Performance of Isotope Ratio Infrared Spectroscopy (IRIS) for analyzing waters containing organic contaminants: Problems and solutions

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Chemical conversion of $\text{H}_2\text{O}$ (and contaminants)

- Contribution of contaminants is mass-dependent (unavoidable)

- No chemical conversion of $\text{H}_2\text{O}$

- Contribution of contaminants can be disproportionate to mass contribution (a positive and a negative feature)

Trace contamination may have huge effect

Some contaminants may be “invisible”
Alcohols interfere with H₂O isotope measurement on IRIS

- Alcohols (especially MeOH) cause large isotope errors
- Highly sensitive
- Quantitative contribution (for pure mixtures)

What about plant waters?

$\delta^2H$ and $\delta^{18}O$ of plant water is critical for:

**Biogeochemistry**
- water cycle
- ecosystem transpiration

**Paleoclimatology**
- tree rings, leaf waxes

**Forensics**
- provenance of materials etc....
Can we reliably measure plant water extracts with IRIS?

- Sampled leaves from 11 plant species
- Extracted water cryogenically
- Treated with activated charcoal

West et al. (2006) *RCMS* 20: 1317-1321
Direct comparison of IRIS and IRMS results

Identical sample sets analyzed on:

**IRMS**
1) TC/EA pyrolysis
2) Chromium combustion
3) CO\textsubscript{2} equilibration

**IRIS**
1) OA-ICOS (Los Gatos Research)

\[ \sigma \text{ for IRMS replicates} \]
\[
\begin{align*}
\delta^{2}\text{H} & \pm 0.4\%o \\
\delta^{18}\text{O} & \pm 0.1\%o
\end{align*}
\]

2) WS-CRDS (Picarro Inc.)
Large discrepancies between IRIS and IRMS

- effect seen for both IRIS instruments
- same relative magnitude, opposite sign
- species-specific effect

\[ \delta^2 H \text{ range} \approx 54\% \\
\delta^{18} O \text{ range} \approx 14\% \]

Example of environmental variation in $\delta^{2}H$ and $\delta^{18}O$
Errors not necessarily predictable, consistent

Sampling repeated
- Sept 2009
- Oct 2010

- temporal variation in contaminants?
Problems

1) Standard methods for IRMS not adequate for IRIS
2) Potential for major errors to occur in both $\delta^{2}H$ and $\delta^{18}O$
3) Not necessarily predictable, consistent

Solutions

Chemical conversion, purification?

Diagnostic software to flag bad samples
Does spectral analysis software catch bad samples?

- following identical methodology to first study
  - identified bad samples by comparison to IRMS
  - compared with samples flagged by software
Flagging software correctly identified major problems

- some false positives, some false negatives

- BUT both systems flag the obvious problems

- Standardization?
Conclusions

1) Our current methods for treating waters containing organics appear insufficient for IRIS
   • Potential for big errors (~ 50‰ $\delta^{2}$H, ~ 15% $\delta^{18}$O)

2) Development of pre-analysis treatment needed
   • Chemical conversion, purification?

3) Interference needs to be continually assessed
   • Spectral analysis software appears promising
   • Methods for standardizing and reporting?

4) Reporting of IRIS data?
   • Cross-checks with IRMS essential at present
   • International standards?

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