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A smog chamber comparison of a microfluidic derivatisation measurement of gas-phase glyoxal and methylglyoxal with other analytical techniques

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A microfluidic lab-on-a-chip derivatisation technique has been developed to measure part per billion (ppbV) mixing ratios of gaseous glyoxal (GLY) and methylglyoxal (MGLY), and the method is compared with other techniques in a smog chamber experiment. The method uses o-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) as a derivatisation reagent and a microfabricated planar glass micro-reactor comprising an inlet, gas and fluid splitting and combining channels, mixing junctions, and a heated capillary reaction microchannel. The enhanced phase contact area-to-volume ratio and the high heat transfer rate in the micro-reactor result in a fast and highly efficient derivatisation reaction, generating an effluent stream ready for direct introduction to a gas chromatograph-mass spectrometer (GC-MS). A linear response for GLY was observed over a calibration range 0.7 to 400 ppbV, and for MGLY of 1.2 to 300 ppbV, when derivatised under optimal reaction conditions. The analytical performance shows good accuracy (6.6 % for GLY and 7.5 % for MGLY), suitable precision (< 12.0 %) and method detection limits (MDLs) (75 pptV for GLY and 185 pptV for MGLY) with a time resolution of 30 minutes. These MDLs are below or close to typical concentrations of these compounds observed in ambient air. The microfluidic derivatisation technique would be appropriate for ambient α-dicarbonyl measurements in a range of field environments based on its performance in a large-scale outdoor atmospheric simulation chamber (EUPHORE). The feasibility of the technique was assessed by applying the methodology to quantify of α-dicarbonyls formed during the photo-oxidation of isoprene in the EUPHORE chamber. Good correlations were found between microfluidic measurements and Fourier Transform InfraRed spectroscopy (FTIR) with the correlation coefficient (r2) of 0.84, Broad Band Cavity Enhanced Absorption Spectroscopy (BBCEAS) (r2 = 0.75), solid phase micro extraction (SPME) (r2 = 0.89), and a photochemical chamber box modelling calculation (r2 = 0.79) in GLY measurements. For MGLY measurements, the microfluidic technique showed good agreement with BBCEAS (r2 = 0.87), SPME (r2 = 0.76), and modeling simulation (r2 = 0.83), FTIR (r2 = 0.72) but displayed a discrepancy with Proton-Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-ToF-MS) with r2 value of 0.39.