Geophysical Research Abstracts
Vol. 21, EGU2019-2988, 2019
EGU General Assembly 2019

Development of a Nafion dryer based chemical amplification instrument for quantifying atmospheric peroxy radicals under ambient conditions

Weixiong Zhao (1), Chengqiang Yang (1), Bo Fang (1), Xuezhe Xu (1), Yanbo Gai (1), Yang Zhang (1), Weijun Zhang (1), Weidong Chen (2), Dean S. Venables (3), and Christa Fittschen (4)

(1) Laboratory of Atmospheric Physico-Chemistry, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, 230031, Anhui, China (wxzhao@aiofm.ac.cn, wjzhang@aiofm.ac.cn), (2) Laboratoire de Physicochimie de l'Atmosphère, Université du Littoral Côte d'Opale, 59140 Dunkerque, France, (3) School of Chemistry and Environmental Research Institute, University College Cork, Cork T23 XE10, Ireland, (4) Université Lille, CNRS, UMR 8522 - PC2A -Physicochimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France

Peroxy radicals (HO_2 and RO_2) play a significant role in the formation of ozone and secondary organic aerosols, and in controlling the atmospheric oxidation capacity. The measurement of total peroxy radical RO_2* (RO_2* = $HO_2 + \Sigma RO_2$) by the PERCA (PEroxy Radical Chemical Amplification) technique is achieved by converting HO_2 and RO_2 to NO_2 by their reaction with NO and reforming HO_2 in a flow reactor in the presence of a chain carrier such as CO, which has been widely used in atmospheric chemistry field studies due to its low-cost and portability.

The number of radical reformation cycles before being lost, defined as the chain length (CL), is a critical parameter determining the accuracy and sensitivity of PERCA instruments. For CO-based chemical amplification, the wall loss and water dependent gas phase reactions are the most important chain termination processes that control CL. Compared to dry conditions, the reported CL value is reduced by half at 40% sample inlet relative humidity (RH_{inlet}) and by a factor of 4 at 70% RH_{inlet}. The strong dependence of CL on sample RH for different instruments makes accurate correction of water vapor effect a real challenge.

In this presentation, we report our progresses made in PERCA by using a large diameter Nafion dryer (18 mm inner diameter, MD-700, Perma Pure) as an amplifier to minimize the impact of water vapor on the chain length (CL). We demonstrate (1) that the Nafion dryer reactor can achieve a higher CL (1.6 times better) than the commonly used PFA tube reactor and (2) that there is a relatively small decrease in CL_{wet} over a wide sample RH (about a 10% reduction at 87% RH). The water sensitivity was strongly suppressed in the Nafion dryer reactor and improved the overall PERCA system performance in quantifying RO_2* concentrations with high sensitivity and high accuracy under most (even very humid) ambient conditions. We suggest that this is a simple and attractive approach for research groups to determine peroxy radical chemistry in field and chamber applications.

References:

1, Chen, Y., Yang, C., Zhao, W., Fang, B., Xu, X., Gai, Y., Lin, X., Chen, W., and Zhang, W.: Ultra-sensitive measurement of peroxy radicals by chemical amplification broadband cavity-enhanced spectroscopy, Analyst, 141, 5870-5878, 2016.

2, Fang, B., Zhao, W., Xu, X., Zhou, J., Ma, X., Wang, S., Zhang, W., Venables, D. S., and Chen, W.: Portable broadband cavity-enhanced spectrometer utilizing Kalman filtering: application to real-time, in situ monitoring of glyoxal and nitrogen dioxide, Opt. Express, 25, 26910-26922, 2017.

3, Yang, C., Zhao, W., Fang, B., Xu, X., Zhang, Y., Gai, Y., Zhang, W., Venables, D. S., and Chen, W.: Removing water vapor interference in peroxy radical chemical amplification with a large diameter Nafion dryer, Anal. Chem., 90, 3307-3312, 2018.

4, Yang, C., Zhao, W., Fang, B., Yu, H., Xu, X., Zhang, Y., Gai, Y., Zhang, W., Chen, W., and Fittschen, C.: Improved chemical amplification instrument by using a Nafion dryer as an amplification reactor for quantifying atmospheric peroxy radicals under ambient conditions, Anal. Chem., 91, 776-779, 2019.