Geophysical Research Abstracts,
Vol. 11, EGU2009-7574-1, 2009
EGU General Assembly 2009

# The effect of relative humidity on the detection of pyrrole by PTR-MS for OH reactivity measurements

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The hydroxyl radical (OH) is the most important atmospheric oxidant. Recently Sinha et al. [1] developed a new method to measure the total OH reactivity of ambient air (OH sink) employing a proton transfer reaction mass spectrometer (PTR-MS) as a detector. The new method uses pyrrole ($C_4H_4NH$) as a reagent and for an OH reactivity measurement this species must be measured under both dry ($\sim$ 0% RH) and humid air ( $>$ 30% RH). Here, we investigate the sensitivity dependence of the PTR-MS for pyrrole, as a function of relative humidity in the sampled air. Various normalizations with respect to the $H_3O^+$ ion and its different hydrated clusters ions $H_3O^+(H_2O)_{n=1,2,3}$ are compared. It is shown that both the primary ion signal ($H_3O^+$ ion m/z = 19) and the first water cluster ion $H_3O^+(H_2O)$ (m/z = 37) should be used for pyrrole quantification. However, in spite of using this normalization, the PTR-MS sensitivity for pyrrole changes by as much as 16 % between dry ($\sim$ 0% RH) and humid air (above 30 % RH), with higher sensitivity when the sampled air is humid. Thus, for accurate quantification of pyrrole using a PTR-MS, calibration factors appropriate to dry and humid air should be employed. We recommend that humidity dependence of the PTR-MS be taken into account when reactivity measurements are performed using the pyrrole based comparative reactivity method (CRM).

[1]. V. Sinha, J. Williams, J.N. Crowley, and J. Lelieveld, Atmos. Chem. Phys. 8 (2008) 2213-2227