EA-irms of sub-micromolar C samples: Concentration and $\delta^{13}C$ of DOC in sediment pore water

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Driven to Discover
Objectives

• Elemental Analyzers coupled with IRMS in their “standard configuration” typically require samples with ~ 30 to 600 µg carbon for $\delta^{13}$C analysis. Performances of two commercial EA-irms systems were evaluated analyzing precise amounts of organic C standards in sub-micromolar range

• Evaluation of carbon backgrounds of tin and silver capsules of various sizes

• Application of sub-micromolar EA-irms: Concentration and $\delta^{13}$C of DOC in sediment pore water (with DOC ~ 2 to 30 mg.L$^{-1}$ and sample volume < 10 mL)
Instrumental setup

**LLO-UMD setup:**
- *Thermo Delta Plus XL IRMS*
- *Conflo-II interface*
- *Costech ECS4010 with Pneumatic autosampler*

**EPS-Northwestern setup:**
- *Thermo Delta V Plus IRMS*
- *Conflo-IV interface*
- *Costech ECS4010 with Zero Blank autosampler*
Preparation of primary standard and DOC samples

• Primary DOC standards were prepared by dissolving IAEA CH-6 Sucrose ($\delta^{13}C \approx -10.45\%_{oo}$) in de-ionized water, to a concentration of 0.3 $\mu g$ C. $\mu L^{-1}$

• Between 1 and 40 $\mu L$ of the primary standard solution were loaded in tin capsules and oven dried at 60 °C for 8 hours

• 2 to 10 mL of sediment pore water samples were taken in pre-combusted 10 mL glass vials, acidified to pH ~2 with dilute HCl, and evaporated to dryness in a vacuum oven at 60 °C. The residual organic matter were re-dissolved in 250 $\mu L$ of de-ionized water, loaded in tin capsules and dried at 60 °C for 8 hours

• DOC concentrations of the pore water samples were measured independently using a Shimadzu TOC Analyzer
Elemental Analyzer (Costech ECS4010) in CHN configuration

<table>
<thead>
<tr>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental Analyzer</td>
<td>Helium flow: 80 mL.min(^{-1}) 4 m SS GC column @80°C</td>
</tr>
<tr>
<td>Conflo (II / IV)</td>
<td>Helium pressure: 1.2 bar 0% sample dilution</td>
</tr>
<tr>
<td>MS ion-source</td>
<td>Delta Plus XL</td>
</tr>
<tr>
<td>Emission</td>
<td>1.00 mA</td>
</tr>
<tr>
<td>Trap</td>
<td>20 V</td>
</tr>
<tr>
<td>Electron energy</td>
<td>83 V</td>
</tr>
<tr>
<td>Extraction</td>
<td>50%</td>
</tr>
</tbody>
</table>

Oxidation furnace (980°C) -> Reduction furnace (650°C) -> Moisture trap -> GC (80°C)
EA-irms analysis of IAEA CH-6 Sucrose: C peak areas

Net area [mV s]

Delta V Plus
Delta Plus XL

6 µg C
Blank
Carbon backgrounds of tin and silver capsules

<table>
<thead>
<tr>
<th>Capsule type</th>
<th>Background [µg C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin (3.5×5 mm)</td>
<td>0.6</td>
</tr>
<tr>
<td>Tin (5×9 mm)</td>
<td>1.4</td>
</tr>
<tr>
<td>Tin (9×10 mm)</td>
<td>2.4</td>
</tr>
<tr>
<td>Silver (5×9 mm)</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Cleaned or un-cleaned tin capsules?

Area all [mV/s] vs. $\delta^{13}$C (‰)
Fitted curves: $y = y_0 + a e^{-bx} + c e^{-dx}$
EA-irms analysis of IAEA CH-6 Sucrose: $\delta^{13}C$ results
(corrected for non-linearity)

Correction eqn. : $\delta^{13}C_{corr} = \delta^{13}C_{meas} - (y_0 + a e^{-bx} + c e^{-dx}) + \delta^{13}C_{CH-6}$
Measurements of pore water DOC and $\delta^{13}$C

- Measured with Delta Plus XL IRMS with Pneumatic Autosampler
- Only for samples with > 3 $\mu$g C
DOC concentrations: IRMS vs TOC analyzer

DOC measured with IRMS were 30% lower than those with TOC analyzer (sample volatilization?)
Conclusions

• Both C amount and $\delta^{13}$C were analyzed in sub-micromolar range using a commercial EA-irms without any significant modification

• Precision of $\delta^{13}$C were better than ±0.2‰ for samples with > 3 µg C

• Carbon background in untreated tin capsules range from 0.6 to 2.4 µg C depending on size; silver capsules have ~ 75% more background C than tin

• Method applied to analyze concentration and $\delta^{13}$C of DOC in sediment pore water samples

• Potential applications of sub-micromolar EA-irms ($\delta^{13}$C in trace non-volatile solids):
  • aerosols
  • pollen grains
  • single microfossil shells
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