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Laser-induced fluorescence instrument (ROxLIF) for measurement of tropospheric RO_2 and HO_2 radicals

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Hydroperoxy (HO₂) and organic peroxy radicals (RO₂) play an important role in the photochemical formation of tropospheric ozone and are chemically linked by chain reactions to the hydroxyl (OH) radicals which constitute the major atmospheric oxidant. In the current work, we have developed a low-pressure laser-induced fluorescence (LIF) instrument to enable the separate measurement of RO₂ and HO₂ with high sensitivity. The instrument uses a two-step chemical conversion of RO₂ to OH radicals, which are subsequently detected by LIF at 308nm. The detection limit for peroxy radicals is about 0.3 pptv in 1 minute measurement time. Here we present the applied conversion technique for peroxy radicals, describe the instrumental characteristics and the calibration for different peroxy radical species. An example of ambient air measurements demonstrates the performance of the new technique which is expected to provide improved understanding of the fast radical chemistry in the troposphere.