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Development of a fast GC/MS-system for airborne measurements of Volatile Organic Compounds

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Volatile Organic Compounds (VOC) determine the radical chemistry of the atmosphere. They can serve both as sources, or sinks for radicals. Mass spectrometry linked to gas chromatography (GC/MS) is a widespread technique in environmental analysis since it can be used to separate and analyze any compound which can be evaporated and pass the analytical column with very high precision and a good sensitivity. The use of special chromatographic phases and long capillary columns enables the quantification of a wide range of compounds with little interference from other sample constituents. An in situ GC/MS consists in principle of three compartments, 1) a preconcentration unit where the sample is extracted from the air, focussed onto a small volume and volatilized, 2) a chromatographic system where the analytes are separated on the analytical column and 3) a mass spectrometer where the compounds are ionized and detected. VOC have to be preconcentrated due to their low concentration level and in order to get enough sensitivity for analysis.

The aim of this project was to develop an in situ GC/MS system to analyze volatile Nonmethane Hydrocarbons (NMHC) and Oxygenated Volatile Organic Compounds (OVOC) for the High Altitude and LOng Range Research Aircraft (HALO).

In contrast to other analytical instruments a GC/MS works discontinuously. The preconcentration unit is either heated up when the compounds are volatilized or cooled down when substances are adsorbed. The same is true for the GC oven. It is heated up when the compounds are separated or it is cooled down to be ready for the next injection. On a system with a single GC oven, these processes will inevitably lengthen the whole analytical procedure. To speed up the analytical process the GC/MS system described here was equipped with two GC ovens and two adsorption units. While the components are adsorbed in one adsorption unit, in the other unit the components are desorbed and transferred to the GC unit. The second GC is heated up to separate the components. The air sample is adsorbed at ambient temperature on graphite based adsorbents in the adsorption unit. Using graphite based adsorbents offers the opportunity to trap even components with high volatility at ambient temperature. Heating the adsorption unit desorbs the concentrated sample. A focus trap with a very low volume and a high heating rate was inserted before the column. This allows a fast injection and separation of very volatile compounds. For gas chromatographic separation a polar DB-Wax column of 20 m length and an inner diameter of 0.18 mm was chosen to provide a good peak resolution. As a compromise between peak resolution and response in the mass spectrometer a column flow of 1.0 ml per minute was taken. Finally the mass spectrometric detector serves for quantification and qualification of the single compounds.

This new GC/MS system enables fast in situ measurements with cycling times of 3 to 4 minutes. 30 components can be quantified. The DB-WAX column is suitable for lower hydrocarbons, alcohols, acetates, aldehydes and ketones with up to 7 carbon atoms. Also, some aromatic compounds can be separated with this setup. The precision of ¼ of these 30 components is better than 3%, while for 2/3 of the components the precision is better than 8 %. The detection limit of a single compound depends on its chromatographic and mass spectrometric properties and possible blank values. The detection limit can be estimated to be lower than 10 ppt.