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D/H Isotope Ratio Measurements of Atmospheric Volatile Organic Compounds

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Analysis of isotope ratios in atmospheric volatile organic compounds (VOC) is a reliable method to allocate their sources, to estimate atmospheric residence times and investigate physical and chemical processes on various temporal and spatial scales. Most investigations yet focus on carbon isotope ratios. Certainly more detailed information can be gained by the ratio of deuterium (D) to hydrogen (H) in VOC, especially due to the high mass ratio. Combining measurements of carbon and hydrogen isotopes could lead to considerable improvement in our understanding of atmospheric processes.

For this purpose we set up and thoroughly characterised a gas chromatograph pyrolysis isotope ratio mass spectrometer to measure the D/H ratio in atmospheric VOC. From a custom-made gas standard mixture VOC were adsorbed on Tenax®TA which has the advantage that CO_2 is not preconcentrated when measuring ambient air samples. Our results show that the pyrolysis method has significant impact on the D/H ratios. A pyrolysis temperature of at least 1723 K and conditioning of the ceramic tube on a regular basis is essential to obtain reproducible D/H isotope ratios. For an independent comparison D/H ratios of the pure VOC used in the gas standard were determined using elemental analysis by Agroisolab (Jülich, Germany). Comparisons of 10 VOC show perfect agreement within the standard deviations of our measurements and the errors given by Agroisolab, e.g. for n-pentane, toluene, 4-methyl-2-pentanone and n-octane. A slight mean difference of 5.1 ‰ was obtained for n-heptane while significant mean differences of 15.5 ‰ and 20.3 ‰ arose for 1,2,4-trimethylbenzene and isoprene, respectively.

We further demonstrate the stability of our system and show that the sample preparation does not affect the isotope ratios. Moreover the applicability of our system to ambient air samples is demonstrated.