

## Introduction

The analysis of multiply substituted isotopologues of CO<sub>2</sub>, or “clumped isotopes” as it is known colloquially, has recently gained world-wide acceptance as a useful tool in paleothermometry as well as atmospheric science. However, the application of clumped isotopes presents significant challenges, in terms of the analysis, since the relative abundance of multiply substituted isotopologues is substantially lower than singly substituted isotopologues (see Application Note 025 for further information). It is also a crucial requirement that the isotopic ratio of the multiply substituted isotopologues are analysed to extremely high precision (on the order of < 0.015 permil) in order to be a useful paleothermometer. Up until now, all successful measurements in the field have been performed using large radius, high sensitivity IRMS instruments as described by Huntington et al. However, these large instruments present significant entry barriers to the field of clumped isotopes due to the large capital investment that is required to purchase these instruments.

## Perceived requirement for ‘large’ IRMS

As discussed previously, all useful measurements of clumped isotopes have so far been performed with instruments that are of large resolution ( $m/\Delta m \approx 200$ ), large mass dispersion (>400mm), and high accelerating voltage (>8kV). However, even these “large” instruments are not sufficiently powerful enough to resolve isobaric contaminants which may interfere with the analysed ion beams, which implies that the additional resolving power is of no additional benefit. The large mass dispersion is similarly non-advantageous, as all IRMS instruments are capable of simultaneously analysing CO<sub>2</sub> masses of 44, 45, 46, 47, 48, 49. Higher accelerating voltages imply a greater ionisation efficiency, and so greater molecules/ion sensitivity. However, source sensitivity must also be considered alongside the capability of the instrument to efficiently introduce the sample and reference gas from the dual inlet system as well as the ion source architecture to give a “real-life” molecules/ion sensitivity.

In this applications note we are able to demonstrate that the IsoPrime100 IRMS, which is specifically designed to be a compact, bench-top IRMS ( $m/\Delta m \approx 100$ ; dispersion >100mm; accelerating voltage = 5kV) is capable of operating at exactly the same level of performance as that which is described by Huntington et al. As such, the IsoPrime100 IRMS offers a viable alternative to high cost instrumentation with no compromise, in terms of precision, of the clumped isotope measurements.

## Results

For several weeks, an IsoPrime100 IRMS system equipped with a modified collector array for masses 44 – 49 has been under investigation for its performance of clumped isotope measurements. Except for the additional collectors and associated amplifiers, the instrument is as standard. For more detailed discussion of the IsoPrime100 configuration for clumped isotopes, see Application Note 025.

Initial testing of the IsoPrime100 IRMS system has focussed on achieving high precision 47/44 ratio measurements in the shortest time possible. After pumping out of the previous sample, a 50 μmol volume of CO<sub>2</sub> (approximately equivalent to 8mg of carbonate material) is introduced into the sample bellows of the dual inlet system. The sample bellows are then balanced to give a 60nA beam as registered through the mass 44 amplifier.

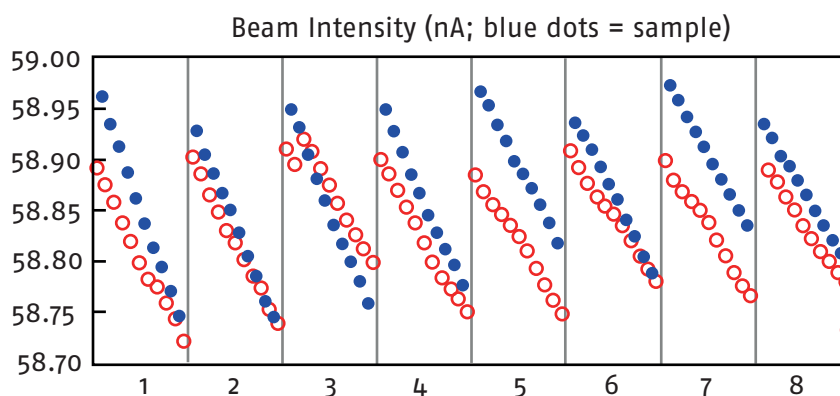


Fig. 1 – Changeover sequence of a single sample

The reference bellows are filled with the same CO<sub>2</sub> as the sample bellows to enable a “zero enrichment” analysis. The reference beam is then matched to the same beam size to an accuracy of 0.2%. Following a period of stabilisation, the instrument then performs 22 changeovers between sample and reference gasses. Each changeover is 32 seconds and the first 6 seconds following the changeover are not integrated to allow the beam to stabilise. Following the changeover sequence, the beam balancing process is repeated and then reanalysed. This is repeated 8 times and the overall precision of the measurements is calculated. The resultant beam intensities are shown in fig 1 below.

The beam intensities of masses 44, 45, 46 & 47 for each changeover are then integrated and the corresponding molecular ratios  $\delta_{45}$ ,  $\delta_{46}$ ,  $\delta_{47}$  are determined. By declaring the bulk isotope composition of the reference gas nominally as  $\delta^{13}\text{C} = 0.00\text{‰}$  (VPDB) and  $\delta^{18}\text{O} = 0.00\text{‰}$  (VSMOW) the resultant elemental ratios are determined and presented in fig 2 below:

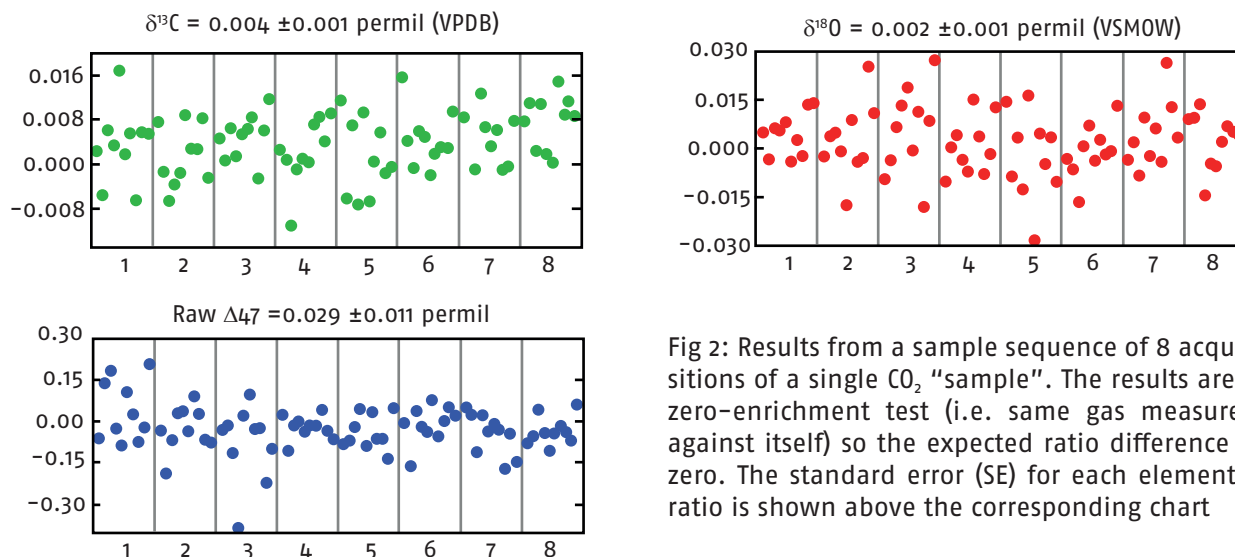


Fig 2: Results from a sample sequence of 8 acquisitions of a single CO<sub>2</sub> “sample”. The results are a zero-enrichment test (i.e. same gas measured against itself) so the expected ratio difference is zero. The standard error (SE) for each elemental ratio is shown above the corresponding chart

The total analysis time for the sample sequence presented in Fig 2 is 1h 50m. In this time  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  performed to very high levels of precision with no isotopic off-set between reference and sample side of the dual inlet. More importantly, a standard error in raw  $\Delta_{47}$  of 0.011‰ is achieved with good accuracy. When compared to the standard analysis described by Huntington et al. it is clear that this level of precision in less than two hours is comparable with the performance of a large radius instrument.

One aspect of the IsoPrime100 which is of particular interest, is the robust nature of the measurements. Following a period of maintenance which involved venting of the IRMS analyser, the IsoPrime100 was able to perform at the same level of precision less than 24hours after the maintenance was completed following a bakeout of the analyser. This demonstrates excellent reliability in this very demanding field.

## Conclusion

The IsoPrime100 IRMS system has consistently performed at a SE for  $\delta_{47}$  of  $\leq 0.015\text{‰}$  over a number of weeks proving that the instrument is capable of analysing clumped isotopes to the same level of precision as the worlds leading laboratories. This presents the IsoPrime100 as a viable low-cost alternative to large radius IRMS.

However, further work is needed to quantify the IsoPrime100 IRMS system. This being:

Quantification of the amount of fractionation/recombination (or scrambling as it is commonly known) of the CO<sub>2</sub> molecule which occurs through the dual inlet capillaries and in the ionisation source. Preliminary testing has shown that comparable levels of scrambling to other systems is obtainable (See Application Note 039)

What size of carbonate CO<sub>2</sub> equivalent can be reasonably analysed to high precision? Again, preliminary testing has shown that 2mg carbonate equivalents can be analysed, though at a reduced precision. Further optimisation will hopefully improve the precision for low sample amounts further.

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### IsoPrime100 Applications



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