

Effect of Matrix Gas Variations on NO₂ Measurements by a PEMS Device for Real Driving Emissions Tests

Mi Eon Kim, Henning Bohlius, Volker Ebert, Jarvis Nwaboh
 Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany,
 Jarvis.Nwaboh@ptb.de

Summary:

For legally required Real Driving Emissions measurements, the quantification of NO₂ amount fractions is performed using Portable Emission Measurement System (PEMS). Although a PEMS must be accurately calibrated, the typical NO₂ calibration gas matrix composition (e.g. synthetic air) differs significantly to that of car exhaust gas. This study shows that a change in matrix composition can cause considerable deviations in PEMS NO₂ results. We found a slope difference of up to about 30 % between measurements performed in synthetic air and a matrix gas mimicking real exhaust gas composition.

Keywords: Nitrogen dioxide (NO₂), Gas matrix effect, Portable emission measurement system (PEMS), Calibration, Optical gas standards (OGS).

Introduction

Nitrogen dioxide (NO₂), one of the major species of nitrogen oxide (NO_x), is a reactive gas and an air pollutant that has hazardous effects on human health. In addition to its health effects, NO₂ further contributes to degradation of air quality as it is a precursor of secondary pollutants [1]. The European Commission has defined rigid emission limits for combustion engine vehicles. NO_x is one of the key pollutant groups under the emission regulation. To overcome the discrepancies between laboratory tests and real vehicle operation, the concept of real driving emission (RDE) measurements was developed and adopted in the European vehicle regulations. RDE measurements should be performed during realistic road emission tests using portable emission measurement system (PEMS) devices [2]. In the last years, there has been a strong need to calibrate PEMS devices using reference gases that better reflect the real application in particular the real exhaust gas composition. Here, the real exhaust gas composition includes additional molecules such as NO, CO, CO₂ and H₂O, while the common components N₂ and O₂ appear in largely different amount fractions. However, for NO₂, PEMS are typically still calibrated using NO₂ in oversimplified gas matrices such as nitrogen or synthetic air, which leads to matrix composition dependent calibration deviations compared to real exhaust gas. Hence, it is important to determine which effect the different matrix gas composition has on the calibration accuracy of the PEMS. Due to the complex composition of real exhaust gases, there has also been a strong necessity to investigate whether

calibration of PEMS devices in nitrogen or synthetic air gas matrix produces valid results when measuring in the real-world application i.e. car exhaust gas analysis. Therefore, in this study, we focused on the investigation of matrix gas effects on the performance of a commercial PEMS device that was calibrated using NO₂ in synthetic air. This is done by measuring NO₂ amount fractions in various gas matrix compositions. The results from the PEMS device are compared to those of a reference device at PTB for a cross check and validation of the observed effects.

Method

Fig. 1 shows a schematic diagram of the setup used for NO₂ measurements. The International System of Units (SI) – traceable static gas reference materials prepared in cylinders or dynamically prepared gas mixtures were used to interrogate the PEMS device. The dynamic gas mixtures are prepared via dilution of the static gas mixtures. In parallel with the PEMS device, there is a reference device (Non-Dispersive Ultraviolet spectrometer) that also monitors the NO₂ amount fraction (concentration) for cross check and validation of the measured effects. Matrix effects on the response of the reference device were previously validated via a comparison with the PTB direct tunable diode laser absorption spectroscopy (dTDLAS) instrument [3] and found to be insignificant. The dTDLAS instrument is being developed to be operated as an optical gas standard (OGS) and fully accounts for matrix gas effects via the fitting of the absorbance data [3]. The work with the dTDLAS instrument is planned for a separate publication.

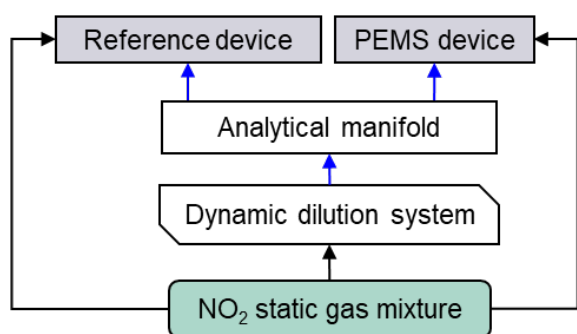


Fig. 1. Schematic diagram of the setup used for NO_2 measurements.

By means of the dynamically generated gas mixtures as shown in Fig. 1, multiple NO_2 amount fraction steps can be measured by both the PEMS device and the reference instrument simultaneously. For the matrix effect studies, dynamically prepared gas mixtures with NO_2 in different matrices, e.g. (a) synthetic air (79 % N_2 , 21 % O_2), (b) synthetic air plus argon (78 % N_2 , 21 % O_2 , 1 % Ar), and (c) 85 % N_2 plus 0.5 % O_2 , 0.2 % NO , 0.02 % C_3H_8 , 0.5 % CO and 14 % CO_2 were used. For all gas matrices, the H_2O level as specified by the producer was well below $2 \mu\text{molmol}^{-1}$. The multi-component matrix (c) was prepared to mimic real car exhaust gas composition.

Results

As shown in Fig. 2, the results from the PEMS device are compared to those from the reference device by plotting the measured NO_2 amount fraction as a function of dynamically generated NO_2 amount fraction values. For the PEMS and reference instrument, a good linearity is derived for the NO_2 amount fraction results for the difference as matrices as presented in Fig. 2. For the reference device, the slope values are almost identical (within ± 0.01) for matrix a, b and c, i.e. 1.09, 1.08 and 1.09, respectively. However, for the PEMS device, the slope values for the different matrix compositions a, b, and c vary up to about 30 % (i.e. 0.98, 0.97, and 1.29 respectively), and demonstrate a strong matrix effect on the PEMS device.

It is concluded here that, if air-based matrix reference materials are applied to calibrate a PEMS device, it can lead to a considerable deviation of the NO_2 amount fraction in car exhaust measurement in real world scenarios. Future measurements are planned to calibrate the PEMS device with the dTDLAS OGS which provides direct traceability of the results to the SI. This will enable the PEMS device to be used in real world applications, providing accurate and reliable NO_2 measurements in car exhaust gases.

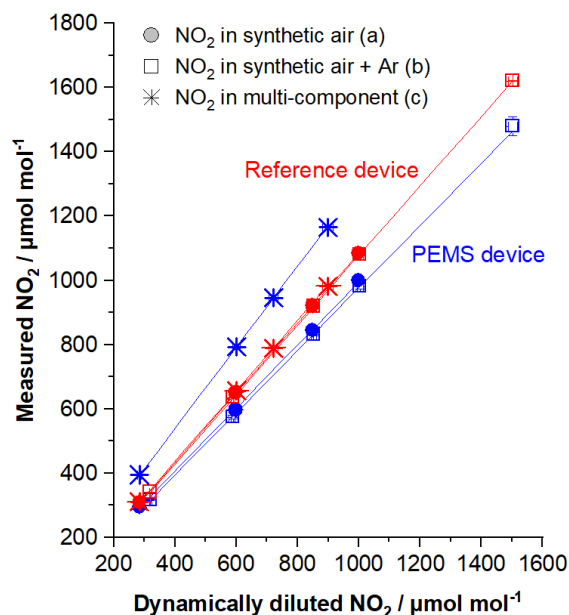


Fig. 2. Plot of measured NO_2 amount fraction as a function of dynamically generated NO_2 amount fraction values, PEMS device (blue) and a reference device (red).

Acknowledgement

This work was supported by the European Metrology Programme for Innovation and Research (EMPIR) project “Improved vehicle exhaust quantification by portable emission measurement systems metrology (MetroPEMS)” and the European Partnership on Metrology (EPM) project “Metrology for green maritime shipping: Emission control through traceable measurements and machine learning approaches (23IND09 MaritimeMET)”. The project 23IND09 MaritimeMET project has received funding from the EPM, co-financed from the European Union’s Horizon Europe Research and Innovation Programme and by the Participating States.

References

- [1] WHO global air quality guidelines: particulate matter (PM_{2.5} and PM₁₀), ozone, nitrogen dioxide, sulfur dioxide and carbon monoxide (2021); <https://iris.who.int/handle/10665/345329>
- [2] European Commission Regulation (EU) 2023/443 of 8 February 2023 amending Regulation (EU) 2017/1151 as regards the emission type approval procedures for light passenger and commercial vehicles (2023); <https://eur-lex.europa.eu/eli/reg/2023/443/oj>
- [3] J. A. Nwaboh, Z. Qu, O. Werhahn, V. Ebert, Towards an Optical Gas Standard for Traceable Calibration-Free and Direct NO_2 Concentration Measurements, *Applied Sciences* 11(12), 5361 (2021); doi: <https://doi.org/10.3390/app11125361>