

Monitoring organic nitrogen species in the UT/LS – a new system for analysis of CARIBIC whole air samples

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The CARIBIC project is a unique program for long term and global scale monitoring of the atmosphere (http://www.caribic-atmospheric.com). An instrument container is installed monthly into a civil aircraft operated by Lufthansa (Airbus A 340-600) and makes atmospheric observations en route from Frankfurt, Germany to various destinations around the globe. In four to six long distance flights at a cruising altitude of 10 to 12 km online measurements of various atmospheric tracers are performed during the flight as well as whole air samples are taken with two different sampling units (116 samples in both glass and stainless steel canisters). These samples are routinely analyzed for greenhouse gases, non-methane hydrocarbons (NMHC) and halogenated compounds.

Nitrogen containing compounds play various important roles in the atmosphere. Alkyl nitrates (RONO₂) are products of the reaction of NMHC with OH and other oxidants in the presence of NO. They can provide information on the oxidative history of an air mass. Moreover they influence photolchemical ozone formation and act as a transport mechanism for reactive nitrogen. Less reactive nitrogen containing species such as HCN and acetonitrile are important markers for biomass burning, while organic amines are involved in gas to particle partitioning. Finally N2O is a long lived nitrogen containing gas important for the Earth's radiative budget. Regular measurements of such nitrogen compounds would therefore be a significant contribution to the CARIBIC data set.

Especially for high altitude samples, in which the mixing ratios of many species are expected to be in the low ppt range, a highly sensitive method for analysis is required. Therefore a new system for measurement of nitrogen compounds has been built up, comprising a gas chromatograph (GC) using a nitrogen chemiluminescence detector (NCD). An important advantage of the NCD is that it is selective for nitrogen and equimolar. The nitrogen compounds are sequentially pre-concentrated, then focused cryogenically, and then separated by GC. The eluting nitrogen compounds are combusted to NO in a plasma burner and reacted with ozone to yield excited NO_2 which emits light in the near infrared detectable by a photomultiplier. The instrument set up and results of method characterization with acetonitrile,N2O and the first organic nitrate measurements of whole air samples will be shown.