



Infrared Electro spray-assisted Laser Desorption Ionization Mass Spectrometry

Introduction

The IR ELDI concept involves desorbing a large quantity of predominately neutral sample molecules in “water-rich” medium at atmospheric pressure by a mid-IR laser pulse into the gas phase and post-ionizing the molecules through fusion with charged solvent droplets generated by ESI. No matrix addition or sample purification is necessary and typical electrospray conditions are used. Mass spectrometry imaging using ESI is possible using IR ELDI. In this application note, IR ELDI MS analysis of aqueous biomolecules will be shown.

Experimental Conditions

A droplet of 1-10 μL of 0.1-2.5 μM aqueous analyte solution was deposited on a metal target isolated from an X-Y-Z stage using delrin. The droplet was desorbed at 2.94 μm using a 20 or 100 Hz IR Opolette before drying. Three Thermo ESI LTQ mass spectrometers (linear ion trap, OrbiTrap and FT ICR) were used for ionization and mass analysis. The electrospray was generated using a 1:1 v/v ACN/ H_2O and 0.2% formic acid with a flow rate of 1 $\mu\text{L}/\text{min}$ through a 50 μm silica capillary and 2-5 kV potential on the tip.

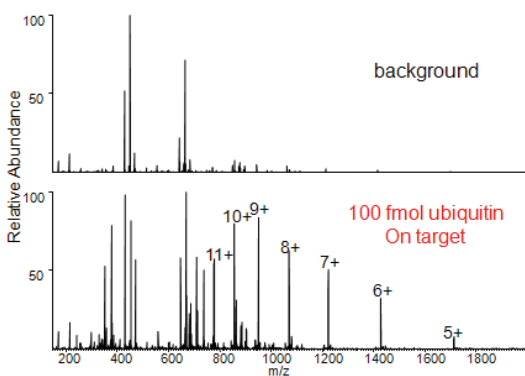


Figure 1. IR ELDI MS of ubiquitin aqueous solution (1 μL of 0.1 μM 100% water) acquired over 10 sec on a Thermo Finnigan LTQ-Orbitrap XL mass spectrometer using 100 Hz IR Opolette.

Results

The lowest detection limit achieved to date was 100 fmoles of ubiquitin loaded on target (Figure 1). IR ELDI was performed on three mass analyzers to determine compatibility and resolution (Figure 2). The ability to analyze mixtures with MS and MSⁿ is

shown in figure 3 for four proteins dissolved in water.

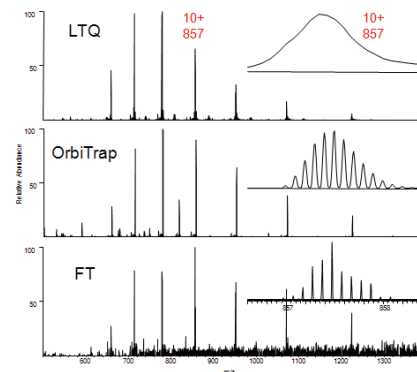


Figure 2. IR ELDI of aqueous ubiquitin solution (100% water) acquired from three mass spectrometers.

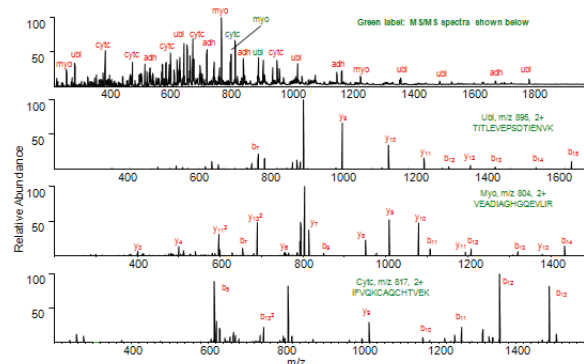


Figure 3. IR ELDI MS and MSⁿ of Tryptic digest protein mixture of ubiquitin, myoglobin, cytochrome C and alcohol dehydrogenase aqueous solutions (10 μL of 2.5 μM 100% water)

Conclusions

Since mid-IR lasers desorb a large amount of material, more sample is available for ESI; therefore increasing sensitivity. The analysis of large biomolecules is possible due to “soft” mid-IR desorption and the multiple-charging effect of ESI. Other tests found that proteins up to 80 kDa can be successfully ionize (data not shown).

Acknowledgements

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