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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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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.

1. Introduction

OH radicals are the primary oxidants of the atmosphere [1]. Due to their high reactivity with ambient trace gases, they act as the cleansing agents of the atmosphere. This is accomplished by oxidizing most of the primary emissions in the presence of oxygen, to products that can be more easily removed from the atmosphere [2] because the products are less volatile and more water soluble. Along with volatile organic compounds (VOCs), OH radicals drive the formation of secondary pollutants such as ozone and secondary organic aerosol [3,4]. The total OH reactivity is defined as the summation over products of the concentration of the OH reactant $[X_i]$ (e.g. $X_i = CO$, VOCs, NO_2 etc.) and its rate coefficient with the hydroxyl radical (k_{OH+X_i}), expressed mathematically as:

$$\text{Total OH reactivity} = \sum k_{OH+X_i}[X_i] \qquad \text{(E1)}$$

Direct measurements of the total OH reactivity of ambient air in combination with measurements of major reactive volatile organic compounds permit investigation of missing reactive emissions [5,6] in atmospheric chemistry field studies. Moreover the total OH-reactivity is a robust proxy for the total reactive pollutant loading of air masses and when combined with measurements of nitrogen oxides, permits derivation of instantaneous ozone production

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regimes [7,8]. While the sources of hydroxyl radicals depend on only few photochemical reactions and hence are better constrained, the total OH reactivity which represents the collective sink term is more difficult to constrain as it depends on the multitude of reactive species present in ambient air. Thus, direct measurements of the total OH reactivity also permit an accurate assessment of the atmospheric hydroxyl radical budget [9], which represents a key test for our understanding of atmospheric chemistry in different environments. For direct measurements of total OH reactivity, there are three well established methods, two of which (namely total OH loss measurement [10,11] and pump-probe method [12]) are based on laser induced fluorescence (LIF) and derive the OH reactivity of ambient air by detecting the decay of artificially produced OH radicals in a flow tube injected with ambient air. The third method, namely the Comparative Reactivity Method (CRM) [13], uses a proton transfer reaction mass spectrometer or a gas chromatograph equipped with a photo-ionization detector (GC-PID) [14] for detection of pyrrole (a reagent molecule) during an in situ competitive kinetics experiment.

In terms of cost and logistical constraints (power consumption, size, weight and laser stability), which are very important considerations for instrumental deployment in field studies, laser induced fluorescence based systems are generally more difficult to deploy than proton transfer reaction mass spectrometers. However, even proton transfer reaction mass spectrometers are expensive and cost upwards of 2,00,000 Euros each. Till date in all field studies either two PTR-MS systems or a GC-PID and a PTR-MS have been required to perform ambient measurements of VOCs as well as the total OH reactivity. As far as the CRM method is concerned, the PTR-MS remains a better choice for the detector as the GC-PID has many limitations for this application [14]. It would thus be extremely beneficial, to be able to deploy a single PTR-MS system configured for rapid measurements of both reactive VOCs and the total OH reactivity, so that meaningful information pertaining to diel VOC and OH reactivity profiles can be obtained using only one instrument.

In this work, we present a new technique, termed VOC–OHM (Volatile Organic Compound–OH reactivity Measurement), that enables a single PTR-MS instrument to be employed for direct and rapid sequential ambient measurements of total OH reactivity and reactive VOCs in a semi-automated manner. The technique was tested in the laboratory for analytical constraints specific to both CRM OH reactivity measurements and ambient PTR-MS VOC measurements, and optimized. Successful acquisition of ambient data at a site in India where the ambient chemical composition shows pronounced diel variability in response to emission activity and meteorological factors is also demonstrated. Finally, the advantages and limitations of VOC–OHM, in comparison to the traditional two PTR-MS systems' deployment are discussed.

2. Experimental

2.1. Measurement of ambient volatile organic compounds and pyrrole using a proton transfer reaction mass spectrometer (PTR-MS)

A high sensitivity quadrupole proton transfer reaction mass spectrometer (PTR-QMS) (Model 11-07HS-088; Ionicon Analytik Gesellschaft, Austria) was used to perform sequential measurements of ambient VOCs and pyrrole (the reagent molecule measured in the comparative reactivity method) [13]. Analyte molecules can be detected in the PTR-MS if their proton affinity (P.A.) exceeds that of water vapour [15] (P.A. = 165.2 kcal/mol). A pure flow of the hydronium reagent ions (>99% purity) is produced in the ion source region of the PTR-MS using a plasma discharge in a hollow cathode which are then directed towards the drift tube. Within the drift tube, analyte VOCs with a proton affinity greater than that of water vapour react with reagent hydronium ions (H_3O^+) to form protonated molecular ions (with m/z = molecular ion + 1). With the exception of few classes of compounds (e.g. higher alcohols where molecular ion – 17 peaks also occur), fragmentation of the molecular ion does not complicate the mass spectra at the typical drift tube conditions of the PTR-MS (E/N < 135 Townsend) for several volatile organic compounds. The ions are then separated based on their m/z ratio using a quadrupole mass analyser and detected using a secondary electron multiplier. The applications of proton transfer reaction mass spectrometry for quantifying ambient VOCs and pyrrole have been discussed extensively elsewhere [16,17]. A comprehensive description of the data quality assurance, calibration protocols for ambient VOCs and technical details of the PTR-MS and other instruments used in this work have already been provided in Sinha et al. [18].

Table 1 lists the detection limits and uncertainties for the ambient VOCs measured in this work along with the m/z ratios at which they were detected. The instrument was calibrated for the measured compounds (range 0.3–20 ppb) using a custom ordered VOC gas standard (Apel-Riemer Environmental, Inc., Colorado, USA; ∼500 ppb for each VOC, stated uncertainty = 5%) containing compounds listed in Table 1. The calibrations were performed by dynamic dilution of the gas standards as described in Sinha et al. [8,17]. The instrumental background was determined by sampling VOC-free zero air generated using a Gas Calibration Unit (GCU-A, Ionimed Analytik). A catalytic converter inside the GCU-A oxidizes VOCs to carbon dioxide. The detection limit for the measured VOCs was defined as 2σ of the measured normalized signal divided by the sensitivity at that m/z, while measuring zero air. The overall uncertainty was calculated using the root mean square propagation of (i) 5% accuracy error inherent in the VOC gas standard, (ii)

Table 1
Nominal protonated m/z, detection limits and uncertainties of VOCs measured during the study period.

Measured species	Nominal protonated m/z (Th)	Detection limit[a]	Uncertainty
Methanol	33	0.46	10.3%
Acetonitrile	42	0.03	10.1%
Acetaldehyde	45	0.12	10.1%
Acetone	59	0.61	10.3%
Isoprene	69	0.06	15.8%
Methyl vinyl ketone	71	0.02	11.6%
Methyl ethyl ketone	73	0.04	10.5%
Benzene	79	0.03	10.1%
Toluene	93	0.05	11.5%
Sum of C8 aromatics[b]	107	0.04	12.4%
Sum of monoterpenes[c]	81 (65% fragment) and 137 (35% fragment)	0.03	12.1%
Sum of C9 aromatics[d]	121	0.09	11.0%

[a] Reported in ppb.
[b] Calibrated using p-xylene.
[c] Calibrated using 1,2,4-trimethylbenzene.
[d] Calibrated using α-pinene.