

$\delta^{13}\text{C}$ AND $\delta^{18}\text{O}$ ANALYSIS OF VERY SMALL CALCIUM CARBONATE SAMPLES ON THE PERSPECTIVE IRMS WITH NUCARB AUTOMATED CARBONATE DEVICE DEMONSTRATING OUTSTANDING LINEARITY AND PRECISION

Introduction

Further to Application Notes AN28 (Routine batch analysis using NuCarb) and AN20 (Small sample analysis of carbonates using NuCarb), the lower limit of sample size that can be analysed with the NuCarb automated carbonate device was investigated. A range of carbonate samples (weight 4 μg to 41 μg) were isotopically analysed using the NuCarb interfaced to the Perspective IRMS.

Settings for sample analysis

33 samples of Nu Carrara marble (NCM grain size 60 μm – 90 μm) and 3 samples of NBS-19 were measured into open top vials and placed into the carousel of the NuCarb. The standard operating parameters were used (see AN28 for further details); the samples were allowed to warm up to the oven temperature of 70°C. Each vial was pumped to high vacuum, and then 120 μl of phosphoric acid was automatically added to the vial. The CO_2 produced was frozen into the 'Prep' cold finger at -170°C, while water was removed using a water trap held at -93°C. The CO_2 was then frozen into the Perspective Dual Inlet cold finger and then analysed by the Perspective against Tank CO_2 reference gas. The acquisition was made with 12 sample / reference changeovers. The integration period was 20 s and the delay after changeover was 12 s.

Results and Discussion

Figure 1 shows the initial sample ion current ($\propto \text{CO}_2$ volume) against the measured sample weight.

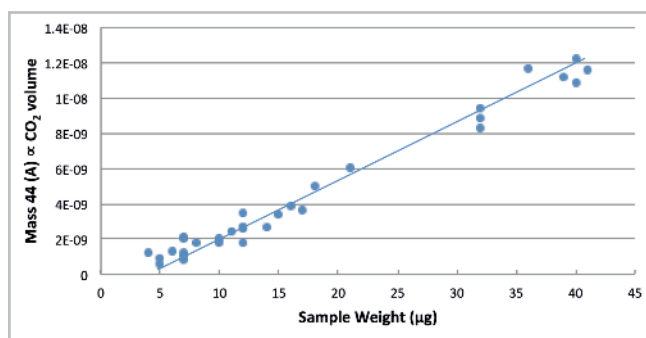


Figure 1: NCM and NBS-19 initial sample ion current vs. weight

The yield of CO_2 from a sample is given by the volume of CO_2 produced divided by the sample weight. This figure shows that the CO_2 yield from the NuCarb is constant when the sample weight is > 10 μg . Below this weight the yield reduced slightly.

The reference bellows were set up to provide a wide range of reference ion current from 1.1 nA to 7 nA. Five extremely small samples (around 5 μg) yielded less than 1.1 nA initially and were rejected for isotopic analysis as the ion currents could not be

balanced. If less reference gas was used these smaller samples could be analysed. Two samples were also rejected because their sample yields were reported as unusually low, suggesting that they had not been processed correctly.

The summary of isotopic values found are shown in Table 1.

Sample	Raw δ_{45}	Raw δ_{46}	μg	n
NCM	36.60	25.62	4 – 41	26
1 σ	0.04	0.04		
NBS-19	36.47	25.35	32– 41	3
1 σ	0.02	0.03		

Table 1: Raw δ w.r.t. tank CO_2 reference gas

The data was then corrected w.r.t. vpdb and is plotted in Figure 2.

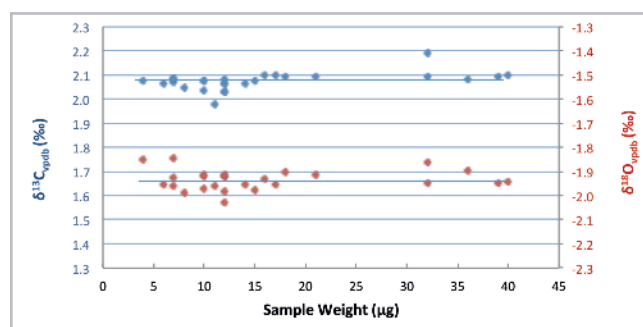


Figure 2: Analysis of NCM weight 4 μg – 41 μg

weight μg	$\delta^{13}\text{C}_{\text{vpdb}}$	$\delta^{18}\text{O}_{\text{vpdb}}$	n
4 – 10	2.07 \pm 0.02	-1.92 \pm 0.05	9
11 – 20	2.06 \pm 0.04	-1.95 \pm 0.04	11
21 – 41	2.11 \pm 0.04	-1.92 \pm 0.04	6

Table 2: Results of a single batch of Nu Carrara Marble standard

Conclusion

This data shows outstanding linearity and precision over the full weight range in the batch. The latest generation Perspective with NuCarb promotes exciting new possibilities for routine small sample carbonate analysis.