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Application Note – Tree Ring Measurements of $\delta^{13}C$ using Laser Ablation LA-IRMS

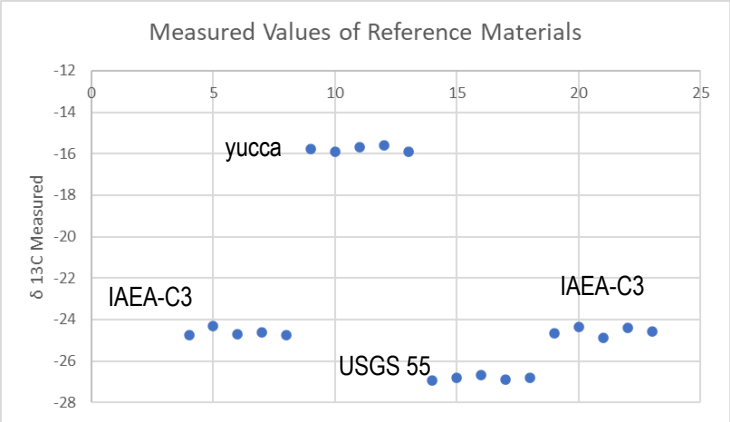
Variations of the stable carbon isotope composition ($\delta^{13}C$) of tree rings depend on multiple environmental and plant physiological factors that are still partly shrouded in mystery. A very fine resolution, intra-annual $\delta^{13}C$ analysis of tree-rings provides a necessary tool to assess the different dependencies. However, current conventional methods for analysing these intra-annual isotopic variations rely on time consuming manual or machine assisted separation methods and can be hindered by material restrictions in cases where the tree rings are very narrow.

To overcome these analytical challenges, the Sercon HS2022 IRMS and Cryoflex interface was coupled to a Teledyne CETAC Technologies LSX-213G2+ laser ablation system fitted with an IsoScell sample cell developed by Terra Analytic and used to analyse the $\delta^{13}C$ composition of three trees (*Pinus sylvestris*) from a forested area in central Finland. The system was installed at Natural Resources Institute Finland (Luke).
LA-IRMS allows the sampling of a tree ring *in situ* using a 213 nm laser, negating the time consuming and laborious manual slicing and weighing of the samples into tin cups for $\delta^{13}C$ analysis. For LA-IRMS analyses, the only required sample preparation steps are the smoothing of sample surface for laser beam focusing and the removal of mobile phases (resins). Further, LA sampling tracks can be easily positioned so that they accurately follow the cell structure of the tree-rngs as desired.

Picture1 Showing the sampling tracks of ablating laser over early and late wood of tree rings. Using this technique many measurements can be made on each tree ring.

Using tree stem growth data obtained from independent measurements, and by knowing the exact position of the laser sampling tracks, we can assign a timeline for the produced intra-annual $\delta^{13}C$ data series. The time resolved, high resolution $\delta^{13}C$ data will allow us to examine the environmental and physiological factors contributing to the changes in the $\delta^{13}C$ of tree-rings by comparing this data to climatological variables and to the carbon isotope composition of sugars (i.e. the building blocks of wood) extracted from needle, twig and phloem samples collected from the tree during the growing season.

Picture 2 The Sercon LA – IRMS system with Teledyne laser system.



Reference	$\delta^{13}C$, ‰/VPDB	Mean Measured $\delta^{13}C$, ‰/VPDB	SD	Difference
IAEA-C3	-24.55	-24.63	0.20	0.08
USGS 55	-27.13	-26.83	0.09	-0.30
yucca	-15.46	-15.77	0.13	0.31

Figure 1 Comparison of reference materials values

LA-IRMS Features

LA-IRMS requires much less sample preparation compared to traditional methods

No weighing of sample amount required as the amount of material sampled is a function of laser parameters

Easy to make replicate and retrospective measurements

High resolution sampling for temporal analysis, of e.g. wood, bone, teeth

Allows precious materials to be sampled with minimal deformation

Further analysis on the same sample is possible after LA-IRMS e.g. ICP-MS, AA

Data from the installed system was shown to give good agreement and precision with reference material values and with an in-house reference Yucca plant measured via EA-IRMS. After the method was established and optimised, measurements were made on the three tree-ring samples. $\delta^{13}C$ values were plotted and aligned to coincide with early- and latewood boundaries. The plot shows the clear variation of $\delta^{13}C$, over time and the large range $\delta^{13}C$ values.

The data shows good agreement of the general trends between the three trees. The distinct offset between tree 1 and the trees 2 and 3 can be accounted for by differences in environmental factors when the sugars were synthesized in the tree.

To summarize, the LA-IRMS gives good performance as an analysis technique in this application with some clear advantages over existing methods. The LA-IRMS method can also be adapted for analyzing the $\delta^{13}C$ in other types of solid organic materials by adjusting the instrument parameters.

Figure 2 $\delta^{13}C$ measured values of the three tree cores (unpublished data)

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