

RAPID NANOMOLAR STABLE ISOTOPE MEASUREMENTS OF NITROGEN AND CARBON FROM ORGANIC SAMPLES

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As part of an ongoing project to measure $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of tetrapyrrole pigments and their derivatives from sediment extracts, we developed a method to decrease sample size requirements for continuous flow elemental analyzer-isotope ratio mass spectrometer (EA-IRMS) systems. Effluent nitrogen and carbon dioxide from the EA are trapped on a silica gel packed column (30cm, 0.75mm ID stainless steel) immersed in liquid nitrogen. The trapped gases are then released in a 1-2 ml min⁻¹ flow of helium by heating to 115°C. Finally nitrogen and carbon dioxide are separated on a carbon PLOT column and introduced to our Finnigan MAT Delta^{plus}XP mass spectrometer through a ConFlo III interface. A single sample can be analyzed for both nitrogen and carbon in 12 minutes, making this system preferable to offline trapping methods for small samples.

We minimized the nitrogen background blank from the EA by reducing the inner diameter of the oxidation and reduction furnaces (Carman and Fry, 2002) and the water trap thus decreasing the mixing volume of the system as well as the required trapping time. We also installed a low-flow bleed valve on the EA autosampler to eliminate the effect of leaks associated with the autosampler seals during sample runs. As a result, the nitrogen blank measured on the mass spectrometer has a magnitude of 87±2 nanomoles N₂ and $\delta^{15}\text{N}$ value of -6.13±0.11‰ (vs. N_{air}). Analyses of samples in the 200-400 nanomole N₂ range yielded a precision of 0.2‰ while samples as low as 60 nanomoles N₂ achieved a precision of 0.5‰. The carbon blank is much smaller (6±3 nanomoles, $\delta^{13}\text{C} = -23.95 \pm 1.22\text{‰}$ VPDB) but also less stable in both size and isotopic composition. Most of the organic materials we analyze for carbon and nitrogen have high C/N ratios so the carbon blank is at least 2 orders of magnitude smaller than the sample and thus does not significantly affect the $\delta^{13}\text{C}$ measurements. With improved carbon blank, we anticipate sample sizes for carbon that can be run in the absence of the helium dilution from the ConFlo III interface.

These new modifications reduced the minimum sample size requirement from ~1000 nanomoles N₂ on the conventional EA system to 60 nanomoles N₂ on our “nanoEA” system. This ~15-fold decrease in sample size enables compound-specific coupled $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements on large molecules such as chlorophyll *a* that are incompatible with GC-IRMS.

The presentation will focus on isotopic measurements of whole extracts and pigment fractions collected after separation using a high performance liquid chromatography quaternary solvent gradient system (Airs et al., 2001).

REFERENCES

- Airs R.L., Atkinson J.E., Keely B.J., 2001. Development and application of a high resolution liquid chromatographic method for the analysis of complex pigment distributions. *Journal of Chromatography* 917, 167-177.
- Carman K.R., Fry B., 2002. Small-sample methods for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis of the diets of marsh meiofaunal species using natural-abundance and tracer-addition isotope techniques. *Marine Ecology Progress Series* 240, 85-92.