UV-Laser-Ablation-Combustion-GC-IRMS
a tool for on-line analysis of intra-annual variation of d13C in tree rings

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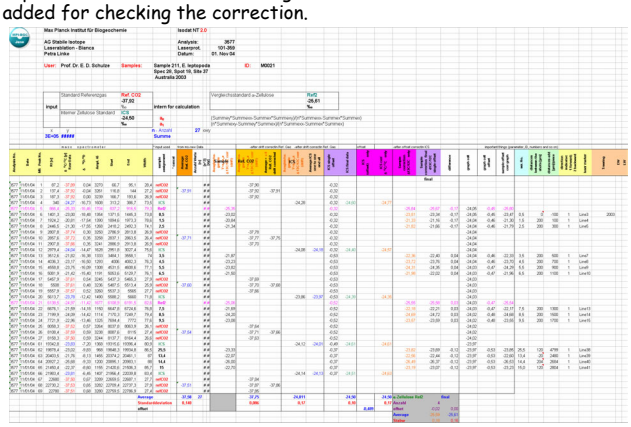
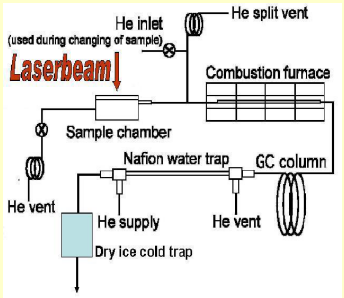
Principle and equipment

A UV-Laser (266nm Nd-YAG) is connected with an isotope mass spectrometer Delta^{plus}XL (Finnigan MAT, Bremen) via a home-made combustion interface. The system is continuously purged with a He-carrier-gas flow (10 ml/min). Every 8.5 minutes woody dust particles are ablated from a tree core. The resulting material is swept to the interface where it is combusted to CO_2 at 700 C. Inside the reactor an oxidized copper wire provides the oxygen for the combustion. The resulting CO_2 is separated from other gases in a GC-column (Haysep Q) and transferred to the mass spectrometer via an open split after removal of water vapour. The measurements are calibrated and checked with external CO_2 Standard gas, injected in the open split region, and in addition with internal cellulose standards which are also ablated by laser shots and combusted.
CO_2 Standard gas is needed for mass spectrometer control throughout the long run-time. Small instabilities of the mass spectrometer within a run can be corrected afterwards by applying a drift correction as a function of retention time. An internal cellulose standard (ICS; $\delta^{13}C$ = -24.50 ‰) is important to correct for altering conditions inside the interface. It is also used for offset correction afterwards. A second cellulose standard is added for checking the correction.



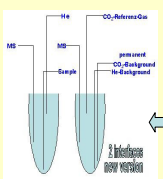
Evaluation

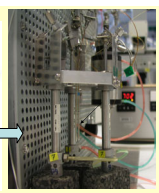
- 1st drift correction of reference CO_2-gas versus time
- 2nd drift correction of all measured raw data depending on CO_2-gas values internal cellulose standard (ICS) averages and the standard deviation
- offset correction; all values are now based on ICS
- 2nd internal standard (EHZ-1) average and the standard deviation
- the averages of ICS and EHZ-1 provide the basis for the long term QA control (standard deviation for ICS ~ 0.20-0.25 ‰; EHZ-1 ~ 0.30 ‰)



Laser parameters
- Nd-YAG Laser System (Merchantec/New Wave, UP Series)
- wavelength 266nm
- pulse width 3-5nsec ~3mJ
- variable repetition rate 1-20 Hz

What is possible?
- different shot sizes and shapes (spots, lines)
- variable distances between the shots
- variable shot duration and delay time
- continuous online measurement





Sample requirements
- Samples must be very dry
- size: length max. 12 mm, width ~ 5 - 7 mm, height ~ 5 mm

Dimensions are limited by the sample chamber size and the peak shape requirements.

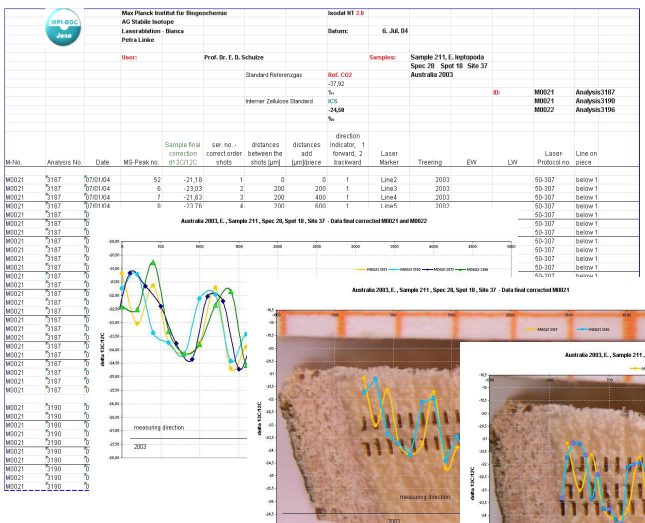
Standards in use
- ICS (internal cellulose standard); $\delta^{13}C$ = -24.50 ‰
- EHZ-1 (second cellulose standard); $\delta^{13}C$ = -26.4 ‰
- CO_2-gas; $\delta^{13}C$ = -37.92 ‰

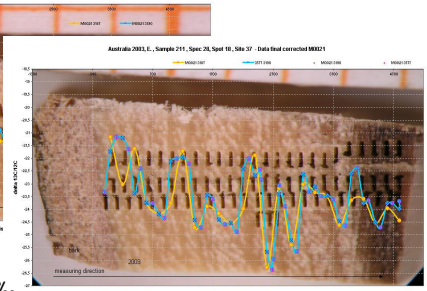
Possibly errors
Incomplete oxidation [1]
Leakages in the sample chamber or along the sample pathway [2]
Incorrect carrier gas flow [3,4]
Temperature stability [5]
Mutual Sample Standard cross contamination [6]

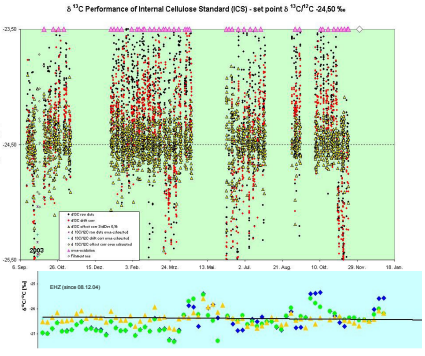
Possible remedies
[1]Complete oxidation is the most important requirement. Frequent oxidation of the Cu (overnight)
[2]Can be checked before analysis using Ar (m/z 40 on the mass spectrometer)
[3]Must be checked routinely using a precision flow meter
[4]Flow changes occur when frozen water or dust particles clog the capillary
[5]Constant temperature in the IsoLab ; maintain constant conditions during a run
[6]Can be prevented by working with utmost care under clean conditions. Dust in the laser sample chamber during a run is inevitable. Possible cross contamination between sample and standard can occur unattended and must be checked post-run.

Example for a sample analysis protocol

- Sample ID by the sample submitting person ('customer')
- Sample ID by IsoLab
- Unique analysis ID numbers for runs, generated by MS software
- Identification numbers for peaks, as analysed by the peak finding algorithm in the instrument software
- Shot identification numbers and distances (analyst)
- document measuring direction (analyst)
- high resolution post-analysis photographs for relating laser shots with isotope results
- Excel diagram for sequence of shots
- Tree ring identification (by customer / sometimes by IsoLab)







- $\delta^{13}C$ patterns along three parallel ablation lines on the same core showed a high level of congruity.
A conservative estimate of the precision is ± 0.24 ‰.
Comparison with a more conventional method (elemental analysis-IRMS) indicated a high level of accuracy of the Laser ablation and Combustion-GC-Isotope Ratio Mass Spectrometry.