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Title:	VOC–OHM: A new technique for rapid measurements of ambient total OH reactivity and volatile organic compounds using a single proton transfer reaction mass spectrometer
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Keywords:	Hydroxyl radical Volatile organic compounds Mass spectrometer Spectrometry
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Abstract:	Measurements of total hydroxyl radical (OH) reactivity and volatile organic compounds (VOC) are necessary for improving our understanding of reactive emissions and atmospheric oxidation in air pollution and atmospheric chemistry studies. Proton transfer reaction mass spectrometers (PTR-MS) can measure ambient VOCs and the total ambient OH reactivity. However, till date this has always required deployment of two PTR-MS instruments, wherein one instrument measures ambient VOCs and the other instrument measures the total OH reactivity using the comparative reactivity method (CRM). Due to material (e.g. power, space) or financial constraints, deploying two PTR-MS instruments is not always possible and yet it is desirable to quantify both VOCs and OH reactivity. Here, we present a novel hyphenated technique christened VOC-OHM (for Volatile Organic Compounds–OH reactivity Measurement) that enables rapid ambient measurements of both VOCs and total OH reactivity using a single PTR-MS. The technique can provide more specificity for identification of compounds using a PTR-QMS through an estimate of the rate coefficient of the major isobaric contributor with the hydroxyl radical as shown in the case of m/z = 69 for isoprene and furan, which are nominal isobars but have rate coefficients that differ by one order of magnitude. It also demonstrates a new safer and portable substitute for pressurized zero air bottles that have been required thus far in CRM OH reactivity deployments. VOC–OHM successfully couples the typical VOC and CRM experimental set ups without undermining the PTR-MS's ability to measure either parameter. The design of the VOC–OHM system, its validation, optimization and results of field tests are described in detail. The VOC–OHM system measures the ambient VOCs and OH reactivity every hour for ~20 min durations each, with an ambient data gap of ~13 min in between. Thus rapid temporal changes in the ambient chemical composition and reactivity are easily quantified. The sampling periods and VOC speciation achieved using VOC–OHM can be customized depending on user preferences, providing more options for the majority of users possessing a single PTR-MS.
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