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A new method for direct total OH reactivity measurements using a fast Gas Chromatographic Photo-Ionization Detector (GC-PID)

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The primary and most important oxidant in the troposphere is the hydroxyl radical (OH). Currently the atmospheric sinks of OH are poorly constrained. One way to characterize the overall sink term of OH is to measure directly the ambient loss rate of OH, the total OH reactivity.

The first direct measurements of total OH reactivity were performed using laser induced fluorescence (LIF) [1], [2]. Recently a new method for determining OH reactivity was developed called the comparative reactivity method (CRM) [3]. The measurement principle is based on a competitive reaction between a reactive molecule not normally present in air with OH, and atmospheric OH reactive molecules with OH. The reactive molecule (X), is passed through a Teflon coated glass reactor and its concentration is monitored with a suitable detector. OH radicals are then introduced into the reactor at a constant rate to react with X, first in the presence of zero air and then in the presence of ambient air containing OH reactive species. Comparing the amount of X exiting the reactor with and without the competing ambient air molecules directly provides the atmospheric total OH reactivity. In the first version of this set up, molecule X is pyrrole (C5H4N) and the detector used is a proton transfer reaction mass spectrometer (PTR-MS). In comparison to the original LIF based system, the PTR-MS has the advantage of being smaller, less expensive, and commercially available. However, using the PTR-MS for total OH reactivity measurements prevents it from probing the broad variety of volatile organic compounds in ambient air. Moreover, even smaller, less expensive and more portable detectors are available. This work examines the potential for a GC-PID in order to make the total OH reactivity measurement accessible to more practitioners.

This study presents measurements of total OH reactivity with a custom built GC-PID (VOC-Analyzer from IUT-Berlin, now ENIT (Environics-IUT GmbH))[4]. The GC-PID is small (260*160*400 mm), light (8 kg) and provides a good time resolution (50-60 sec). The method is able to operate in ambient conditions, requires no external carrier gas, and an internal battery provides power for ca. 12 hours which makes the instrument suitable for outdoor field campaigns. The GC-PID detection limit for pyrrole is 3 ppb, which is adequate for this application and total OH reactivity can be measured under optimum conditions down to 4 sec-1.

The new set-up has been tested in parallel to previously validated PTR-MS measurements for CRM in laboratory experiments, a plant chamber, and boreal forest field studies. Advantages and drawbacks of the new technique are discussed. Although the polymerization of pyrrole on the detector window remains a weakness in the present version of the system, in general the GC-PID produces acceptable results.

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[3] V. Sinha et al, 2008, Atmos. Chem. Phys., 8, 2213–2227
[4] http://www.environics-iut.de/