

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

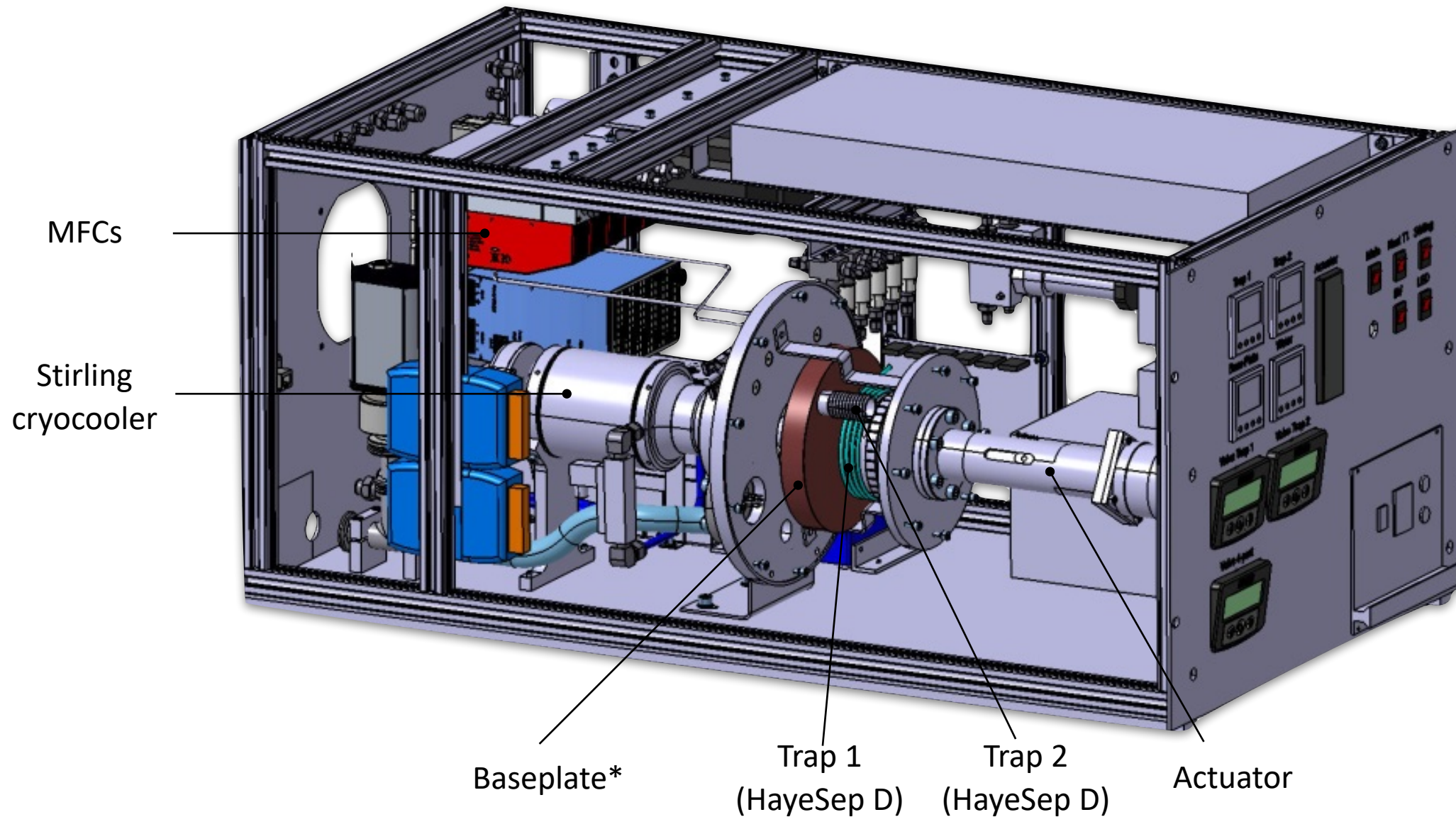
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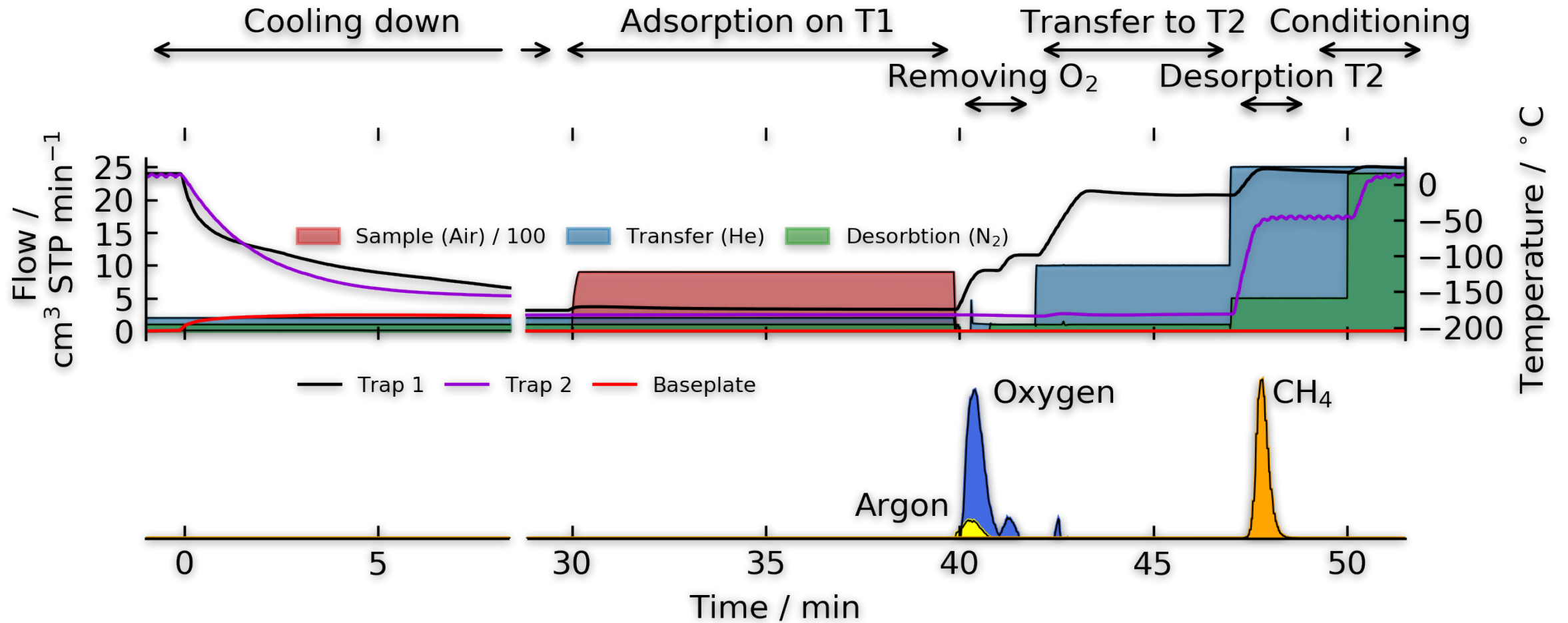


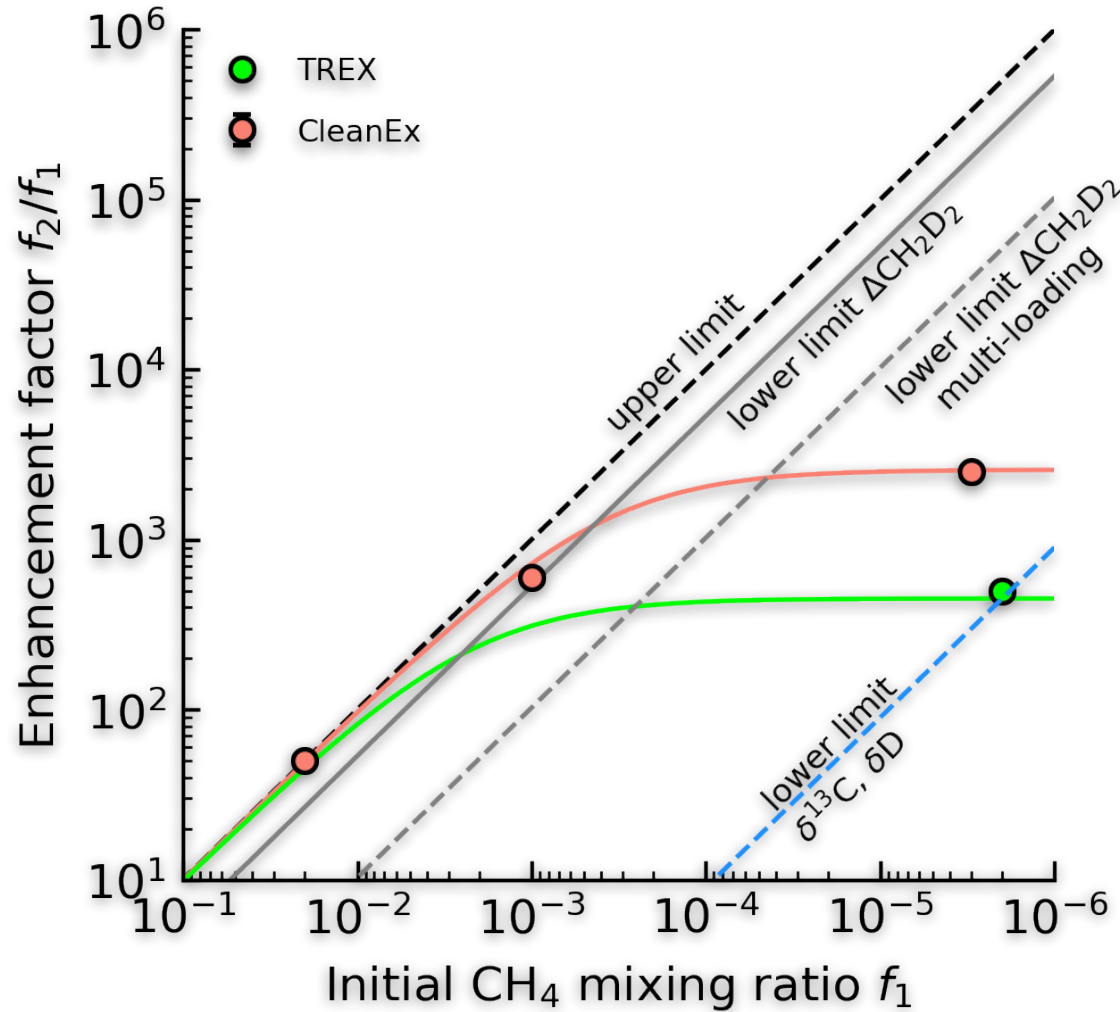
- Clumped isotope, $\delta^{13}\text{C}$, and δD analysis are powerful tools to constrain methane's origin in various geological, biogeochemical, and environmental settings.
- The extremely low abundance of doubly substituted $^{12}\text{CH}_2\text{D}_2$ ($1.44 \cdot 10^{-7}$) and $^{13}\text{CH}_3\text{D}$ ($6.92 \cdot 10^{-6}$) 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 .
- Remaining impurities bias spectroscopic analysis due to influence on spectral line shapes and potential spectral interferences. It is particularly relevant for oxygen, argon, and krypton.
- Sequential desorption of methane (boiling point -161.5°C) ensures complete separation from oxygen (-183°C), argon (-185.8°C), and substances with higher boiling points CO_2 , N_2O , H_2O , C_nH_m .

Methane *Cleaner* and Extractor (*CleanEx*)

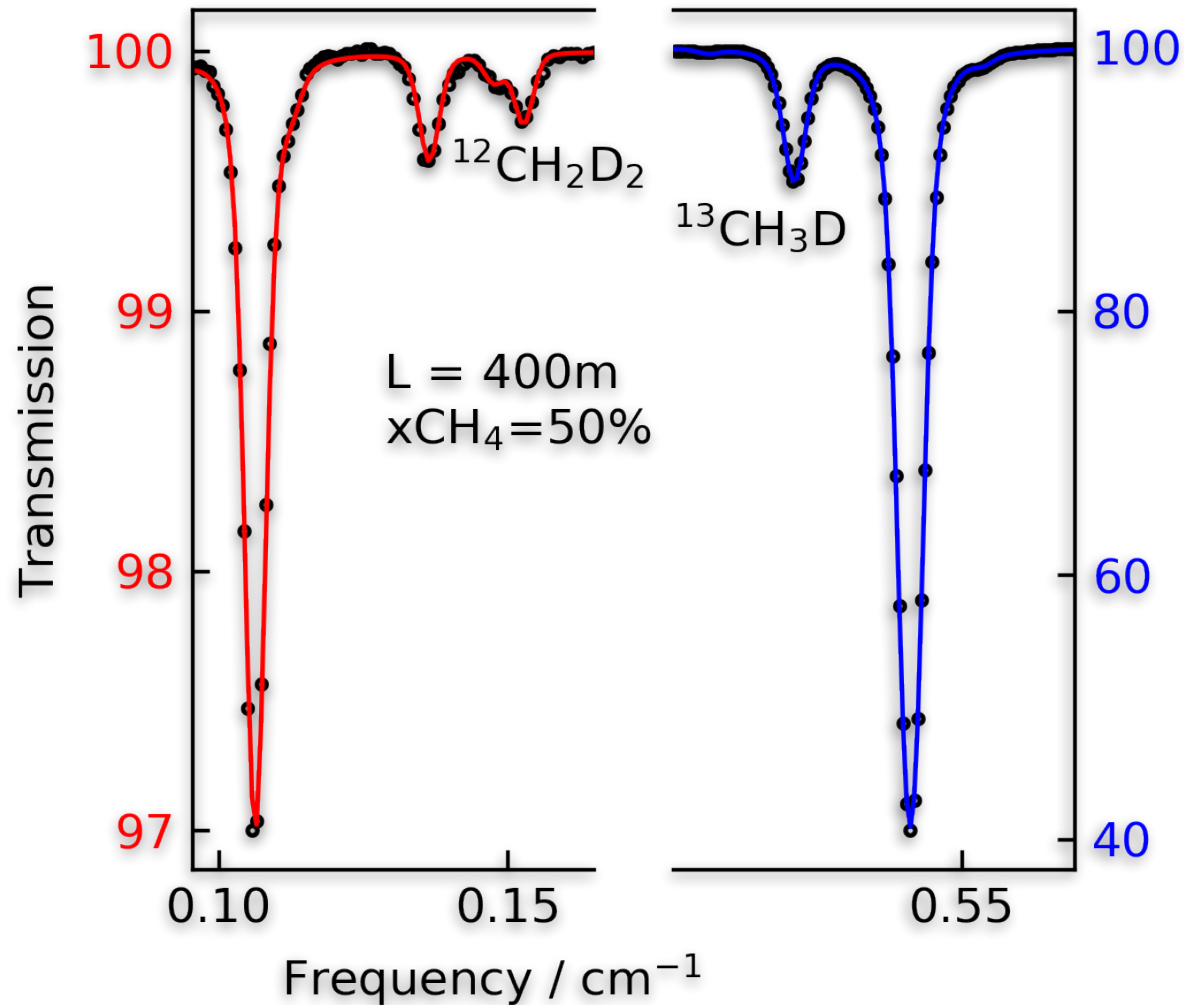


* vacuum chamber and pipings are not shown





- **Breakthrough volume of Trap 1**
 - 18 liters STP at -176°C
 - 11 liters STP at -166°C
- **Low volume of Trap 2**
 - Full desorption with 2 to 10 ml STP of N_2
 - Mole fraction enhancement up to 3'000 for atmospheric CH_4
- **Complete recovery**
 - >99% recovery has been demonstrated for atmospheric air samples
- **Reproducible amount fraction and isotope ratios in preconcentrated samples**



- **Multipass cell (MPC)**
 - Astigmatic Herriott-type cell
 - Volume 2000 cm^3
 - Optical path length (OPL) = 400 m
- **Quantum-cascade lasers (QCLs)**
 - Mid-IR spectral region
 - $\lambda_1 \approx 8.6\text{ }\mu\text{m}$, $\lambda_2 \approx 9.3\text{ }\mu\text{m}$
- **Gas inlet system**
 - Rapid switching between sample and reference gas

- We have developed a new preconcentration unit for CH₄ extraction and cleaning.
- High mole fraction enhancement of 3'000 for ambient air CH₄ combined with almost complete separation from other atmospheric gases enables automated monitoring of $\delta^{13}\text{C}$ and δD in atmospheric CH₄
- CleanEx can extract sufficient amount of CH₄ for doubly-substituted isotopologue analysis from samples with elevated methane mole fraction $>1000 \text{ nmol mol}^{-1}$

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