Overview

Purpose: The use of Thermo Scientific 253 Plus 10 kV IRMS technology in combination with the 10^13 ohm technology and LIDI software control to evaluate the one degree Celcius boundary, e.g. Clumped CO_2 isotope research (Eiler, 2007).

Methods: A Thermo Scientific Kiel IV Carbonate Device and a 253 Plus 10kV IRMS prototype (without 10^13 ohm technology) and a 253 Plus 10kV IRMS - equipped with low noise 10^13 ohm technology- were used to explore the new collector design including baseline monitoring and the new magnet design. We focused our research on low abundance clumped CO_2 using pure CO_2 gas and carbonate extracted CO_2 (100 ug to 1200 ug carbonate). The Long integration time dual inlet (LIDI; Hu et al. 2014) in combination with the 10^13 ohm technology has been optimized to improve the precision on clumped CO_2. All microvolume modes, e.g Kiel IV, have been run in LIDI workflow (Long Integration Dual Inlet). The Kiel IV has been equiped with an in-built, automated hydrocarbon cleaning trap (Schmidt and Bernasconi 2010).

Results: The 10^13 ohm technology significantly improves the signal to noise ratio for small ion beam measurements. Benefits in throughput and sample size reduction are seen if this technology is applied together with the LIDI software workflow. The new collector array with baseline detection and improved magnet design of the 253 Plus 10kV IRMS enhanced the precision to get results beyond the 2 degree boundary. In general, the 10^13 ohm technology and the baseline monitoring can be applied to similar isotopologue abundances, i.e. nobles gases (Ne, Ar, Kr, Xe), clumped O_2, Sulfur isotopologues (SFs).

Introduction

The clumped isotope application requires precise and accurate measurements of rare isotopologues on small sample sizes. Careful ion optical design investigations led to reshaping of the magnet which significantly improved peak shapes. The new collector design takes care about minor secondary effects that can be amplified together with the minor ion beam and shows best performance in baseline stability and clumped isotope temperature reconstruction.

Figure 1. The Thermo Scientific 253 Plus 10 kV IRMS.

Additionally, a Faraday cup between mass positions in the collector array is introduced to monitor the baseline during analysis (patent pending). A new software workflow, LIDI, is integrated into ISODAT Software Suite to support higher productivity, reduced sample consumption, improved sample utilization and hence increased sensitivity. The LIDI workflow allows analysis of smaller samples to enable high resolution studies. High-gain 10^13 ohm amplifier technology is integrated into the 253 Plus 10kV IRMS, to further reduce the amplifier noise by a factor of 3. These instrumental improvements will push the boundaries for clumped isotope applications as well as for GC-IRMS where sensitivity, precision, stability and low noise are key features for high precision measurements.
Sample Preparation
Commercial gas has been used for Dual inlet LIDI. ETH 1 to 4 clumped CO$_2$ calcite standards for the Kiel IV carbonate device were measured and data processed as in Meckler et al. 2014 and Kele et al. 2015.

Noise and decay of new 10$^{13}$ amplifier technology
Introduction of CO$_2$ gas for decay determination.

253 Plus ratio stability for 45/44, 46/44 and 47/44
Introduction of CO$_2$ gas for 2h with a signal decay from 5 to 4.7 [V] for 44-CO$_2$ and 7.7 [V] to 3V for 47-CO$_2$, (253 Plus sensitivity as specified, capillary valves open).

Baseline stability at the half mass cup
During 5 months ion beam peakshapes of mass 44-45-46-47-47.5-48-49 CO$_2$ were recorded before each sequence in steps from 5, 10, 15, 20, 25-30 [V] 44CO$_2$ and compared to the online baseline monitoring 47.5 cup (see 253 Plus 10kV IRMS brochure). We tested the statistical significance of the slope between the two to dependent regressions.

Microvolume simulation mode for Dual inlet with and without LIDI
253 Plus 10kV IRMS prototype: LIDI with Dual inlet ("signal depletion mode") and Kiel IV and Dual inlet with 60 cycles on sample side, 10 second block integration, for DI 10 acquisitions. 253 Plus 10kV IRMS: Microvolume simulations mode ("signal depletion mode"). A workflow has been applied to simulate a microvolume or a Kiel measurement. All Data processed in Easotope (John & Bowen, in preparation).

Precisely investigation of the 253 Plus 10kV IRMS amplifier system showed excellent three times better noise of the 10$^{13}$ ohm technology versus the 10$^{12}$ ohm amplifier system.

FIGURE 2. Johnson Noise of the 10$^{13}$ ohm technology and 10$^{12}$ ohm amplifier over 30 min.
Each Faraday cup is connected to an individual amplifier. As a consequence the 10$^{13}$ ohm technology provides
- Small ion beams amplification by the factor of 10
- A Johnson noise only amplified by the square root of 10
- A signal to noise ratio increase by a factor of 3
- Improved decay times with 10 times higher gain

FIGURE 3. Decay time of a 10$^{13}$ ohm amplifier (3 sec) ensures fast response time of smallest ion beam changes

253 Plus 10kV IRMS ratio stability
The signal to noise ratio of the 47-48 CO$_2$ ion beams resulted in excellent ratio stability. For 2 hours CO$_2$ constant signal depletion from 5 to 4.7 [V] 44-CO$_2$ a 45/44 ratio stability of better than 0.5 ppm and of better than 0.65 for 46/44 have been achieved. The 253 Plus had an internal precision of 5.6 ppm for the 47/44 ratio with an signal intensity of 7.5 [V] on 47 at 10$^{13}$ ohm amplification, i.e. 5 [V] 44-CO$_2$.  

Conclusion
- Improved baseline stability and low noise are key features for high precision as well as for GC analysis (patent pending). A new software workflow, LIDI, collector array is introduced to monitor the baseline during measurements. All Data processed in Easotope (John & Bowen, in preparation).
- High peak shapes. The new collector design takes care about the signal to noise ratio for small ion beam measurements.
- In general, the 10$^{13}$ ohm technology and LIDI enhanced the precision to get results beyond the 2 degree boundary. In general, the 10$^{13}$ ohm technology and LIDI enhanced the precision to get results beyond the 2 degree boundary.
- 10$^{13}$ amplifier technology and LIDI technology and LIDI exemplifies its capability to decrease the sample consumption.
- Over the agreement to the ratio stabilities shown above. Over the agreement to the ratio stabilities shown above.
253 Plus 10kV IRMS baseline monitoring

As expected we found perfect statistical relationship of the two regression slopes, the off peak detected baseline (ETH PBL) and the online baseline monitoring at mass 47.5 (n = 47, >= 5 months). Consequently, the automated baseline monitoring is indistinguishable from the off-peak detection.

FIGURE 4. Linear regression slope of the 47.5 monitor cup versus the off-peak baseline detection. The mean 47.5-CO$_2$ baseline cup detection from 5 to 30 [ V ] 44 CO$_2$ has been -3.78 [mV] with a mean standard deviation of 0.9 [mV] over three months.

253 Plus 10kV IRMS - $\Delta^{47}$ reproducibility with 10$^{13}$ ohm technology and LIDI

An excellent $\Delta^{47}$ and $\Delta^{48}$ reproducibility is in perfect agreement to the ratio stabilities shown above. Over the whole range of signals the 10$^{13}$ ohm technology exemplifies its capability to decrease the sample consumption.

Table 1. $\Delta^{47}$ and $\Delta^{48}$ reproducibility of CO$_2$ reference gas measured at 10$^{13}$ ohm amplification, with LIDI workflow and microvolume simulation.

<table>
<thead>
<tr>
<th>44-CO$_2$ [V]</th>
<th>47-CO$_2$ [V]</th>
<th>raw $\Delta^{47}$CO$_2$</th>
<th>raw $\Delta^{48}$CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 to 12.5</td>
<td>30.5 to 20</td>
<td>0.094</td>
<td>0.261</td>
</tr>
<tr>
<td>15 to 9.7</td>
<td>22.6 to 15.3</td>
<td>0.036</td>
<td>0.679</td>
</tr>
<tr>
<td>10 to 6.8</td>
<td>15.0 to 8.7</td>
<td>0.02</td>
<td>0.844</td>
</tr>
<tr>
<td>7.5 to 5.2</td>
<td>11.5 to 8.1</td>
<td>0.043</td>
<td>0.425</td>
</tr>
<tr>
<td>5 to 3.6</td>
<td>7.7 to 5.5</td>
<td>0.055</td>
<td>0.418</td>
</tr>
<tr>
<td>Mean</td>
<td>0.050</td>
<td>0.525</td>
<td></td>
</tr>
<tr>
<td>1-sigma</td>
<td>0.027</td>
<td>0.230</td>
<td></td>
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</tbody>
</table>

Our collaboration partner from the ETH Zürich evaluated the reproducibility and temperature reconstruction with a 253 Plus 10kV IRMS prototype.

FIGURE 5. Offset from the accepted $\Delta^{47}$ value of ETH 1 to 4 standards. Each data point is one of the standards, treated as an unknown and averaged over 1 to 2 consecutive days (LIDI run, 8 to 12 aliquots of 100 µg, consecutive over two month, February-March ‘16).

FIGURE 6A. Aliquots to reach statistical significance on $\Delta^{47}$ of natural samples (100 µg per aliquot). B. Sample material, aliquots and $\Delta^{47}$ results with inferred temperatures. Note: The different temperature calibration for corals has not been applied.
Conclusion

- Stability in isotope ratios from low abundance isotopologue signals is a result from the improvements in peak flatness over the full simultaneous mass range of the 253 Plus 10kV IRMS, i.e. the new magnet design, the new collector arrays with baseline monitoring, low noise 10^{13} ohm technology and the new software LIDI measurement mode.

- The automated baseline monitoring and the 10^{13} ohm technology make it possible to develop new correction schemes for applications with low abundance isotopologues, e.g. 48-CO\textsubscript{2} clumped, noble gas, O\textsubscript{2} clumped, SF\textsubscript{6}.

- The 10 kV IRMS system (253 Plus) operated with Kiel IV Carbonate Device in LIDI workflow and proved it is possible to analyse smaller sample weights and to improve the throughput. With those prerequisites it allows to reach the 1 degree temperature reconstruction with the clumped CO\textsubscript{2} carbonate measurement.

References

5. Kele et al. 2015, GCA, 168, 172-192