Characterization of Ocean Realms and Life Signatures (CORALS) Prototype

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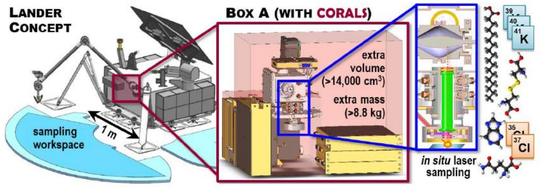
INTRODUCTION

The CORALS instrument is a development under NASA's Instrument Concepts for Europa Exploration-2 program for investigation of life signatures on the surface of Jupiter's moon Europa. Europa is known to have liquid water in contact with an icy mantle, and as such, it represents a compelling target for the search for life. Indicators of life include molecular building blocks such as long chain fatty acids, amino acids, and nucleobases, and a preference for certain molecular and isotopic distributions. The CORALS instrument (Fig. 1; Box A) interfaces a CosmOrbitrap mass analyzer[1] with a high-energy solid-state UV laser via a custom ion inlet that accelerates and focuses ions into the CosmOrbitrap analyzer. This study focuses on testing of a CORALs prototype with a commercial Orbitrap™ analyzer.



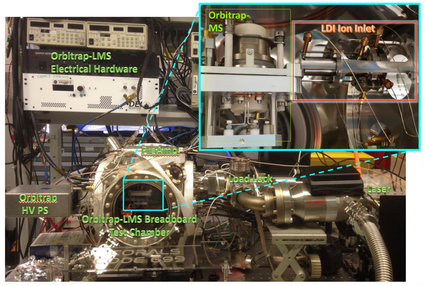
OBJECTIVES

- Mass resolution (FWHM) >100,000 (*m/z 100*).
- Mass accuracy of 3 ppm (internal calibration over mass range of 23-900 u).
- Demonstration of negative/positive ion mode

METHODS

Our setup integrates a commercial 266 nm sub-ns laser (Passat), an ion inlet prototype, and a commercial orbitrap analyzer (see bottom right). Instrument characterization was done using a CsI pellet embedded in a stainless steel target or by drop casting chlorophyll A, NaCl, and KCl onto the target. Ions formed at the target were focused and accelerated to 1100 eV by the ion inlet and then injected into a d30 Orbitrap under ultrahigh vacuum (<1E-8 torr). Voltage levels were set with bipolar supplies (Spectrum Solutions, SRS, ISEG, and Thermo Fisher).

A NI scope card monitored the amplified image current signal (Thermo Fisher preamplifier 2078900) and a custom FPGA board controlled high speed timing.



RESULTS

To demonstrate a **mass resolution** (FWHM) >100,000 (*m/z 100*) we focused on the Cs peak (m/z 133) and performed FFTs on 800 ms transients. Sets of 10 spectra were averaged in the time domain to reduce background noise (~3x reduction). Initial reproducibility of mass resolution during repeated trials was poor so we examined whether its dependence on transient length was linear as expected. Even after some success with zero-filling (Fig. 3a) applying Hanning apodization to the time domain data, adjusting our zero fill to 1.67 s, we found that a Gaussian fitting function gave better fits to the Cs peak and from the fitted FWHM of the peaks we obtained the expected linear relationship (see Fig. 3b). Hence, this post processing method was used to process all other spectra.

Fig. 3a: Mass resolution vs. transient length using Lorentz fits of Cs peaks in the FFT. Raw fft (black); After 2x zerofilling(red)

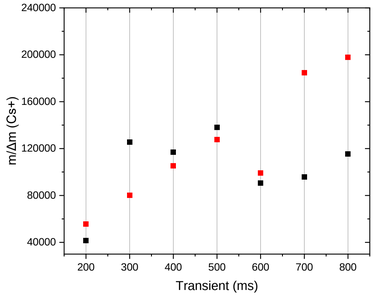
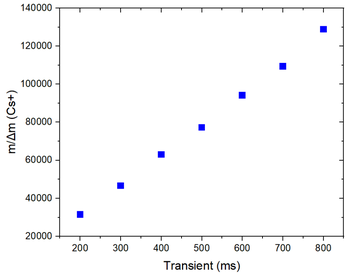


Fig. 3b: Mass resolution vs. transient length after zerofilling and hanning apodization



Mass accuracy was routinely checked by calibration using the most intense peak, Cs, [2]. Some spectra, such as the one shown in Fig. 4a (averaged 200 ms transients) included Na. The presence of Na allowed us to demonstrate detection of lower mass ions. The $Cs(CsI)_2$ peak with height of 7E-6 was 2-3x the background level of 2E-6. Hence, a mass range from 23 to 653 u could be demonstrated with sufficient intensity. The mass accuracy of Na and $Cs(CsI)_2$ were -4.3 and -0.8 ppm, respectively, using this method. The worst accuracy came from ^{40}Ca and $Cs_2{}^{37}Cl$ with mass errors of -12.5 and 18.7 ppm, respectively. Better mass accuracy using a 800 ms transient. One such example, included a fortuitous contamination species, Pb. Calibration to ^{208}PbI reduced the rms errors in mass accuracy from 3.62 obtained with Cs to 2.68 ppm (Fig. 4b).

Fig. 4a: Demonstrating mass range from 23 to 653 u using averaged 200 ms transient spectra

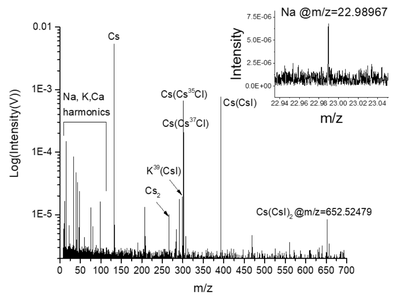
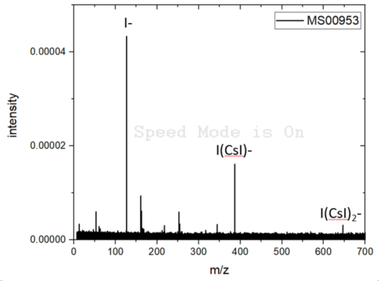


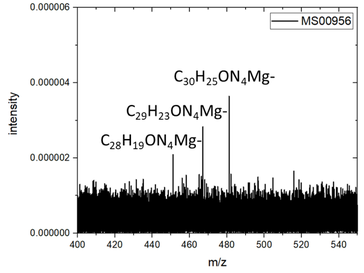
Fig. 4a: Mass accuracy (in ppm) calibrating to Cs (second column) and ^{208}PbI

Cs	0	-4.4
^{206}Pb	1.1	-3.3
^{207}Pb	0.6	-3.8
^{208}Pb	1.1	-3.4
$Cs_2{}^{35}Cl$	2.7	-1.7
$Cs_2{}^{37}Cl$	2.3	-2.1
^{206}PbI	5	0.5
^{207}PbI	4.8	0.4
^{208}PbI	4.4	0
Cs(CsI)	2.5	-1.9
$Cs(CsI)_2$	6.5	2.1
RMS (ppm)	**3.62**	**2.68**

Negative ion mode was demonstrated using CsI (left) as well as Chlorophyll A (right). The internal calibrants used for these spectra were Iodine and Cl_3Fe (not shown), respectively. A mass resolution of 130,000 was determined for Iodine in the left most spectra. The molecular ion of Chlorophyll was not detected but three known fragments were identified with mass accuracy of 25-31 ppm.

Fig. 5a-b: Negative ion mode spectrum of CsI (left) and Chlorophyll A (right)





CONCLUSIONS

- Preliminary data using the CORALS prototype indicates that 700 ms transients with zero filling and Hanning apodization enable a mass resolution of over 100,000 for Cesium, successfully meeting objective 1.
- Obtaining mass accuracy of 3 ppm, will also likely require a transient of similar length and will necessitate additional noise reduction measures and/or more signal from higher mass analytes to demonstrate accuracy over the 23-900 u mass range. Averaging in the time domain is compromised by jitter in the timing of the laser fire (standard deviation of 500 ns) with respect to the timing of electrodynamic squeezing, the result of using an FPGA to trigger the laser and CE/DE pulser. Triggering of the pulser using a photodiode detector largely removes the jitter effect but relies on a low latency between CE/DE trigger and pulse.
- Negative ion mode was demonstrated and is expected to be a useful and complimentary tool to positive ion mode.

FUTURE WORK

- Testing of a prototype laser capable of much higher laser energies (up to 400 µJ) should enable identification of amino acids (Arevalo 2018)
- A new, more compact, engineer test unit will be built that integrates the before mentioned laser, the Cosmorbitrap analyzer and mature pulser/preamplifier. The test unit will also include a MEMS mirror to be used in conjunction with steering lenses in the LDI inlet to allow for imaging mass spectrometry over a 200,000 µm² field of view.

REFERENCES

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[2] A. Makarov "Electrostatic Axially Harmonic Orbital Trapping: A High-Performance Technique of Mass Analysis" *Anal. Chem.* 2000.

[3] R. Arevalo "An Orbitrap-based laser desorption/ablation mass spectrometer designed for spaceflight**"** *IEEE* **2018.**

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