

Large-Volume Methane Separation and Purification for Clumped Isotope Analysis

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The study of the doubly-substituted (or “clumped”) methane isotopologues $^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$ offers new avenues for deepening our understanding of methane sources, sinks, reaction pathways, and formation temperature. Two measurement techniques are currently available for methane clumped isotope analysis: high-resolution isotope ratio mass spectrometry (HR-IRMS)^[1] and quantum cascade laser absorption spectroscopy (QCLAS)^[2,3]. Both techniques, however, necessitate thorough purification of methane to mitigate interferences from contaminants such as N_2 , O_2 , CO_2 , and higher alkanes.

Most published gas chromatography-based purification methods were designed for small methane volumes (< 5 ml) in HR-IRMS applications^[4]. However, QCLAS requires significantly larger volumes (10–25 ml) to achieve comparable precision, requiring method adaptation. Hence, processing CO_2 -rich gas samples—such as methane derived from ruminants, biogas/landfill sites, or carbonate rocks via acid dissolution—becomes particularly challenging, for instance, due to the problem of trap-clogging by CO_2 -ice and methane isotope fractionation by CO_2 -ice trapping.

We present a sample preparation method that employs cryogen-aided gas chromatography to purify larger methane volumes (≤ 50 ml) prior to clumped isotope analysis. For CO_2 -rich gas samples, our protocol includes an additional pretreatment step that utilizes an N-methyldiethanolamine (MDEA) solution to efficiently remove excess CO_2 in a closed-loop reactor.

We optimized and validated our method for quantitative methane recovery and minimal isotopic fractionation using a set of reference gases in a series of test measurements. Our results demonstrate high reproducibility and confirm that the isotopic signature of the processed methane is preserved within analytical uncertainties.

As a case study, we recovered methane from bituminous limestones through acid digestion, MDEA treatment, and gas chromatographic separation for QCLAS-based clumped isotope analysis. The obtained Δ -values align with the theoretical prediction of thermodynamic equilibrium^[5] and, therefore, combined with carbonate clumped isotope thermometry, are promising for reconstructing the thermal history of sedimentary sequences.

[1] Stolper, D. et al. (2014), *Geochimica Et Cosmochimica*

Acta 126, 169–191.

[2] Zhang, N. et al. (2025), *Analytical Chemistry* 97, 1291–1299

[3] Gonzalez et al. (2019), *Analytical Chemistry* 91(23), 14967–14974.

[4] Sivan, M. et al. (2023), *EGUsphere* 2023, 1–35.

[5] Eldridge et al. (2019), *ACS* 3, 2747–2764.