Development of a New Method for the Study of the Global Distribution of the OH-Radical

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The hydroxyl-radical is of utmost importance for the removal of both anthropogenic and biogenic pollutants from the atmosphere. However, the understanding of the global OH-cycle and budget is very limited to date. These limitations are caused by the high reactivity and short lifetime of the OH-radical. Therefore, direct measurements are very elaborate and expensive. Previously applied methods include multipath laser absorption, laser-induced fluorescence and long-path spectrometry. All of these methods have in common that they cover only a short amount of time and a small geographic area.. The longest continuous documentation stems from the Global Atmospheric Gases Experiment/Advanced Global Atmospheric Gases Experiment (GAGE/AGAGE) campaign in Mace Head, Ireland. This campaign uses an indirect method by analyzing the atmospheric depletion of methyl-chloroform (CH_3CCl_3) that occurs mainly by oxidation with the OH-radical.

Similarly as for methyl-chloroform, other light, saturated hydrocarbons (C_2-C_7) are mainly depleted by reaction with OH. Therefore a new approach to study the global distribution of light hydrocarbons and methyl-chloroform is developed. This technique relies on air samples collected from the CMDL flask project. Currently air samples are taken from more than 50 sites worldwide and are analyzed in Boulder for the atmospheric trace gases CO_2, CH_4, SF_6, N_2O, CO, and H_2 as well as $^{18}O/^{16}O$, and $^{13}C/^{12}C$ isotope ratios. After these measurements, approximately 1 liter of sample air remains in the flasks that will now be used for C_2 to C_7 quantification.

An Instrument was developed to analyze light hydrocarbons in the flasks. This instrument uses a vacuum reservoir to draw a sample out of the flasks through a cooled solid adsorbent trap. After the preconcentration step, the trap is heated up rapidly, and the sample is transferred onto a GC-column and quantified using a flame-ionization detector (Figure 1).
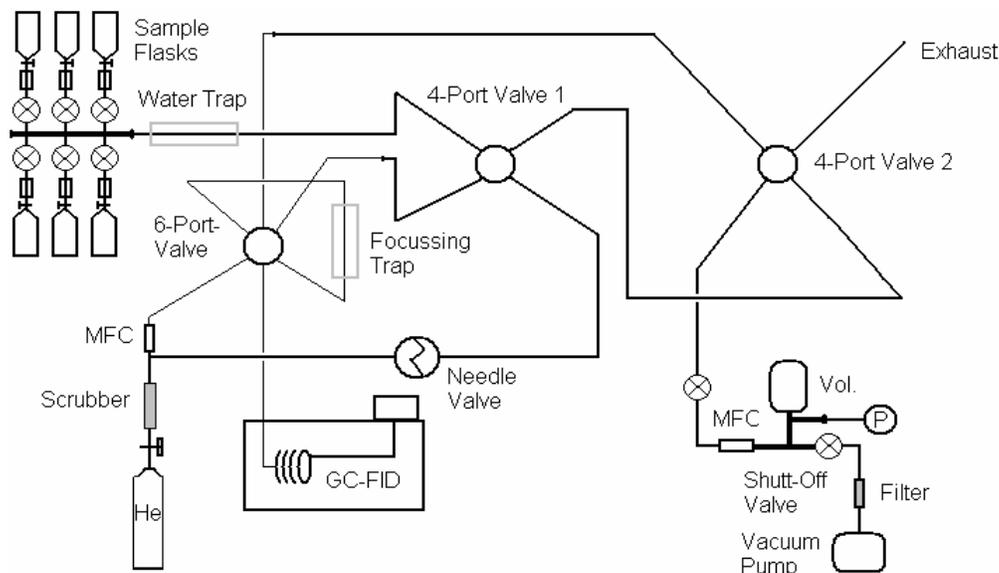

Figiure 1. Schematic of the GC system for C2-C7 hydrocarbon sampling from the CMDL glass flasks.