Cryogen-free fully automated preconcentration unit to enable $\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$ analysis

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Clumped isotope analysis is a powerful tool to constrain methane's origin in various geological, biogeochemical, and environmental settings. The extremely low abundance of $^{12}\text{CH}_2\text{D}_2$ and $^{13}\text{CH}_3\text{D}$ isotopologues poses a challenge for the existing analytical systems. Mole fraction enhancement and cleaning of the environmental samples are necessary to fully exploit the potential of modern analyzers, requiring 50 to 1000 μmol of pure CH$_4$. To enable high-precision $\Delta^{12}\text{CH}_2\text{D}_2$ and $\Delta^{13}\text{CH}_3\text{D}$ analysis with dual-QCL (8.6 μm and 9.3 μm) absorption spectroscopy in a multipass cell (400 m), we have developed a new automated cryogen-free unit for methane Cleaning and Extraction – CleanEx.

The unit can process up to 18 liters of sample air at a high flow rate of 900 ml min$^{-1}$. Methane ($T_{BP} = -161 ^\circ\text{C}$) is separated from major air components on a high capacity trap filled with HayeSep D (Trap 1, $-176 ^\circ\text{C}$). Sequential desorption and transfer to a second trap (Trap 2, $-181 ^\circ\text{C}$) ensure complete O$_2$ and Ar removal. Substances with a higher boiling point, i.e., CO$_2$, N$_2$O, H$_2$O, C$_n$H$_{m+n}$, remain on Trap 1 to be removed at a later conditioning phase. CleanEx demonstrates equal performance for gas mixtures with initial methane mole fraction ranging from 2 ppm up to 2%. In contrast to the previously developed single trap TREX system (Eyer et al., 2016), atmospheric O$_2$ and Ar are effectively separated by cryo-focusing of CH$_4$ on the second trap. Ongoing work is focused on the separation of atmospheric gases with boiling points close to methane, e.g., Kr ($T_{BP} = -153 ^\circ\text{C}$).

We present the instrument design, performance, and details of its operation. Fractionation effects, methane recovery efficiency, and implications for high-precision $\delta^{13}\text{C-CH}_4$, $\delta\text{D-CH}_4$, $\Delta^{12}\text{CH}_3\text{D}$, and $\Delta^{12}\text{CH}_2\text{D}_2$ analyses are being discussed.

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