

## Do you need a PBL on a 253 Plus? Uncertainty in $\Delta 47$ measurements

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Carbonate clumped thermometry relies on the precise and stable measurement of  $m/z$  44 through 47 of both sample and standard  $\text{CO}_2$  gas over weeks to months. Stability and precision of standard (gas or carbonate) measurements are necessary to create an instrument-specific  $\delta_{47}$ - $\Delta_{47}$  reference frame. The stability of this reference frame determines the absolute accuracy with which any precise sample measurement can be converted into a temperature for that given run period. He et al.<sup>1</sup> introduced a pressure baseline (PBL) measurement and correction on a MAT 253 resulting in an instrument reference frame that was stable for longer periods of time, in addition to correcting out non linearity for flatter reference gas lines. The original PBL approach involves measuring off-peak signals while the reference and sample gas are flowing to ascertain the negative voltage well associated with the on-peak voltage of each Faraday cup. Two hardware changes of Thermo Scientific's 253 Plus are intended to eliminate the causes of negative baseline as well as monitor the baseline without peak hopping through the addition of a half-mass cup between the  $m/z$  47 and 48. One issue this new half mass cup introduces is the need to intercalibrate the  $m/z$ 47 Faraday with the  $m/z$ 47.5 Faraday, which typically do not see the same ion beam.

Here, we present a method for inter-cup calibration that directly compares the 47 and 47.5 Faradays. The Isodat script collects data while directing a beam from one cup to the other. Data from each cup are then linearly fit to an arbitrary time ( $t_0$ ) so that the intensities can be compared directly, correcting for decreasing signals due to consumption from a finite bellows ("bleed out"). This script is run at multiple voltages, 0-16mV, ultimately creating a cup 47 intensity vs. cup 47.5 intensity data set that allows for comparison of either cup and amplifier circuitry at any signal intensity. Our new data from the Thermo Scientific 253 Plus demonstrate that negative baselines are still present, but here they must be caused by something other than the  $\text{CO}_2$  ion beam clipping the flight tube<sup>1</sup>. We detail a method for correlating the off-peak hopping method of PBL measurement with the simultaneous collection of "half-mass" data. We will also show the long-term effect (6 months of data) of applying a scaled correction with the new  $m/z$  47.5 cup.

1. He, B., Olack, G. & Colman, A. Pressure baseline correction and high-precision  $\text{CO}_2$  clumped-isotope ( $\Delta_{47}$ ) measurements in bellows and micro-volume modes. *Rapid Commun. mass Spectrom.* **26**, 2837–53 (2012).