



Stability of Halocarbons in UTLS Whole Air Samples in Stainless Steel Canisters

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Halogenated trace gases occur in the atmosphere at very low mixing ratios of only a few hundred parts per trillion or even less. Still, they have a significant impact on the atmosphere because many long-lived halogenated tracers are climate active gases with high radiative efficiencies. In addition, chlorinated and brominated halocarbons are responsible for stratospheric ozone depletion. Their mixing ratios are particularly relevant in the upper troposphere as it constitutes an entry point for transport of chlorine and bromine into the stratosphere.

Airborne measurements of halocarbons in the atmosphere often rely on canister sampling followed by offline laboratory analysis using gas chromatograph-mass spectrometry with sample preconcentration. This allows for a large number of compounds to be analyzed, however, individual gases might be affected during storage of the canister samples. In order to assess halocarbon stability in whole air samples from the upper troposphere and lowermost stratosphere, we performed stability tests using the air sampling unit High REsolution Sampler (HIRES) which is part of the CARIBIC (Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container) instrument package. HIRES holds light-weight stainless steel cylinders that are pressurized in flight using metal bellows pumps.

The HIRES sampling unit was first deployed in 2010, but has up to now not been used for halocarbon analysis. It was now tested for sampling and storage effects on halogenated compounds. The focus was on compound stability in the stainless steel canisters during storage of up to five weeks and on the influence of ozone, since sampling during CARIBIC flight takes place in the upper troposphere and the lowermost stratosphere with ozone mixing ratios of up to several hundred ppbV.

Most of the investigated (hydro)chlorofluorocarbons and long-lived hydrofluorocarbons were found to be stable over a storage time of up to five weeks and were unaltered by ozone being present during pressurization. Some compounds, such as for example dichloromethane, trichloromethane or tetrachloroethene, started to decrease in the canisters after a storage time of more than two weeks or exhibited too low mixing ratios in samples pressurized in the presence of ozone. Few compounds, such as for example tetrachloromethane or tribromomethane, turned out to be not stable in the HIRES stainless-steel canisters independent of ozone levels.