



## TNA User Report

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Project title	Testing of a new instrument for the detection of glyoxal based on cavity enhanced absorption spectroscopy
Name of the accessed chamber	SAPHIR
Number of users in the project	2
Project objectives (max 100 words)	The goal of this project is to test a new instrument (OVOC-CEAS) based on cavity enhanced absorption spectroscopy for measuring glyoxal (GLY) and methylglyoxal (MGLY) under controlled conditions in SAPHIR chamber. By injecting different precursors into the chamber, instrument's performance on measuring GLY and MGLY separately and simultaneously can be tested. Moreover, instrumental anti-interference ability under NO <sub>2</sub> rich environments can also be tested by mixing NO <sub>2</sub> with GLY or MGLY in the chamber.
Description of work (max 100 words):	The OVOC-CEAS developed by Peking University (PKU) was installed at SAPHIR and people from PKU were trained to performed experiments at the chamber. Certain amounts of acetylene, hydroxy-acetone, and toluene were injected into the chamber respectively to test the instrumental performance on measuring GLY and MGLY. Different concentration gradients of NO <sub>2</sub> were mixed into the chamber when conducted above experiments. Furthermore, the OVOC-CEAS was deployed in JULIAC campaign (Phase II) to further test the instrumental detection of GLY.

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New user	Yes

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<sup>1</sup> Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

<sup>2</sup> UNI= University and Other Higher Education Organisation;

RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);

SME= Small and Medium Enterprise;

PRV= Other Industrial and/or Profit Private Organisation;

OTH= Other type of organization.

<sup>3</sup> UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

<sup>4</sup> Reproduce the table for each user who accessed the infrastructure

## Trans-National Access (TNA) Scientific Report

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### Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the [eurochamp.org](http://eurochamp.org) website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

**Name of the PI: Xin Li**

**Chamber name and location: SAPHIR, Forschungszentrum Jülich GmbH**

**Campaign name and period: Testing of a new instrument for the detection of glyoxal based on cavity-enhanced absorption spectroscopy (7 May and 12 May to 14 May, 2019)**

**Text:**

#### Introduction and motivation

Glyoxal (GLY) and methyl-glyoxal (MGLY) are atmospheric relevant species since they are key intermediates produced during VOCs degradations (e.g., Toluene + OH reaction) (Fu et al., 2008) and important precursors of SOA formation (Washenfelder et al., 2011; Meng et al., 2018). Accurate quantification of GLY and MGLY is critical for the understanding and improvement of current atmospheric chemical mechanisms.

Cavity enhanced absorption spectroscopy (CEAS) is considered as a sensitive technology for measuring GLY and MGLY simultaneously (Washenfelder et al., 2008; Min et al., 2016). However, recent studies found that high NO<sub>2</sub> concentrations will interfere the accuracy of GLY and MGLY concentrations measured by CEAS (Thalman et al., 2015). In order to minimize such an effect, a new

OVOC-CEAS was developed by integrating a NO<sub>2</sub> photolytic convertor (NPC) which removes sampled NO<sub>2</sub> to a custom-built CEAS unit.

### Scientific objectives

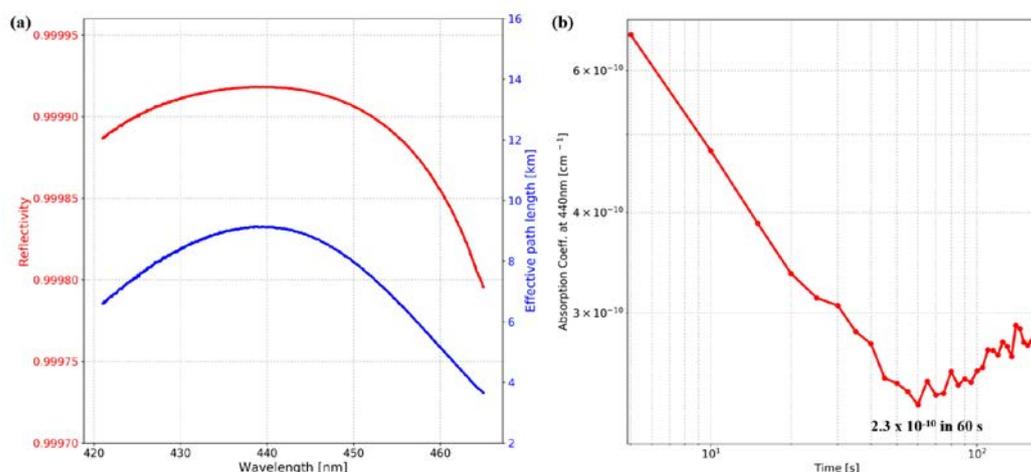
The scientific objective of this project is to test the OVOC-CEAS for measuring GLY and MGLY under controlled conditions in SAPHIR chamber. Specifically, it mainly includes (1) testing instrument's performance on measuring GLY and MGLY separately and simultaneously by injecting different precursors (acetylene, hydroxy-acetone, and toluene), and (2) testing instrumental anti-interference ability under NO<sub>2</sub> rich environments by mixing NO<sub>2</sub> with GLY or MGLY in the chamber.

### Reason for choosing the simulation chamber / calibration facility

The major reasons to use SAPHIR as a platform to test the OVOC-CEAS are, (1) SAPHIR can provide controlled conditions which are similar as in the real atmosphere, (2) SAPHIR is equipped with instruments of LIF, GS-MS/FID, PTR-ToF-MS, etc. which are helpful for the instrument characterization and (3) the OVOC-CEAS can be used at SAPHIR during the JULIAC campaign.

### Method and experimental set-up

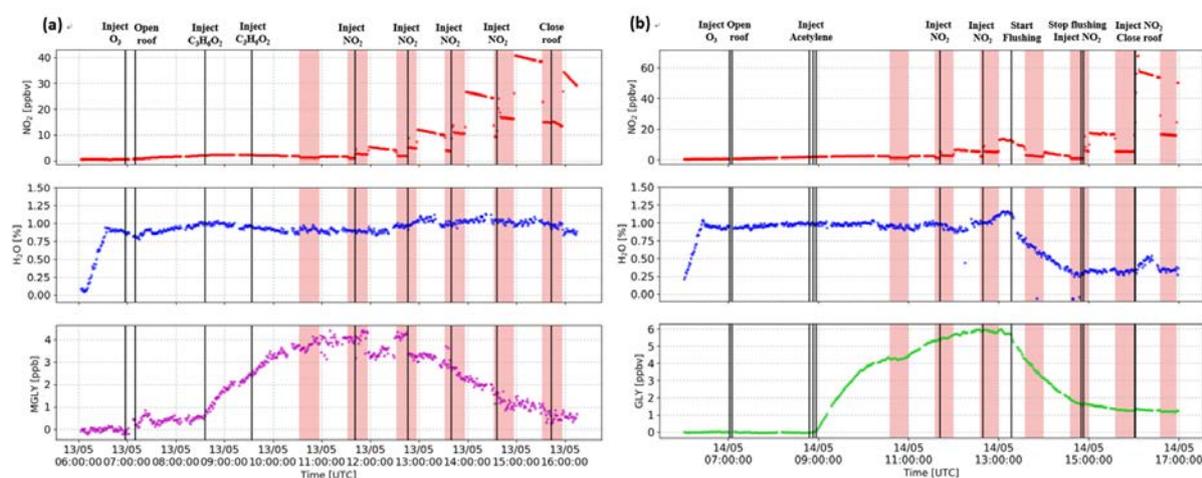
The OVOC-CEAS and other instruments provided by the host were connected to the SAPHIR air and at the beginning of the project, a zero air experiment was conducted to check the background formation of GLY and MGLY in SAPHIR. Certain amounts of three different precursors, acetylene, hydroxy-acetone, and toluene were injected to the chamber respectively to test the instrument's performance on measuring chemically formed GLY, chemically formed MGLY, and both GLY and MGLY simultaneously. The reflectivity of mirrors of the OVOC-CEAS was calibrated before and after the experiments to guarantee the data quality. Mirror reflectivity and corresponding effective path length during the experiments are shown in Fig. 1a. Allan deviation, which is believed as a key parameter of CEAS to characterize the precision (Langridge et al., 2008), is plotted in Fig. 1b. The best precision of the system is  $2.3 \times 10^{-10} \text{ cm}^{-1}$  for an integration time of 60 s.



**Figure 1.** (a) Mirror reflectivity and corresponding effective path length. (b) Allan deviation at 440 nm. The precision ( $1\sigma$ ) of the instrument is  $2.3 \times 10^{-10} \text{ cm}^{-1}$  for an integration time of 60 s.

### Data description

Experiments of OH radicals with acetylene, hydroxy-acetone, and toluene were conducted on different days. Data of OVOC-CEAS and other instruments as planned (e.g., LIF) were recorded during these experiments. Since  $\text{NO}_2$  and water vapor ( $\text{H}_2\text{O}$ ) molecules have strong absorption within the spectral working range of the OVOC-CEAS, their concentrations were also yield during the data processing. Time series of concentrations of  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ , MGLY, and GLY when performed hydroxy-acetone + OH and acetylene + OH experiments were shown in Fig. 2a and Fig. 2b, respectively. Red overlay in the Fig. 2 means the NPC module of the OVOC-CEAS was turned on and black lines and upper labels means corresponding operations during the experiments. Time resolutions of all the data were normalized to 1 minute and corresponding model simulations of these experiments will be conducted after all the data are finalized.

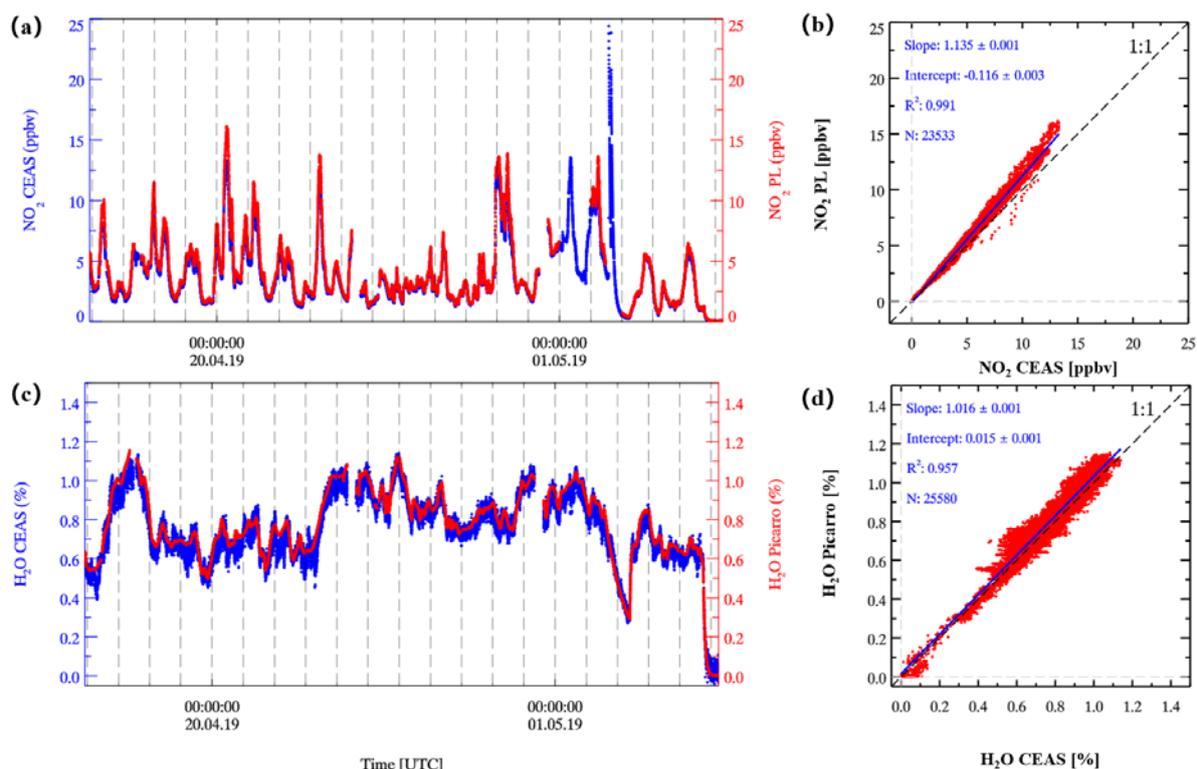


**Figure 2.** (a) Time series of concentrations of  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ , and MGLY during OH + hydroxy-acetone experiment. (b) Time series of concentrations of  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ , and GLY during OH + acetylene experiment.

### Preliminary results and conclusions

As is shown in Fig.2, experiments with different precursors proved that the OVOC-CEAS is sensitive enough to measure chemically formed GLY and MGLY. With respect to the  $\text{NO}_2$  interference, experimental results of MGLY concentration from 11:40 to 12:40 in Fig. 2a were consistent with our results in the laboratory, which indicated that the presence of  $\text{NO}_2$  can cause an underestimation of MGLY concentration and such an effect can be minimized with NPC was working. However, MGLY concentrations after 12:40 seemed to be no longer affected by  $\text{NO}_2$ . The interference of  $\text{NO}_2$  on GLY measurements (see Fig.2 b) was not as significant as the results acquired in the laboratory, which may be caused by two reasons, (1) the GLY concentration was too high, which is at least ten times of the atmospheric concentration and (2) the GLY gases were supplied from different methods (elution from pure solids and chemical formation).

As the data discussed are preliminary, the inconsistency between these results and laboratory results need to be further studied. Nevertheless, our instrumental performance on measuring GLY and MGLY was well verified. In addition, the comparison between OVOC-CEAS's measurements and measurements provided by host showed a good agreement (see Fig.3) during JULIAC campaign. Since GLY has not been well quantified in SAPHIR chamber so far, the comparison was performed on concentrations of  $\text{NO}_2$  and  $\text{H}_2\text{O}$ . Continuous measurement for nearly one month also indicated the stability of the new OVOC-CEAS.



**Figure 3.** (a) Time series and (b) correlation plot of NO<sub>2</sub> concentrations measured by OVOC-CEAS and PL. (c) Time series and (d) correlation plot of H<sub>2</sub>O concentrations measured by OVOC-CEAS and Picarro.

### Outcome and future studies

Experiments in the project verified the instrument's ability of measuring GLY and MGLY. Moreover, instrumental performance during JULIAC campaign (phase II) proved the possibility that the OVOC-CEAS can serve as one of the standard instruments at SAPHIR.

The next steps of the experiments will be focused on improving the detection limit of MGLY and utilizing this new OVOC-CEAS to study the oxidation mechanism of aromatics in SAPHIR chamber, which may provide a deep insight into the details of VOCs degradations and its environmental effects.

### References

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