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Title: Storage stability studies and field application of low cost glass flasks for analyses of thirteen

ambient VOCs using proton transfer reaction mass spectrometry

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Abstract:

Ambient volatile organic compounds play a key role in atmospheric chemistry and air pollution studies due to their chemical reactivity and in several instances high toxicity. Quantification of ambient whole air samples which contain reactive and short-lived VOCs such as acetaldehyde, isoprene, dimethylsulphide and trimethylbenzenes at ppt-ppb concentrations is analytically challenging and generally accomplished using online proton transfer reaction mass spectrometry. Deployment of online instrumentation is still not feasible in several regions of the world due to practical constraints (power, safety issues). Consequently there is paucity of VOC data in vast regions of the world. We present here, the validation and application of a novel method for ambient VOC speciation and emission factor studies using low cost (<100 USD) whole air glass flask samplers and offline proton transfer reaction mass spectrometry that can help reduce the paucity of VOC datasets. Experiments to assess the stability during storage of thirteen VOCs, many of which are very reactive, showed that acetaldehyde, acetonitrile, acetone, dimethylsulphide, methyl vinyl and methyl ethyl ketones, benzene, xylenes, trimethylbenzenes and monoterpenes can be quantified reproducibly within the respective precision error (e.g. 40% at 100ppt α -pinene and 3% at 13 ppb acetaldehyde) between collection and storage (at >95% confidence), for samples analyzed within 10 days of collection. For toluene and isoprene, similar results were obtained until day 9 and 1, respectively and at confidence >70%, over the 10 day period. A storage artefact was observed for methanol resulting in higher analytical uncertainty of upto 40%. We applied the method for measuring toluene/benzene emission ratios and aromatic VOCs in traffic plumes, and determining VOC emission factors (gVOC/kg fuel) from an agricultural wheat straw fire in India. The results of this study demonstrate that use of the low cost glass flask samplers described herein can significantly improve acquisition of spatially and temporally resolved datasets for atmospheric chemistry and air quality studies at sites where online deployment of instruments remains

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