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An automated system for NMHC isotope analysis on trace gases from ambient and CARIBIC samples

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Isotope analysis can be a useful tool in constraining the budgets (sources and sinks) of atmospheric trace species and is increasingly applied for organic constituents. This may be useful in particular for investigating the oxidative capacity of the atmosphere and studying long-range transport.

We present setup and initial results from a new automated system for isotope ratio measurements on atmospheric hydrocarbons. The inlet system is flexible and allows analysis of trace gases from medium size to large ambient air samples (5-300L) as well as CO_2-concentrates from samples that have been extracted offline. Handling of large samples requires a special treatment to remove water and CO_2. In a first step, water, CO_2 and all trace gases are trapped in a high volume trap at liquid nitrogen temperature, which is subsequently heated to release CO_2 and trace gases, whereas most of the water stays behind. CO2 is separated from other gases by means of a PoraPAK Q GC column (10m, i.d. 4mm, at room temperature). After CO_2 breakthrough, the column is heated and the flow is reversed to flush back hydrocarbons and halocarbons from this separation column onto the analytical column, via several focusing steps, where the different constituents are separated by chromatography for subsequent isotope ratio mass spectrometer injection.

The system has been extensively tested and the stability across a broad sample size range has been quantified. Repeatability of 0.1â in δ^{13}C has been achieved for several compounds. The first scientific project is the analysis of a set of large air concentrates

from the CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container) project, which provides a unique archive of atmospheric samples taken in the upper troposphere and lower stratosphere, a region that is rarely sampled. In this initial step, focus is on the isotope signatures of ethane and methyl chloride. These components have sources in combustion and degradation of plant matter and fossil fuels, but are mainly anthropogenic in origin.