIX-MG5 due to a spectral resolution of below 0.5 cm⁻¹.

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