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Perspective Note **PS03**

Routine Batch Analysis Performance Using Nu Carb Automated Carbonate Device

Introduction

The Nu Instruments Nu carb automated carbonate device interfaced to the Nu Instruments Perspective IRMS has been applied to the measurement of multiple batches of the same carbonate sample using the same reference gas. A number of important analytical characteristics of interest to the user are evaluated and discussed. Characteristics such as long term isotope measurement precision, rate of sample throughput, rejected sample frequency and instrument setup parameters will be discussed.

Long term stability measurements were also undertaken by a second Nu carb device interfaced to the same IRMS and the data sets generated by both devices are compared.

Figure 1: Nu carb

Instrumentation

Figure 1 shows the Nu carb automated carbonate device. Up to 50 individual carbonate samples contained in glass vials are sequentially analysed. Once evacuated, a user defined quantity of phosphoric acid is dispensed into the vial using a simple injection system, and the resultant CO_2 from the acid/carbonate reaction is transferred cryogenically to an external cold-finger at -196 °C. Water from the reaction is trapped in a high efficiency water trap at -85 °C. The yield of CO_2 evolved is measured using a baratron pressure transducer, after which the sample is transferred to the micro dual inlet. Isotopic measurement is then performed on the high resolution, high sensitivity Perspective IRMS. Total turn round time between batches can be as low as 20 minutes if a second preloaded carousel has been prepared.

Table 1

nucarb Operating Parameters	
Reaction temperature	70° C
Vial pumpout time	120 s
Quantity of acid injected	120 µl
Reaction time	800 s
External trap release temperature	-70° C
Transfer time to micro dual inlet	180 s
Dual inlet trap release temperature	-20° C
Acquisition temperature	Ambient
Data Acquisition Parameters	
Number of sample/reference	12
Integration period	20 s
C/O delay	12 s

Analysis: Batch and sample size considerations

Although the combination of Nu carb and the Perspective IRMS is capable of sub 10 µg carbonate analysis, there are applications where available sample size (within reason) is not restricted. For example, the analysis of growth bands in coral involves the use of micro milling techniques to generate large numbers of calcite samples typically between 30 and 60 µg. To demonstrate the ability of the Nu carb-Perspective combination in addressing applications of this kind, the decision was made to analyse multiple batches of carbonate samples in the weight range 25-110 µg. The carbonate chosen was a carrara marble that was ground and sieved to a size range of 60-90 µm.

Reference Gas Introduction

As part of the batch analysis sequence, the dual inlet reference gas bellows are refilled after every 10 samples from a large (5 litre) capacity container of reference CO_2 obtained from reacting carrara marble with phosphoric or equivalent acid. Each container has sufficient gas to provide reference refills every 10 samples for more than 10000 samples.

Table 2 shows the overall data from both Nu carbs 1 and 2, including number of samples and number of rejected samples for each prep system. The data shows an extremely high degree of equivalence between the two prep systems as well as the reliability of measurement. The individual data points were generated from a total number of 15 batches for Nu carb 1, and 24 batches for Nu carb 2. The number of rejected samples is small, and the longest sequence of samples without a rejection occurring is 480 in Nu carb 2. The results quoted are for the raw, uncorrected δ^{45} and δ^{46} values. Note that this value does not change over time or between prep systems.

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Table 2

External Sample Stastistics						
	No	δ^{45}raw	1 σ	δ^{46}raw	1 σ	rej.
Nu carb -1	570	-0.10	0.03	-0.42	0.03	3
Nu carb -2	1009	-0.08	0.02	-0.44	0.04	9
Total	1579					12

Sample size versus raw delta

Sample sizes ranging from 24 -104 µg of carrara marble with a sieve size of 60-90 µm were routinely analysed. Figure 3 shows the results for all 1567 individual data points.

Long term reproducibility data

Figure 2 illustrates the long term reproducibility obtained by the Nu carb for a total of 39 batches of samples analysed over the time period 6 March 2013 to 09 July 2013. Two different Nu carb units were used, the transition occuring between 03 April and 05 June. Each batch contained an average of 40 samples. A comparison of batch average values gives a standard deviation in average value of 0.012‰ δ^{45}_{raw} and 0.024‰ δ^{46}_{raw} across all batches.

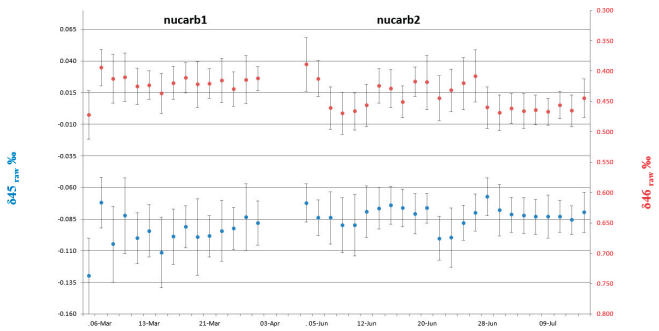

Figure 2: Long term reproducibility of Nu carb batch analysis

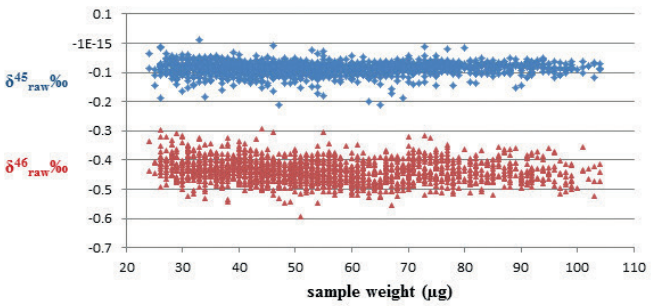

Figure 3: Routine analsis of 24-104 µg carbonate samples

Sample Yield

Sample Yield is a measure of the amount of CO2 generated by the carbonate-acid reaction and is an important parameter. Low yields can be an indication of either: An incomplete reaction between the sample and acid, or that some of the sample has been lost. Losing sample could occur if, in the initial vial evacuation stage, the rate at which air was evacuated caused the small sample grains to move or scatter in such a manner that the acid could not make contact and react. To avoid this possibility, a slow pump facility has been incorporated into the Nu carb design. Figure 4 shows a typical response of the baratron pressure transducer measurement, with respect to sample weight and shows that the response is linear across the size range.

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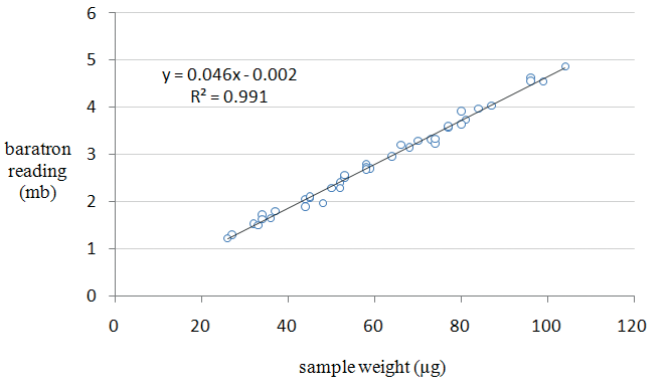

Figure 4: Baratron response vs sample weight

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Conclusion

The Nu Instruments Nu carb automated carbonate device with the Nu Perspective IRMS was tested for routine carbonate analysis performance. 39 batches of carrara marble samples ranging in size from 24 to 104 µg with an average 40 samples per batch and a total of 1579 samples, were analysed. Two Nu carb systems were used, each in turn attached to the same mass spectrometer using the same reference gas and dual inlet sample analysis protocol. Nu carb 1 analysed 15 batches, whilst Nu carb 2 analysed 24 batches. The system is highly reliable with only 12 samples that failed to be analysed in close to 1600 analysis. The external standard deviation of the mean δ^{45}_{raw} and δ^{46}_{raw} values for all 39 batches is 0.01‰ and 0.02‰ respectively, illustrating the long term reproducibility of the Nu carb measurements.