DEVELOPMENT OF NOVEL EXPERIMENTAL METHODS AND CALCULATIONS FOR THE DETERMINATION AND OPTIMIZATION OF THE RESPONSE TIME OF A PHOTOACOUSTIC GAS ANALYSER

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Abstract
Monitoring and controlling of short-term physico-chemical processes frequently require gas analyzers with high time resolution. The scope of the present study was to shorten the response time of the longitudinal-differential cell-based photoacoustic systems. Finite element analysis and visual investigation of the gas flow were used to improve the purge of the gas sample through the photoacoustic cell. A diffuser providing quick purging was attached to the first buffer of the cell. The optimization of the measurement parameters (including temperature, tube materials, flow rate) and the use of the diffuser resulted in a reduced response time, which was found to be around 1 second. In addition, response time characteristics was determined by measurement of instantaneous injection of analyte.

Introduction
In-situ and real time gas measurements are essential to detect rapid changes and allow continuous optimization of industrial processes. Photoacoustic (PA) spectroscopy-based gas measuring systems meet the requirements of process analysis due to their high sensitivity, wide dynamic range, robust construction, automatic operation and short response time. The typical response time of a PA system is around 2-3 seconds, it is expected that the scope of applications can be extended by improving response time of the analyzers [1-2].

Experimental
Response time measurement
NO, NO_2 and N_2 gases were used for the measurement of response time. Figure 1. shows the experimental setup. The gas flows were continuously 3 l/min. A four-way switching valve generated Heaviside function like concentration changes (NO-N_2 and NO_2-N_2). The materials, length and temperature of the pipe between the four-way switching valve and the photoacoustic chamber were changed to measure their effect on the response time. The PA chamber with and without diffuser were measured. The needle valve was set to maintain 1 l/min gas flow. The gas was drawn by a membrane pump. The NO gas was measured with the addition of water vapor. The NO gas was measured with QCL and NO_2 gas was measured with diode lasers.

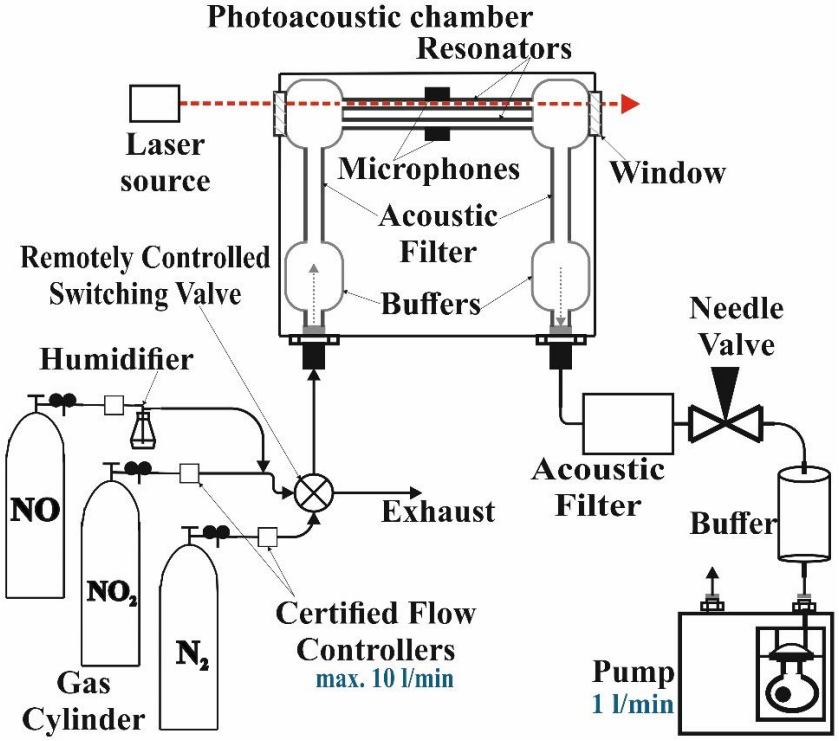

Figure. 1. Response time measurement system

Transfer function measurement

NO and N_2 gases were used for the measurement the transfer function. The gas flows were continuously 2 l/min. 0.5 ml and then 0.25 ml NO (157 ppm in N_2) gas were injected in the N_2 flow through a membrane with a Hamilton syringe (Figure 2.). The needle valve was set to maintain 1 l/min gas flow. The gas was drawn by a membrane pump. The NO gas was measured with the addition of water vapor. The NO gas was measured with QCL lasers.

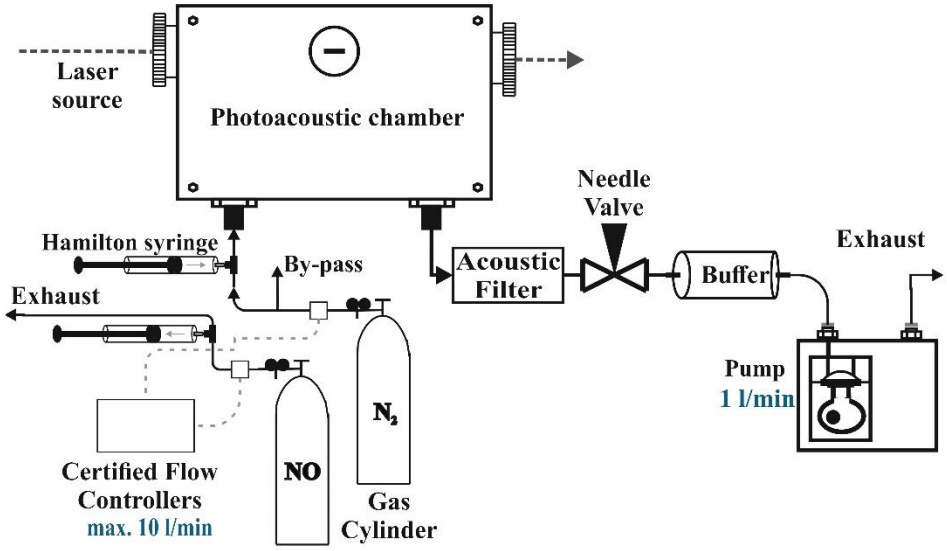

Figure. 2. Measurement system for determination of the transfer function

Results and discussion

Finite element analysis and visual investigation of the gas flow indicated that in the longitudinal-differential PA cell the purge of the gas sample is limited. Therefore, a diffuser allowing quicker purging was attached to the first buffer of the cell. Response time measurements of a PA system with longitudinal-differential cell (with and without diffuser)

were performed with nitrogen monoxide (NO) and nitrogen dioxide (NO_2). Results showed that the diffuser reduces the response time on average by 35%. Furthermore, several factors influencing the response time were investigated (e.g. material of the cell and pipes, temperature, flow rate etc.). For NO and NO_2 measurement, heated polytetrafluoroethylene (PTFE) pipe was found to have the lowest response time. In case of NO and NO_2 measurement it is also important to operate the PA cell at elevated temperature, the optimal temperature was found to be 80°C. Moreover, the most important parameter is the flow rate of the gas sampling, which is highly limited by the PA cell, because above a certain flow rate the flow becomes turbulent resulting in rapidly decreasing signal-to-noise-ratio. It was found that the present system can be operated with a flow rate up to 1 liter/min, which in combination with the low volume of the cell results in short rinse time [3]. The optimization of these parameters and the use of the diffuser resulted in a reduced response time, which was found to be around 1 second. The efficiency of the diffuser was investigated by a finite element modelling performed in COMSOL Multiphysics 5.3. The results of the model proved efficiency of the diffuser. Figure 3. shows the streamlines of a PA cell without diffuser (a) and with diffuser (b).

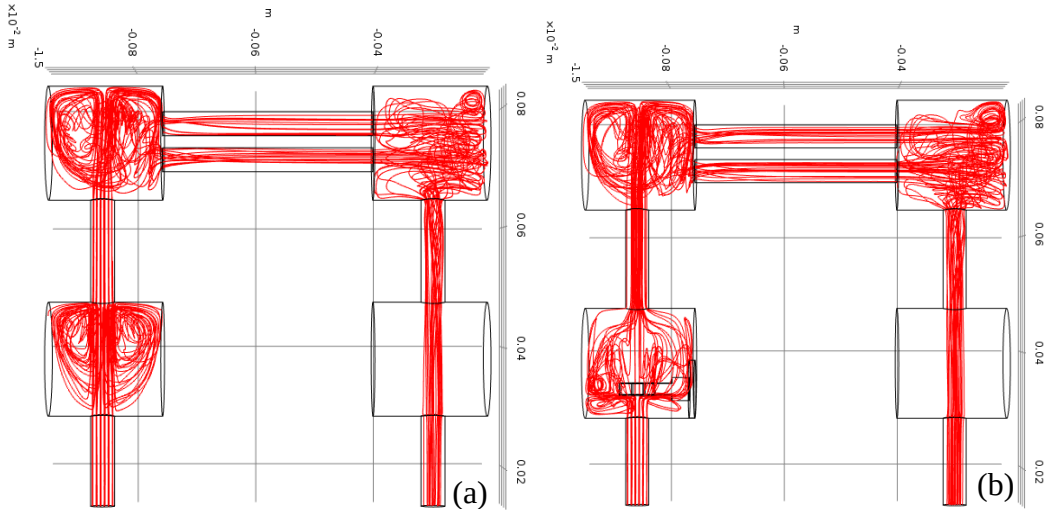

Figure. 3. Streamlines (a) PA cell without diffuser (b) PA cell with diffuser

In addition, the transfer function of the system can be calculated based on response time characteristics. If the transfer function of the system is known and the response of the system is measured, then convolution based analysis can be used to study real-time physico-chemical processes affecting the response time (e.g. adsorption-desorption).

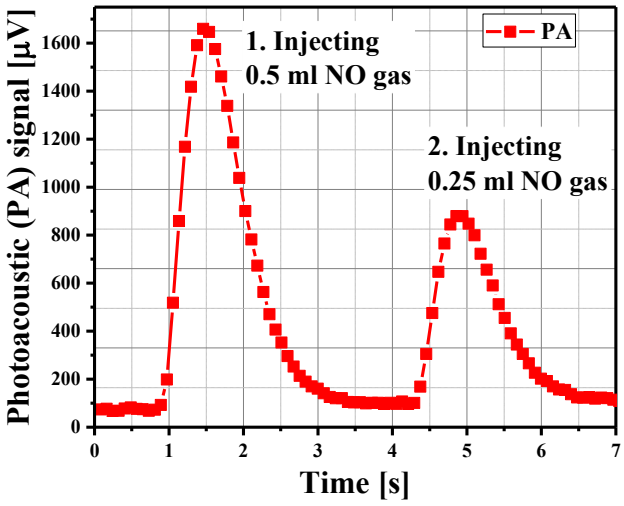

Figure. 4. Response time characteristics of the PA system

Response time characteristics was determined by measurement of instantaneous injection of analyte. The results (Fig. 4.) clearly show that the response of the system extended. Our further aim is to develop a system theory based method that allows the calculation of the concentration changes occurring at the inlet of the PA system with a time resolution below the response time of the system.

Conclusion

The PA system response time was reduced to 1 second. The influencing factors of response time were defined. A method was designed to determine the transfer function of the system and the first measurement was made.

Acknowledgements

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References

1. D. Tátrai, Z. Bozóki, H. Smit, C. Rolf, N. Spelten, M. Kramer, A. Filegs, C. Gerbig, G. Gulyás, G. Szabó Atmos. Meas. Tech. Discuss., 7, 6359-6384, (2014) doi:10.5194/amtd-7-6359-2014
2. A. Miklós, P. Hess, Z. Bozóki, AIP Review of Scientific Instruments, 72, 4, (2001) doi:10.1063/1.1353198
3. A. *Schmohl*, A. *Miklos*, P. *Hess*, *Applied Optics*, *40*, *15*, (*2001*) doi:10.1364/AO.40.002571