Application Note 43

Laser-Induced Fractionation Effects in Hyphenated Laser Ablation Systems

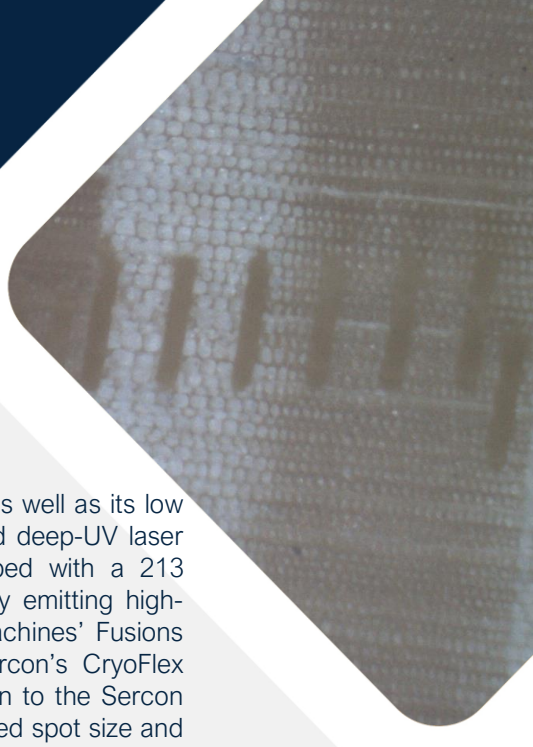
Introduction

The hyphenated laser ablation – isotope ratio mass spectrometer (LA IRMS) analytical setup allows for highly accurate and precise, as well as spatially resolved light isotope ratio measurements (e.g., $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, etc.). It is an unparalleled tool for samples that grow through time (e.g., hair, fingernails, wood, bivalves, speleothems, teeth, etc.), that require a minimally invasive approach (e.g., archaeological artefacts), or where multiple replicates are needed on a size-limited sample (e.g., crystal). It drastically reduces sample preparation time and costs, consumables, and it minimizes sample waste.

Fractionation Effects

Traditionally, laser ablation (LA) as solid sample introduction technique for the measurement of stable isotopes (e.g., $\delta^{13}C$, $\delta^{18}O$, etc.) via isotope ratio mass spectrometry (IRMS) was believed to be strongly affected by laser-induced fractionation. In most cases, especially when looking at $\delta^{13}C$ in organic samples, the laser energy has been shown to induce measurable fractionation (ZHANG et al. 2020; Rodionov et al. 2019).
Increasing the laser energy delivered to the sample surface has been shown to generally decrease $\delta^{13}C$ as compared to referenced values, independent of the matrix. This is believed to be caused either by local heating effects, aerosol particle size and size distribution, or transport efficiency.

However, the analytical conditions used for the experiments were typically constrained by the level of blank achievable using different ablation chambers (van Roij et al. 2017; Rodionov et al. 2019). In other words, the sample trapping time was reduced to the bare minimum such that blank contribution from the sample chamber as well as transport lines was kept within manageable values. While this approach is valid given the technical limitations of the hardware used, it doesn't consider the fact that most organic matrices are prone to yielding a two-phase ablation product – aerosol particulates and gaseous compounds (Todoli and Mermet 1998; Frick and Günther 2012). These products will behave differently during the collection and transport phases, and it is safe to assume that by reducing the trapping time, the two phases are either preferentially collected and transported or processes similar to inertial deposition (as well as gravitational settling) will interfere with the laminar flow required for fast and efficient transport.



Experimental Method

To test the collection and transport efficiency of Terra Analitic's isoScell , as well as its low blank capabilities, two different experiments were designed using a pulsed deep-UV laser ablation system – the Teledyne Photon Machines LSX213 G2+ equipped with a 213 nanometer wavelength laser at a pulse width of 5 ns; and a continuously emitting high-power (55 W) RF-excited water cooled CO2 laser – Teledyne Photon Machines' Fusions CO2 laser. The lasers were coupled via Terra Analitic's isoScell to Sercon's CryoFlex automated gas purification and pre-concentration accessory and further on to the Sercon HS2022 IRMS. Both lasers were fired at increasing energy levels using a fixed spot size and ablation duration (see Table 1 for experimental conditions). The IAEA-C-3 cellulose standard reference material ($\delta^{13}C$ = -24.91 ‰) was used for the experiments.

Instrument	Parameter	Unit	Value
LSX213 G2+	Carrier gas (He)	$mLmin^{-1}$	25
	Energy output	%	5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100
	Spot size	µm	50
	Scan time	s	15
	Scanning speed (for line scans)	μms^{-1}	50
Fusions CO2	Carrier gas (He)	$mLmin^{-1}$	25
	Energy output	%	1, 1.5, 2, 2.5, 3, 4, 5, 6, 7, 8, 9, 10
	Spot size	µm	150
	Scan time	s	2
	Scanning speed (for line scans)	μms^{-1}	N/A
CryoFlex	Trapping time	s	200
Combustion furnace	Temperature	°C	850

TABLE 1: Instrument Conditions

Discussion

The data shows that there is minimal laser-induced isotopic fractionation, even when extremely high laser energy values are used. We believe this is caused by:

1. Efficient collection and transport of the ablation products, both aerosol and gaseous phase.
2. Robustness of the CryoFlex accessory allowing long trapping times without compromising the blank.
3. Low initial blank of the IsoScell ablation chamber.

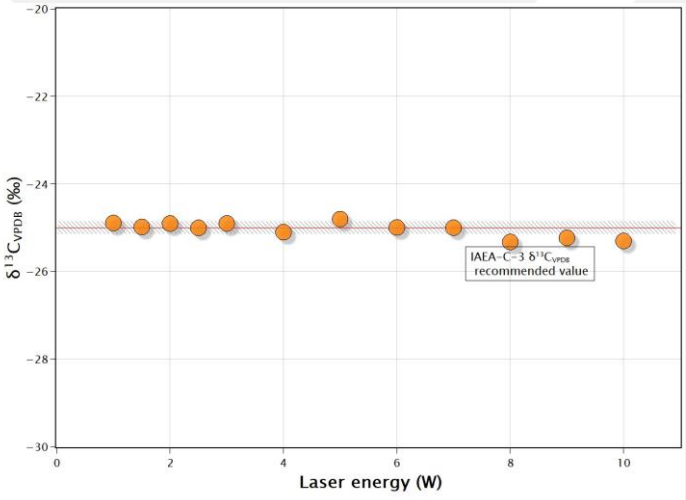


Figure 1. Variation of the $\delta^{13}C$ value of the IAEA-C-3 as a function of the laser energy (Fusions CO2). Shaded area represents the recommended ratio value.

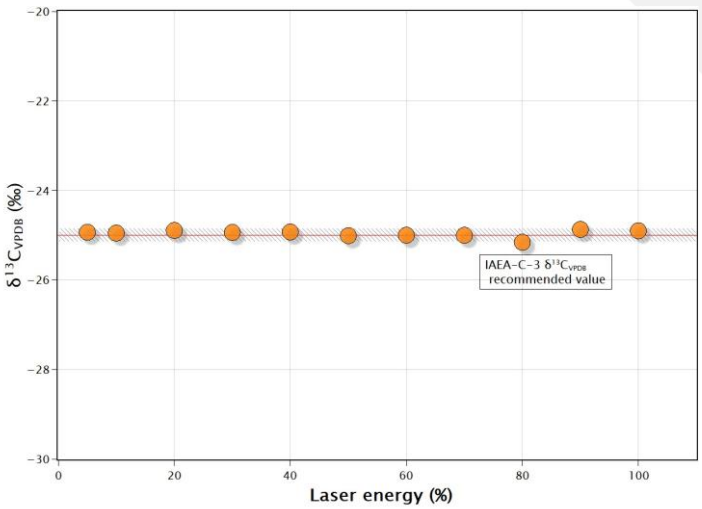


Figure 2. Variation of the $\delta^{13}C$ value of the IAEA-C-3 as a function of the laser energy (LSX213 G2+). Shaded area represents the recommended ratio value.

Conclusion

The data shown above suggests that an optimized instrumental setup is key to addressing a whole series of issues that are often interconnected and can result in data errors that are difficult to detect and correct. Equipment designed based on a good understanding of each component in the LA IRMS system and of every step of the analytical process can insure that acquired data is accurate, reproducible, and reliable.

References:
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