

FINAL REPORT PROGRAM LEFE

Program LEFE/CHAT	Project title: Intercomparison of PERCA, FAGE and CIMS for measurements of peroxy radicals in the laboratory and in the field	Years 2017 – 2018
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<p><i>Context:</i> Atmospheric free radicals, collectively known as RO_x (OH, HO₂ and RO₂), are key species in atmospheric chemistry. They are produced during the oxidation of volatile organic compounds and are involved in the formation of secondary pollutants such as ozone and secondary organic aerosols. However, ambient measurements of these reactive species are still challenging and only a few techniques are currently used for ambient measurements, e.g. FAGE (Fluorescence Assay by Gas Expansion), CIMS (Chemical Ionisation Mass Spectrometry) and PERCA (PERoxy Radical Chemical Amplifier).</p> <p><i>Objectives:</i> The objectives of this project were to (1) equip a one-channel PERCA instrument developed at IMT Lille Douai (LEFE/CHAT AO 2015) with a second sampling channel, (2) implement the RO_x-LIF technique on a FAGE instrument developed at the university of Lille to extend its measurement capability to RO₂, and (3) perform an intercomparison between PERCA (IMT Lille Douai), FAGE (Univ. of Lille) and CIMS (SAMU, Spectromètre de masse Aéroporté Multi-espèces par réactions ions-molécules, Univ. of Orléans).</p> <p><i>Main results:</i></p> <ul style="list-style-type: none"> - Objective (1): The PERCA instrument has been equipped with a second sampling channel to simultaneously measure the peroxy radical signal (with amplification chemistry) and the background signal (without amplification) that needs to be subtracted from the former. This improvement allowed to reach a time resolution of 6-min with 3σ detection limits of 0.7, 1.3 and 3.0 ppt at relative humidity values of 10, 50 and 80%, which are sufficient for ambient measurements of peroxy radicals (usually in the range of 0.4-125 ppt). <p>The 2-channel PERCA instrument has been calibrated under various operating conditions (radical concentration, humidity, CO and NO reagent concentrations). The Chain Length (CL) values calibrated under these conditions have been compared to values simulated by a 0-D box model implementing the Master Chemical Mechanism (MCM V3.2) to investigate our understanding of the PERCA amplification chemistry. The results showed a model overestimation of a factor of two when the (HO₂+NO → HNO₃) channel (competing with HO₂+NO → OH) was not included in the model (Duncan et al., Atmos. Environ., 2020). It was shown that a better characterization of the water-dependent branching ratio for the above-mentioned reaction (HO₂+NO) was necessary to better model the amplification chemistry.</p> <p>Additional experiments were also performed to investigate whether PERCA measurements could be directly compared to the sum of peroxy radicals simulated by atmospheric models. Indeed, PERCA only detects the fraction of peroxy radicals propagated to HO₂ when the reagent gases (NO and CO) are mixed with ambient air and PERCA is blind to the fraction leading to the formation of organic nitrites and nitrates. The results have shown that the CL measured for different types of RO₂ could be computed from the measured HO₂ CL and the known nitrate and nitrite yields (Duncan et al., 2020). It is therefore possible to compare the PERCA measurements to the sum of peroxy radicals modelled by atmospheric models if the modelled concentration of each RO₂ is weighted by a detection efficiency factor (≤1) calculated from its nitrate and nitrite yields.</p> <ul style="list-style-type: none"> - Objective (2): A RO_x-LIF conversion reactor was constructed at the PC2A laboratory based on the design proposed by Fuchs et al. (Rev. Sci. Instrum., 2008) and was coupled to FAGE to perform RO_x (OH, HO₂ and RO₂) measurements. Ambient RO_x radicals sampled in this reactor are converted into HO₂ by adding NO and CO. The reagent concentrations are adjusted to favor the formation of HO₂ from the rapid RO₂-to-HO₂ conversion chemistry and the concomitant HO₂-OH interconversion chemistry. The resulting HO₂ is then sampled inside FAGE, converted into OH by adding NO, and quantified by laser induced fluorescence at low pressure. Unfortunately, technical difficulties were encountered in the coupling of this reactor to FAGE and a full optimization of operating conditions was not possible before the intercomparison exercise described below. 		

- Objective (3): An intercomparison campaign involving PERCA, FAGE (+ROxLIF reactor) and SAMU was performed on the HELIOS atmospheric chamber at ICARE (Institut de Combustion Aérodynamique Réactivité Environnement) from 8-19 October 2018. The three instruments were coupled to HELIOS to measure concentrations of HO₂+RO₂ (PERCA, RO_x-LIF/FAGE, SAMU), HO₂ (FAGE) and HO₂* (HO₂+alkene-based RO₂, FAGE) from different matrix of peroxy radicals. Additional instrumentation was also coupled to the chamber (PTR-MS, FTIR, analyzers for HCHO, NO, NO₂, O₃, spectroradiometer, temperature, RH, pressure).

The radical instruments were calibrated using homemade calibrators (water photolysis) brought by each group. A first step consisted in cross-calibration experiments involving the use of one calibrator (SAMU) on both PERCA and FAGE. Figure 1 shows that concentrations of peroxy radicals measured by PERCA from the SAMU calibration cell are in good agreement with the generated concentrations, indicating no systematic bias in the calibration of these two instruments. Similar results were observed when the calibrator was used on FAGE, with measured and generated concentrations of approximately $1 \times 10^9 \text{ cm}^{-3}$ being within 20%.

Several experiments were conducted in HELIOS to generate different pools of peroxy radicals: only HO₂ (solar irradiation of H₂/(ClCO)₂), HO₂+CH₃O₂ (solar irradiation of H₂+CH₄/(ClCO)₂), a simple mixture of RO₂ (dark ozonolysis of 1-pentene) and a more complex mixture of RO₂ (dark ozonolysis of α-pinene). Two additional experiments were also performed: solar irradiation of isoprene/H₂O₂ and α-pinene/H₂O₂ mixtures.

The two experiments conducted to generate HO₂ and HO₂+CH₃O₂ showed that the 3 instruments were in agreement within 30%. However, a significant concentration of RO₂ radicals was observed in the HELIOS when only HO₂ should have been present (Figure 2), leading to the difference observed between FAGE and the 2 other instruments. The origin of RO₂ needs to be investigated. In contrast, the two dark ozonolysis experiments and the additional isoprene and α-pinene oxidation experiments (H₂O₂/irradiation) highlighted an O₃-dependent artifact on PERCA (positive bias, not shown). This artifact is thought to arise from secondary chemistry occurring in PERCA due to the use of long reactors (necessary to couple PERCA to HELIOS). This artifact is not observed when short reactors are used on PERCA to perform measurements in ambient air.

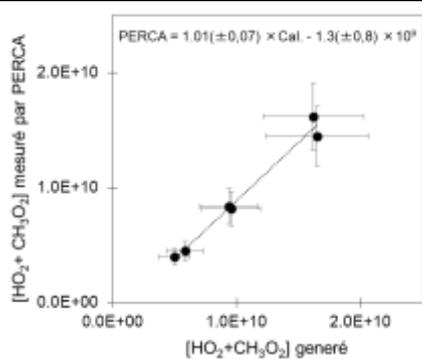


Figure 1: Comparison of peroxy radical concentrations measured by PERCA and generated by the SAMU calibrator. Error bars are 1σ

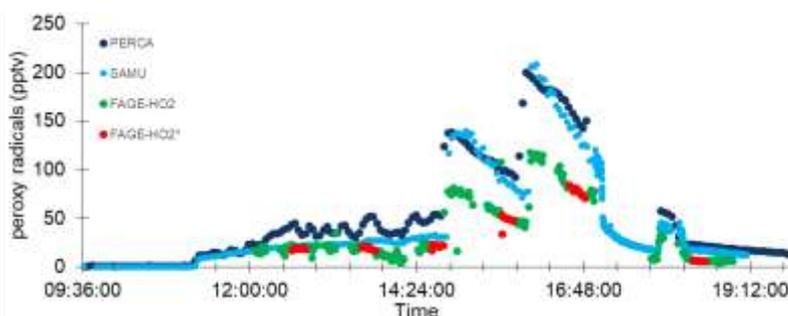


Figure 2: Time series for PERCA (black), SAMU (blue), FAGE-HO₂ (green) and HO₂* (red) for the H₂/(ClCO)₂ experiment

Future of the project: 1/ Experiments performed in this project are being analyzed using a box model. The results will provide additional information on the kinetics of isoprene and monoterpenes under low-NO (dark ozonolysis). 2/ This work highlighted a potential artifact on PERCA that will be further investigated. 3/ These instruments will be deployed during future field campaigns such as ACROSS with the idea to continue the intercomparison under ambient air conditions.

Ph.D Dissertations, Communications, Publications related to the project:

M. Al Ajami, Caractérisation et déploiement d'un instrument FAGE pour l'étude des processus d'oxydation atmosphériques, Ph.D. dissertation, University of Lille, Oct. 2018

A. Lahib, Analytical Developments for Measuring Atmospheric Peroxy Radicals, Ph.D. dissertation, IMT Lille Douai, University of Lille, Dec. 2019

A. Lahib et al., Intercomparison of peroxy radical instruments at the HELIOS atmospheric simulation chamber, AGU Fall meeting, San Francisco, USA, December 9-13, 2019

M. Duncianu, A. Lahib, A. Tomas, P. S. Stevens, S. Dusanter, Characterization of a chemical amplifier for peroxy radical measurements in the atmosphere, Atmospheric Environment (2020), 222, 117106