

Methane isotopologue measurements by high resolution IRMS

MATTHIEU CLOG¹, ROBERT ELLAM², ULF FROEHLICH³

¹SUERC, East Kilbride, United Kingdom,
matthieu.clog@glasgow.ac.uk

²SUERC, East Kilbride, United Kingdom,
rob.ellam@glasgow.ac.uk

³Thermo Fisher Scientific, Bremen, Germany,
ulf.froehlich@thermofisher.com

The development of high resolution stable isotopes mass spectrometry has broadened the field of possible investigation of position-specific and clumped isotopes. A few years ago the only common analytes were N₂O (for N-position-specific isotopic compositions) and CO₂ (for clumped isotopes). The main challenge was reaching high mass resolving power to separate the isotopologues that we may want to measure from isobars, which can be contaminants (e.g. water in the case of methane clumped isotopes), other isotopologues of the analyte or ions produced by source chemistry processes (fragments or adducts of the analyte are the most common). Additionally, the position of the ion beams in the image plane of the mass spectrometer has to be stable over timescales greater than the duration of an acquisition cycle. One of the key steps to reaching high resolution is using thin slits at the exit of the ion source, and optionally apertures further on the way towards the detectors. For the highest resolution, often more than 95% of the ions are then lost, which leads to long integration times to reach the necessary precisions to yield geochemically relevant information. Minute adjustments to magnet current may also be necessary to counter-act instrumental drift, which contributes to make high resolution measurements labour-intensive and limits sample throughput.

We present the results of hardware and software development of the ThermoFisher Scientific 253 Ultra platform, a double-focusing, multi-collection and high resolution (mass resolving power >40,000) IRMS. We observe drifts in peak position over 30 minutes of less than 1ppm. Through a system of automatic compensation, the exact position of the peak shapes in the image plane does not depend on the pressure of gas in the source, which alleviate the need for operator corrections during measurements. To illustrate those capacities, we set up a 0-enrichment measurement scheme with no operator intervention where we measured the ratio of (¹³CDH₃ + ¹²CD₂H₂ + adducts) over (¹²CH₄) for 8 hours. The final standard error reached was 0.05±/-0.1 permil (±/-0.08 expected from counting statistics), demonstrating the capability of making measurements at geochemically relevant precision and to reach a high sample throughput (4 hours to reach a precision of 0.25 permil on Δ₁₈) with less operator labour.