DESI with polymer applications

NIST workshop on soft ionization of polymers

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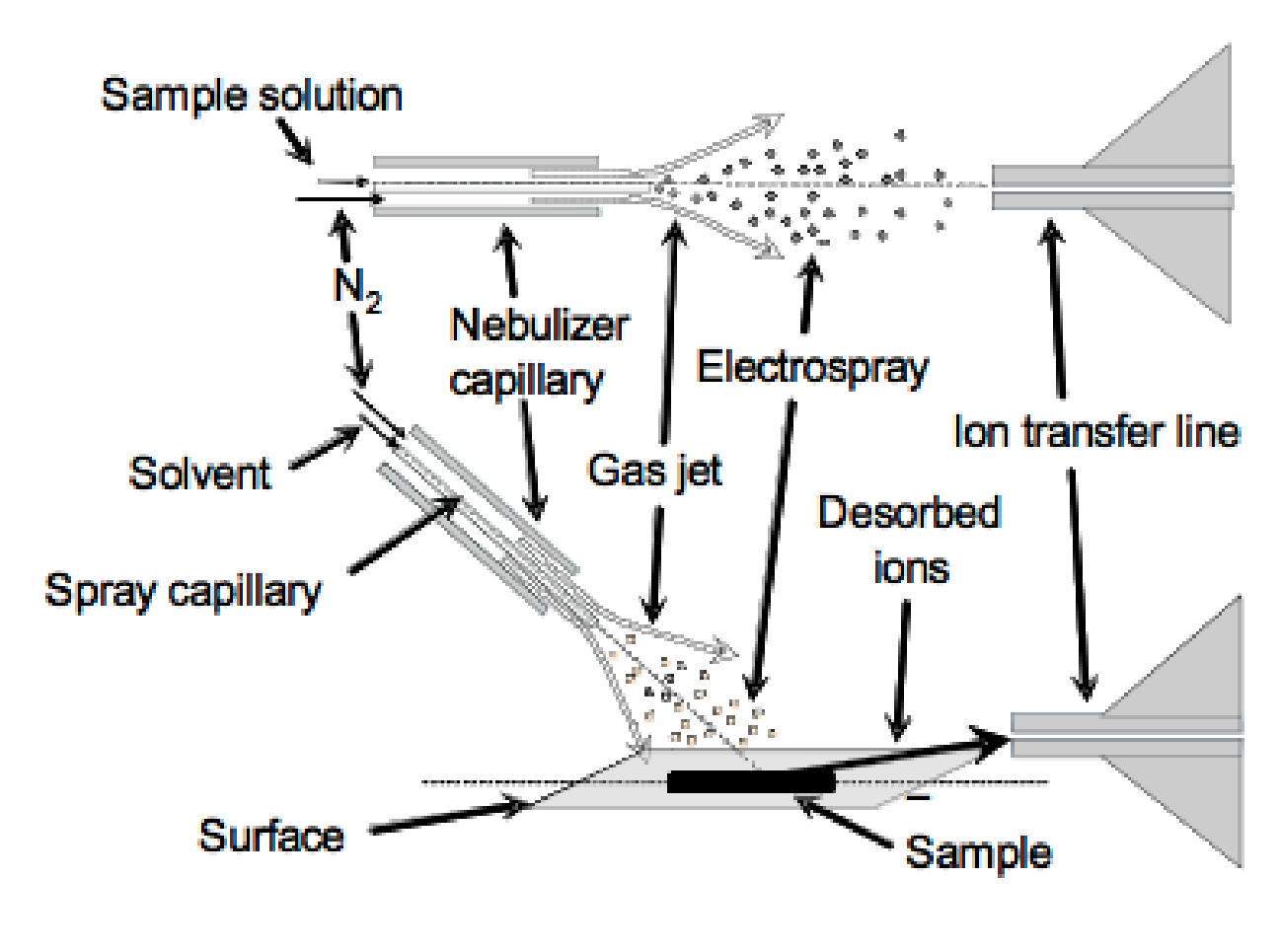
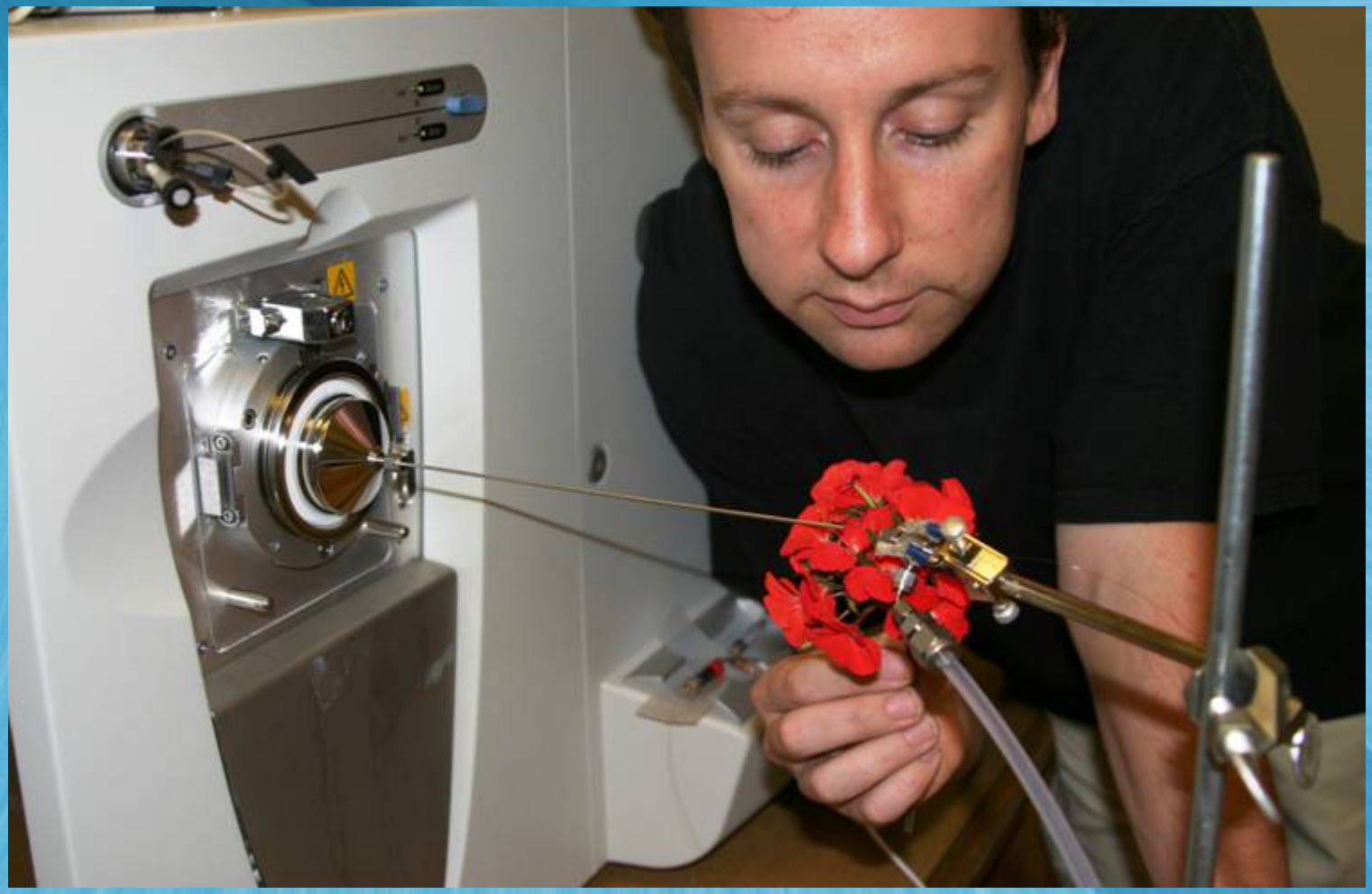
Outline

- DESI and ESSI
- Operational parameters
- Applications
  - Other applications
  - Polymer analysis
  - Polymer additives

Schematic diagram of DESI and ESSI

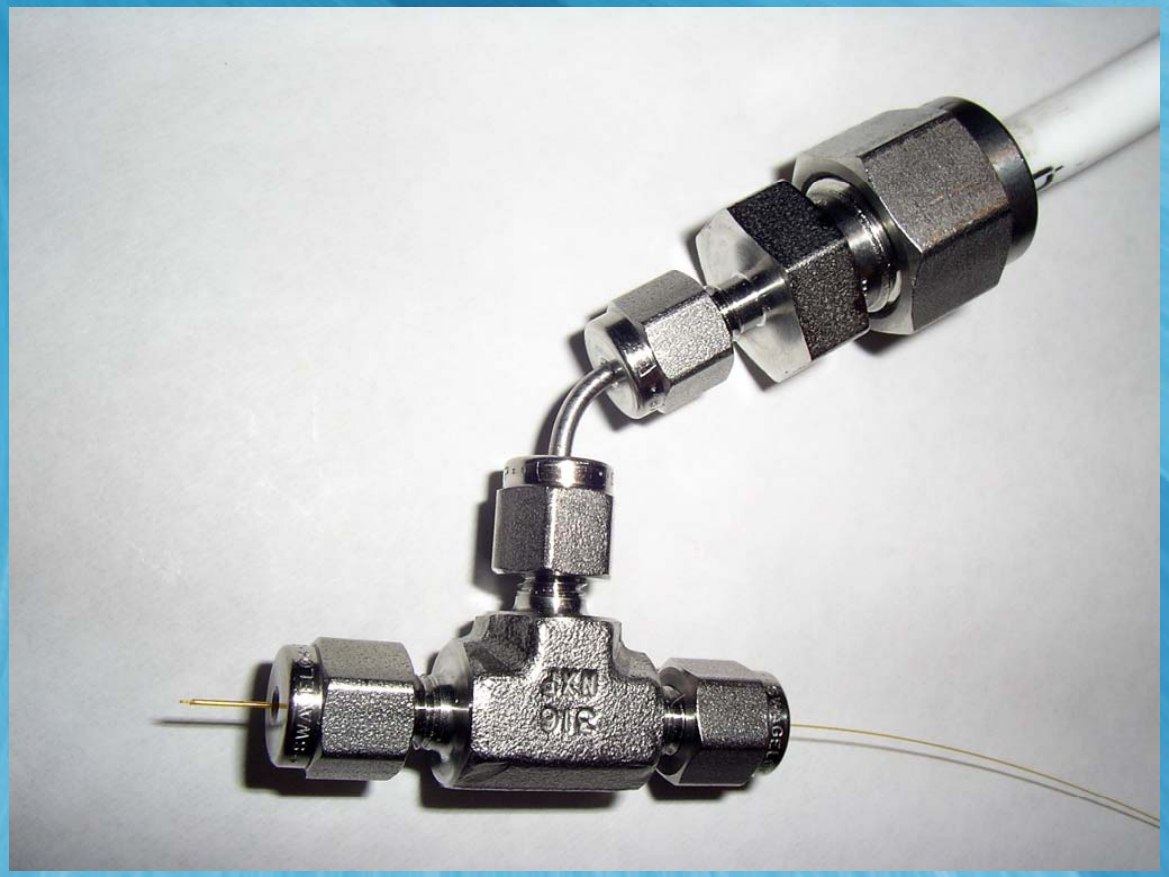


Analysis in the ambient environment



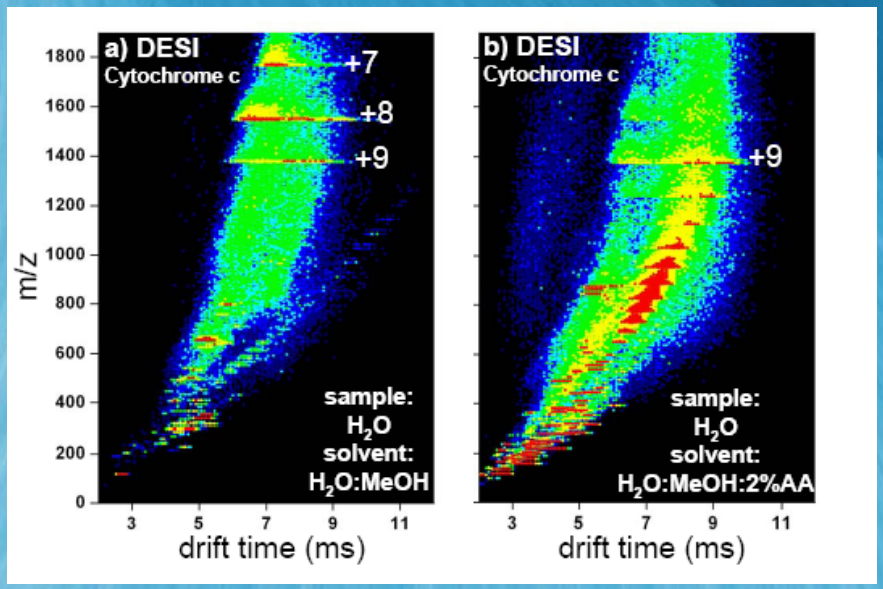
Zoltan Takats

Homebuilt ESSI source used for DESI

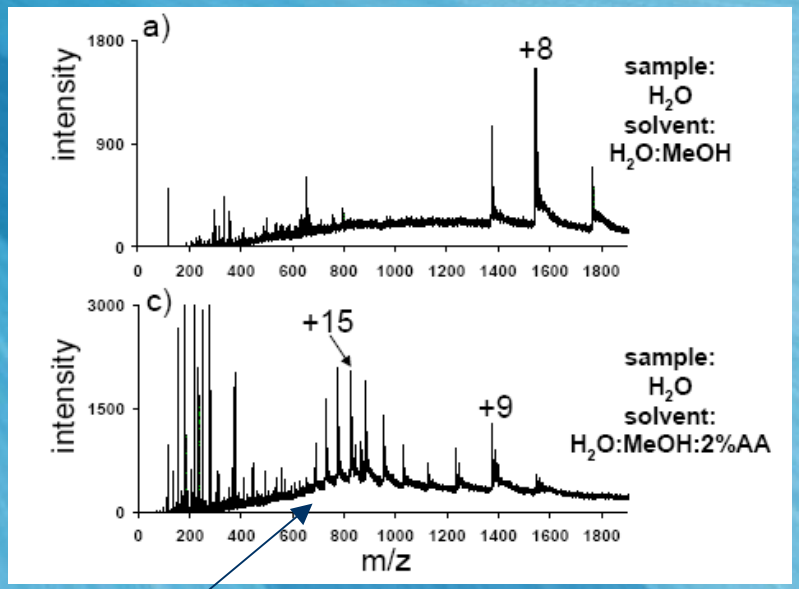


Comparison of Cytochrome C conformations using DESI IMS-TOF

Arrival time distributions



Total integrated mass spectra



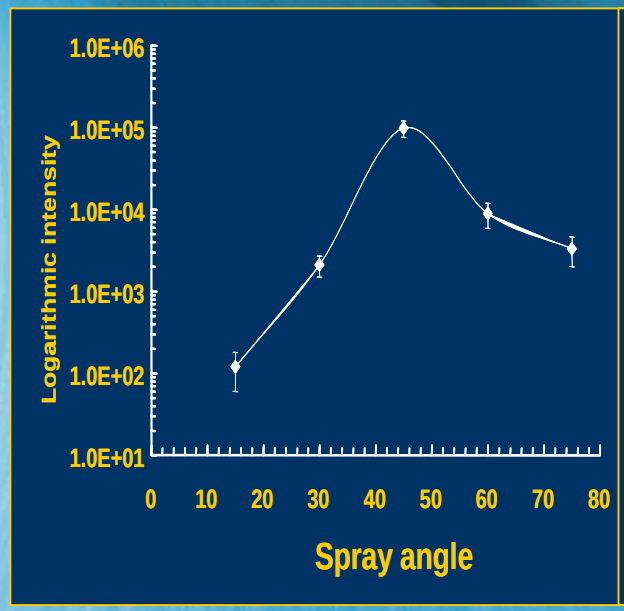
Unfolded conformations

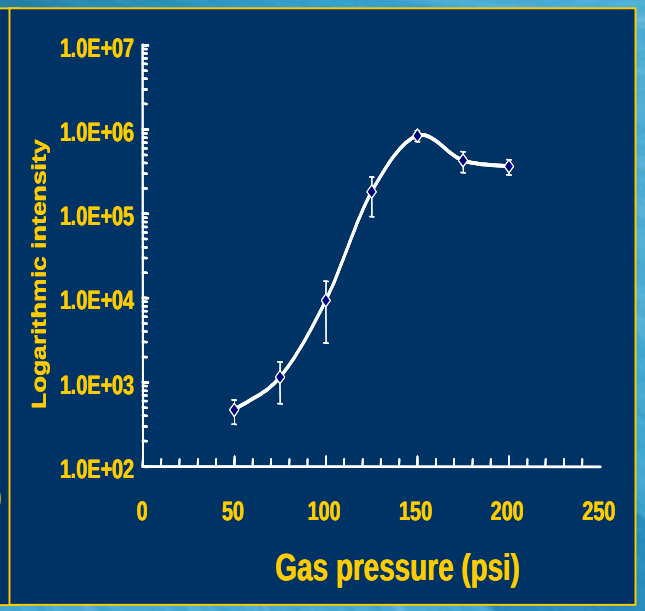
J. M. Wiseman, S. Myung, D. Clemmer

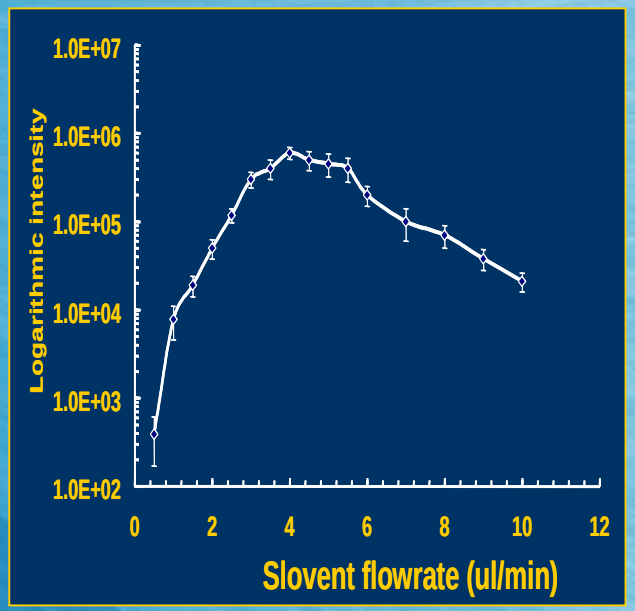
Operating conditions for the two DESI modes

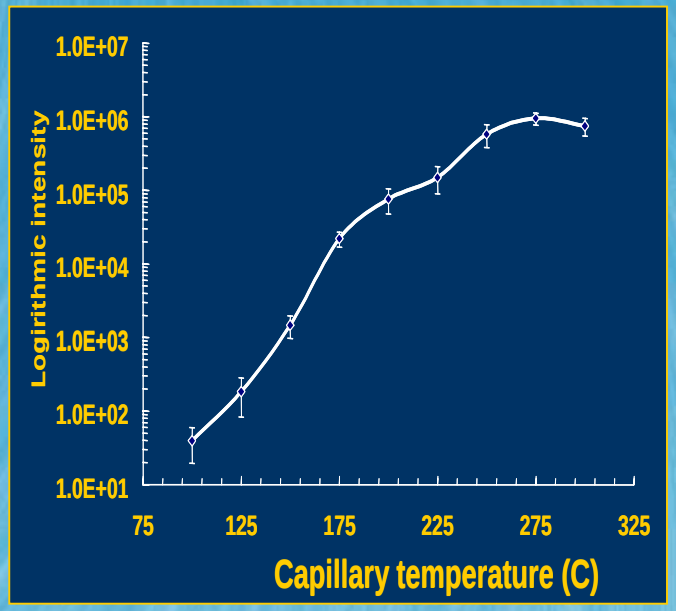
Parameter	**Optimal Setting**	
Analyte type	Peptides, proteins, carbohydrates, nucleic acids	Explosives, lipids, aromatic hydrocarbons
Electrospray voltage	1-4 kV	3-8 kV
Electrospray flow rate	0.1-3 μl/min	
Nebulizing gas linear velocity	>350 m/s	
Heated capillary temperature	200-350 °C	200 °C
Tube lens potential	200-250 V for proteins, 30-150 V for small molecules	
Capillary inlet-sample distance	1-2 mm	2-8 mm
Tip-sample distance	1-2 mm	5-8 mm
Incident angle (α in Fig.1)	60-90 degrees	20-50 degrees
Collection angle (β)	<10 degrees	5-15 degrees

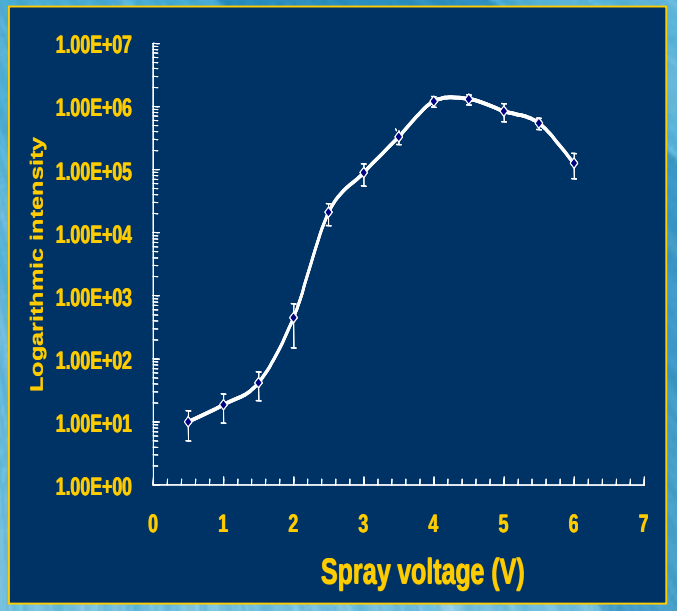
Optimization of Experimental Conditions



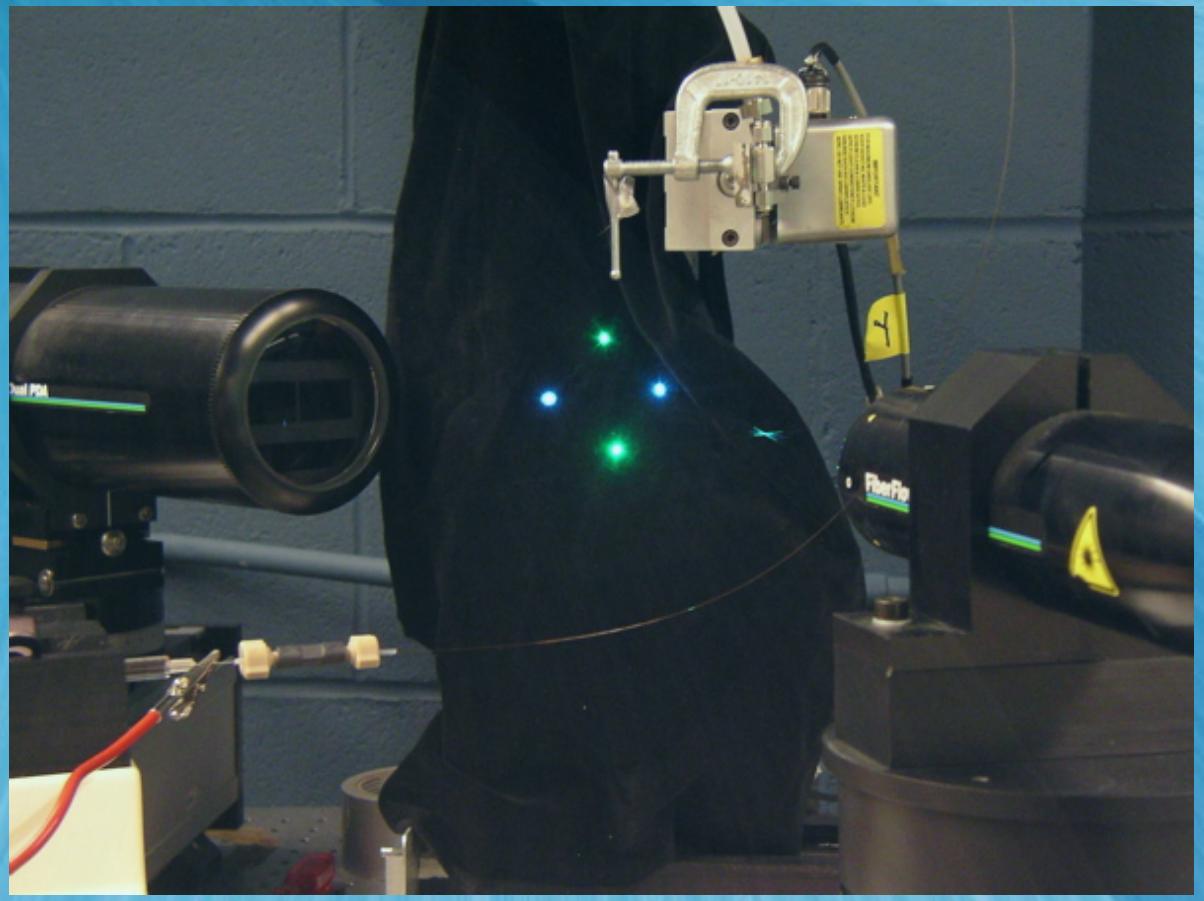




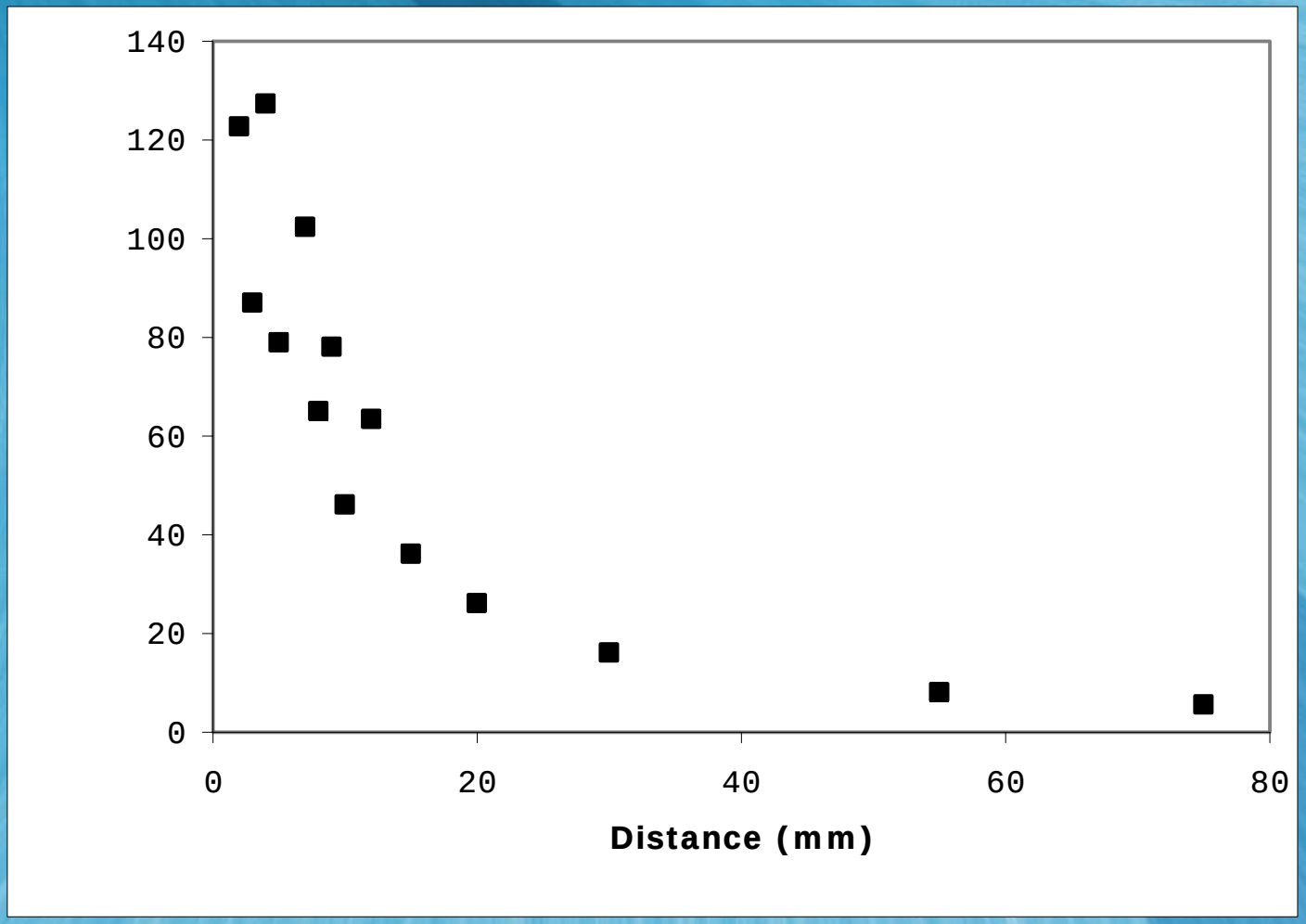




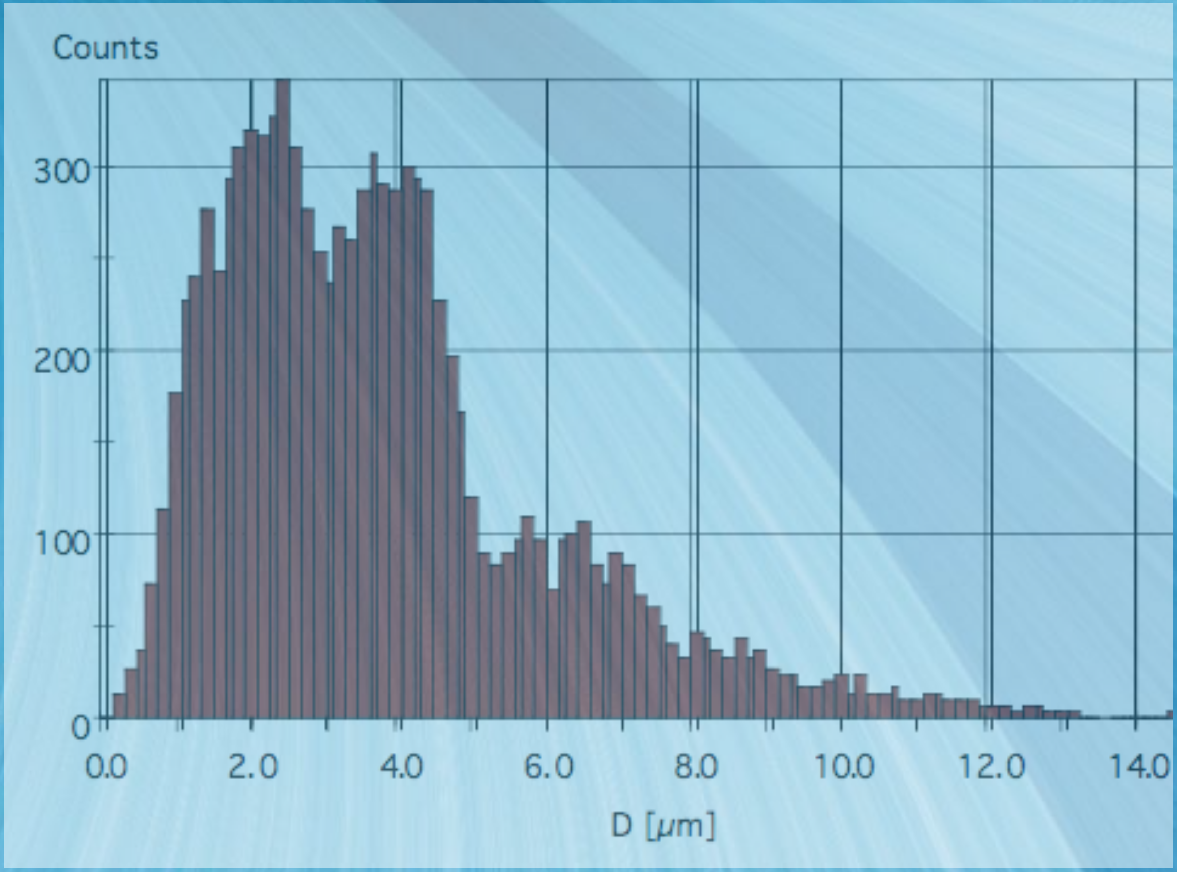
PDA measurements



Velocity change of inbound spray with distance from surface

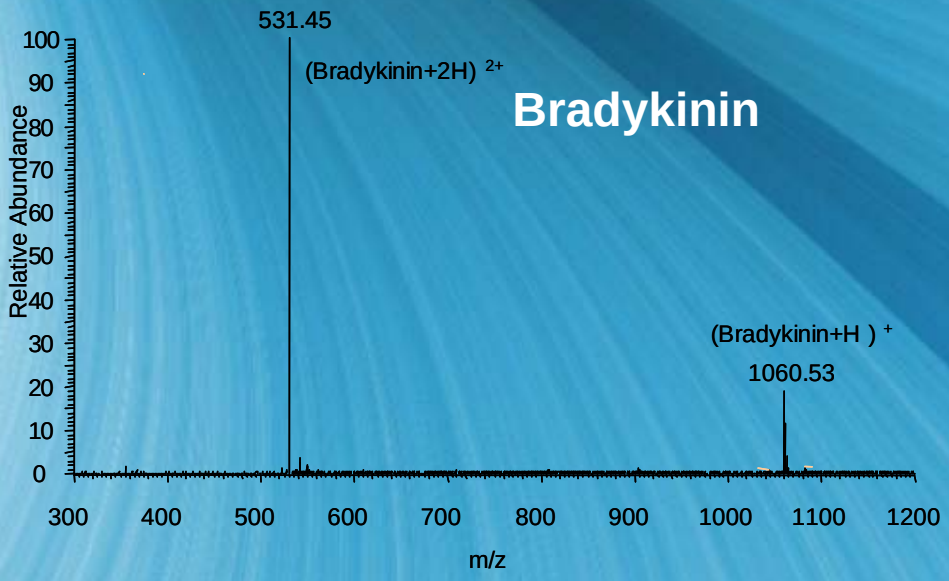


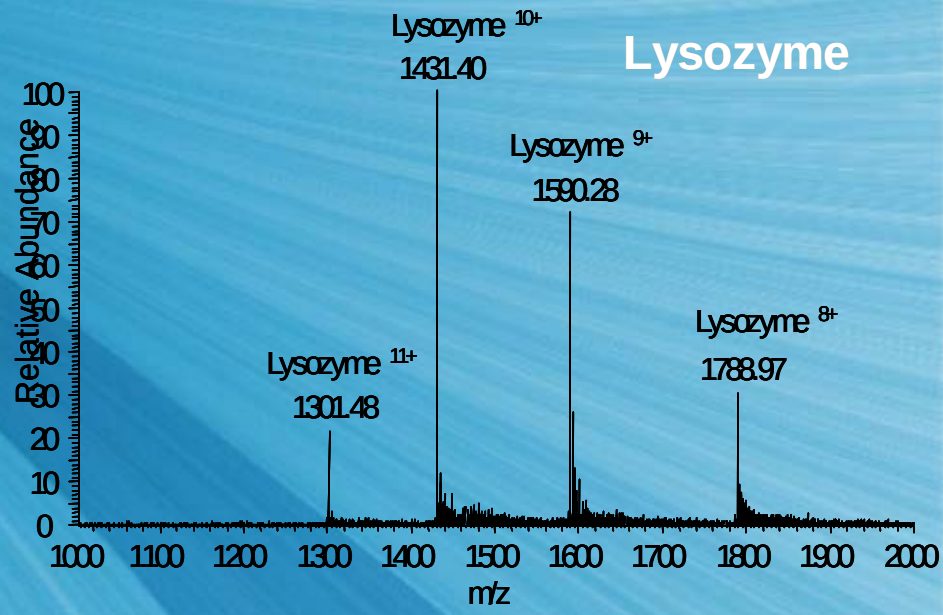
PDA measurements of inbound droplet diameters

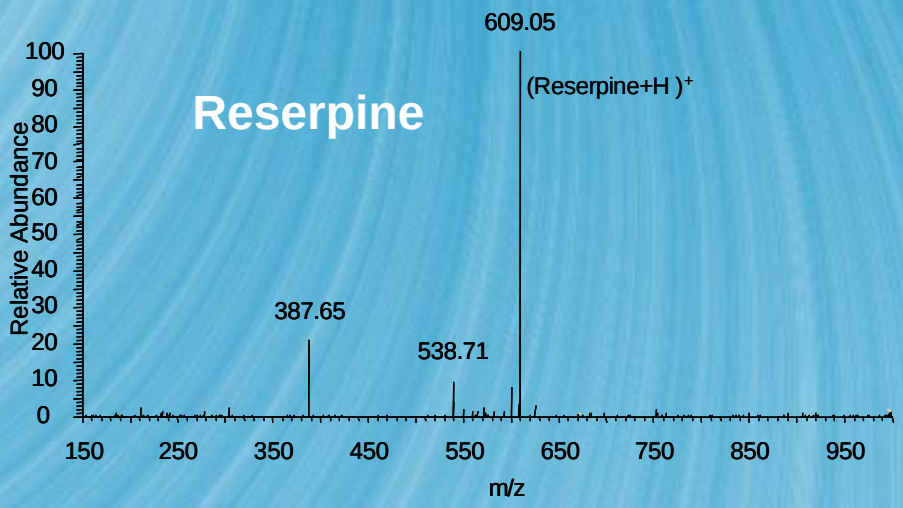


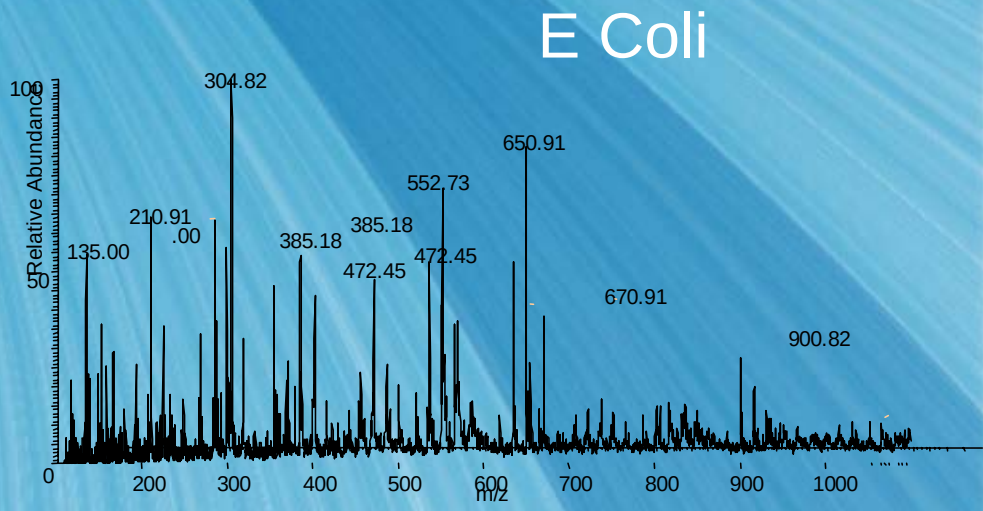
- Ambient samples; 1-10 ng/cm^2; PTFE surface;
- Methanol/water spray; 5 sec analysis time

DESI applications

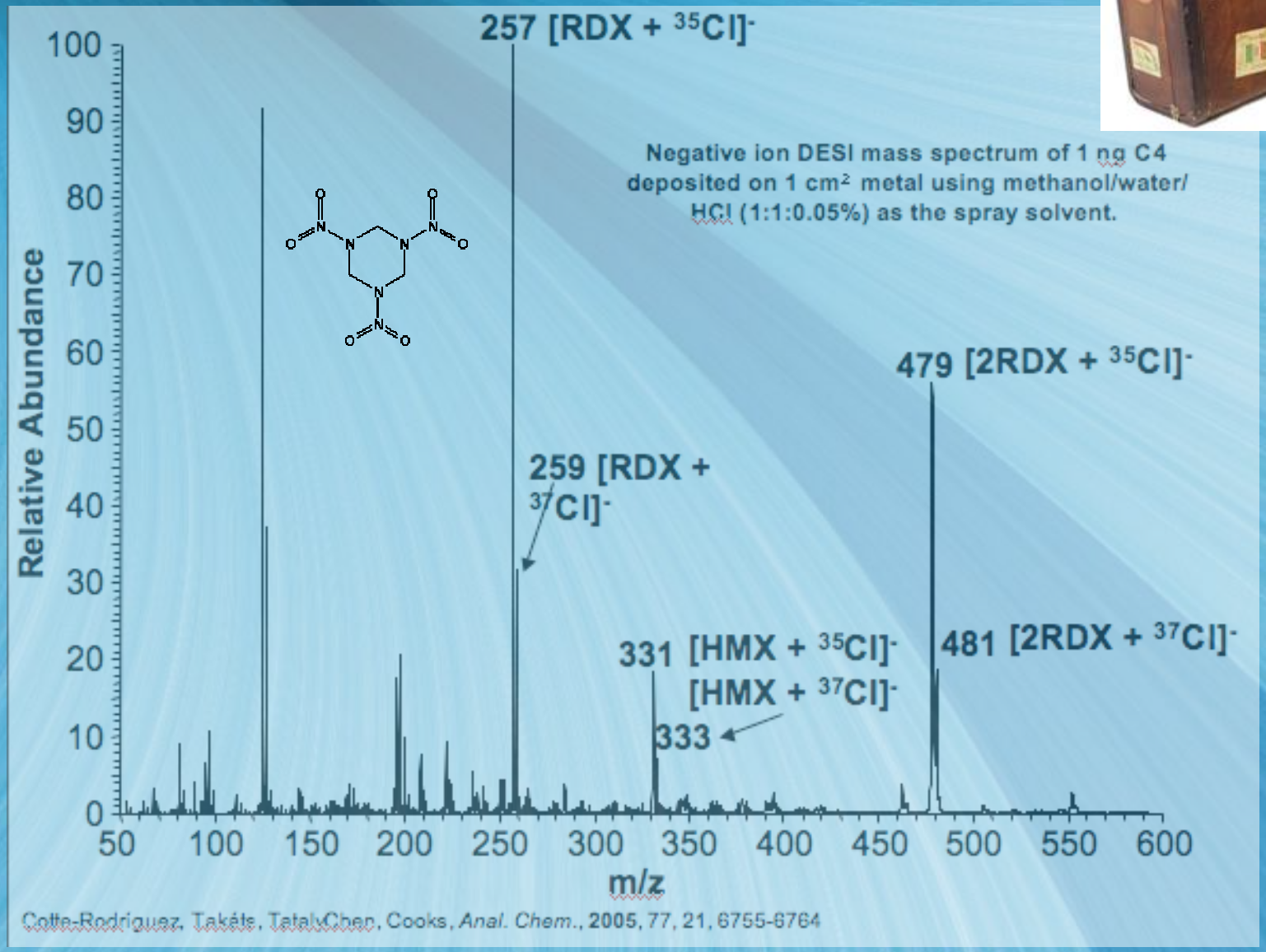








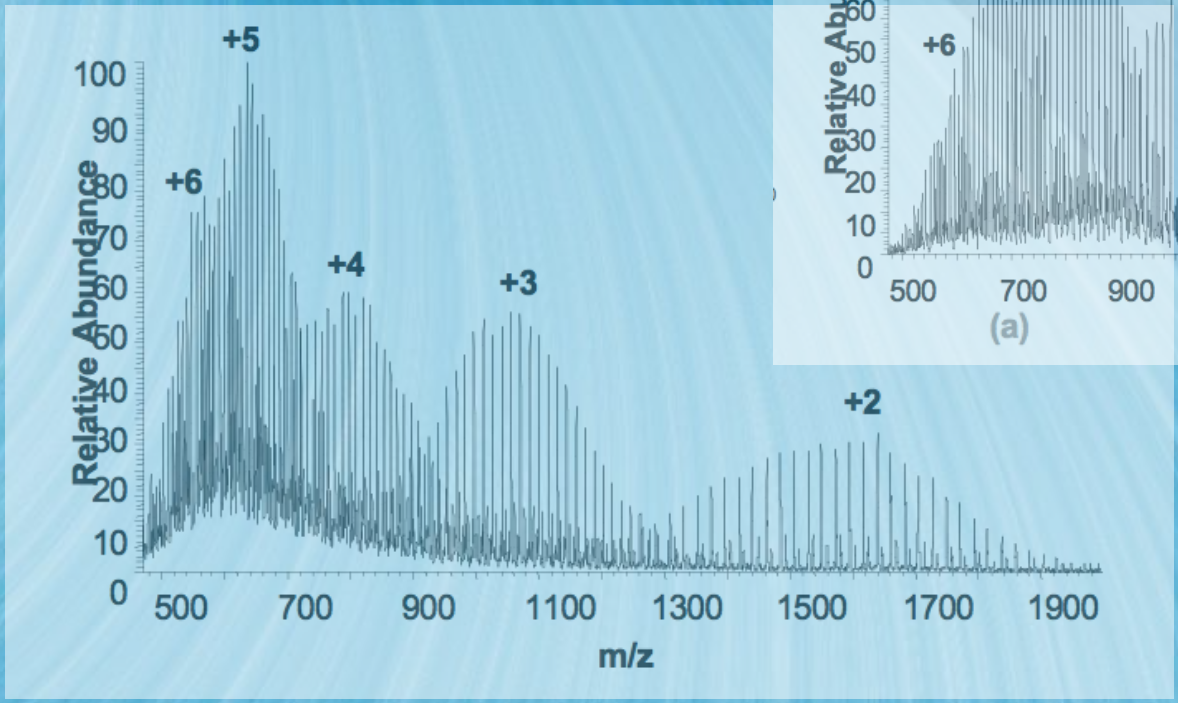
Plastic explosives

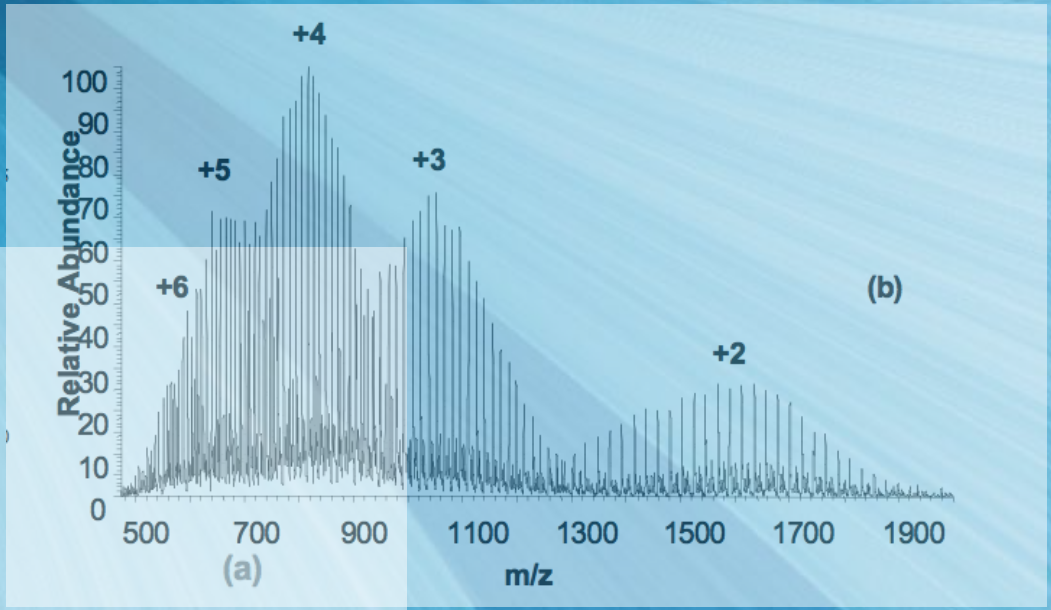


Cotte-Rodriguez, Takáts, Talaty, Chen, Cooks, *Anal. Chem.*, **2005**, 77, 21, 6755-6764

DESI and ESSI spectra of PEG

DESI





ESSI

Tables of results

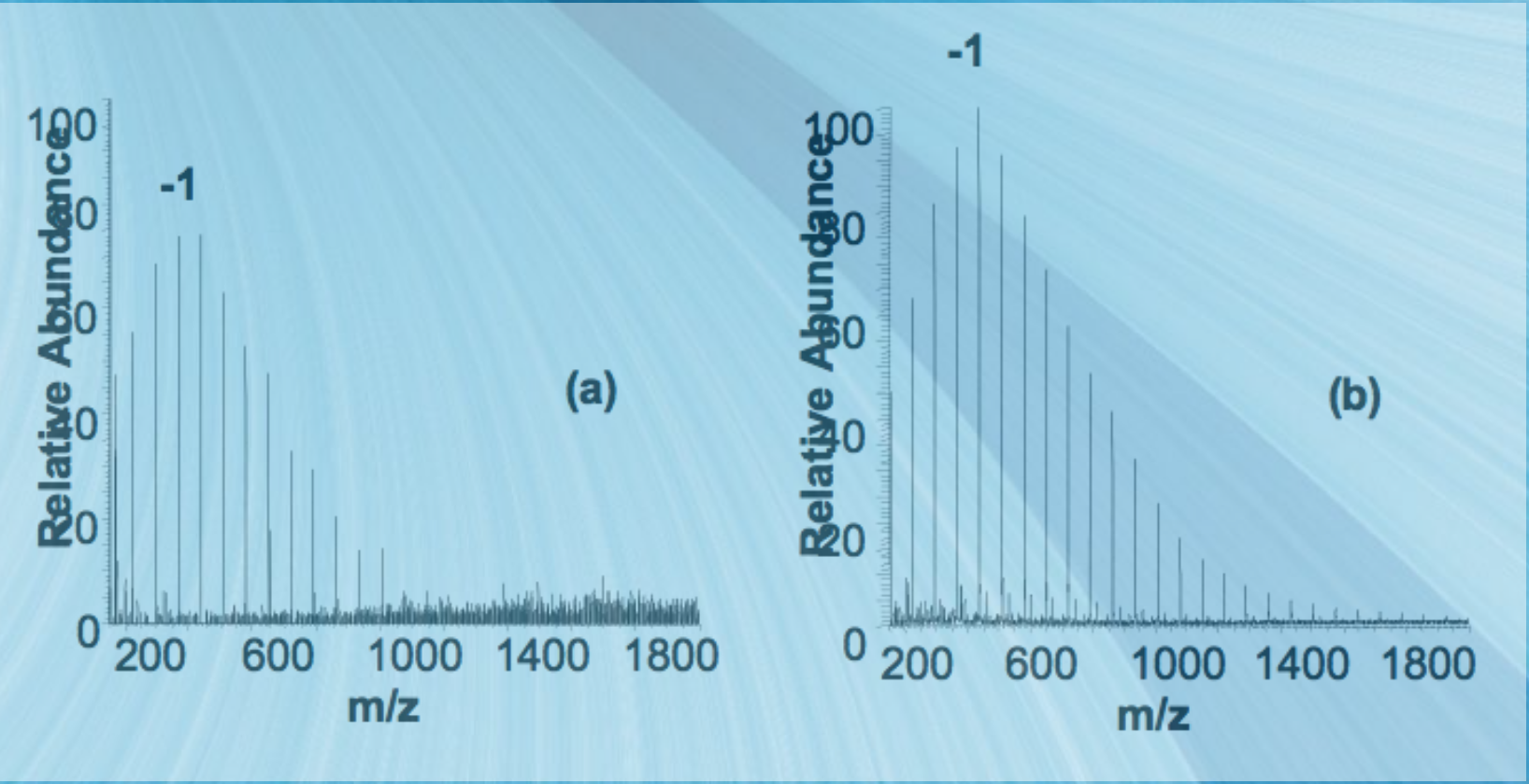
DESI

	+2		+3		+4	+5	+6
	$[M+2Na]^{2+}$	$[M+Na+K]^{2+}$	$[M+3Na]^{3+}$	$[M+2Na+K]^{3+}$	$[M+4Na]^{4+}$	$[M+5Na]^{5+}$	$[M+6Na]^{6+}$
MWD	2219-3936	2483-3716	2351-3936	2527-3716	2351-3892	2483-3848	2747-3936
Mp	3231	3055	3099	3099	3055	3055	3275
Ave MWD (RSD)	2452 (6.9%) – 3854 (2.6%) (32 repeat units)						
Ave Mp (RSD)	3124 (2.9%)						
Mn (RSD)	**3105 (0.60%)**						

ESSI

	+2		+3		+4	+5	+6
	$[M+2NH_4]^{2+}$	$[M+NH_4+K]^{2+}$	$[M+3NH_4]^{3+}$	$[M+2NH_4+K]^{3+}$	$[M+4NH_4]^{4+}$	$[M+5NH_4]^{5+}$	$[M+6NH_4]^{6+}$
MWD	2307-3936	2483-3716	2439-4024	2615-3628	2351-3980	2571-3716	2747-3848
Mp	3099	3055	3099	3099	3188	3099	3408
Ave MWD (RSD)	2502 (6.2%) – 3835 (4.0%) (30 repeat units)						
Ave Mp (RSD)	3150 (3.8%)						
Mn (RSD)	**3172 (0.20%)**						

DESI spectrum of PAM



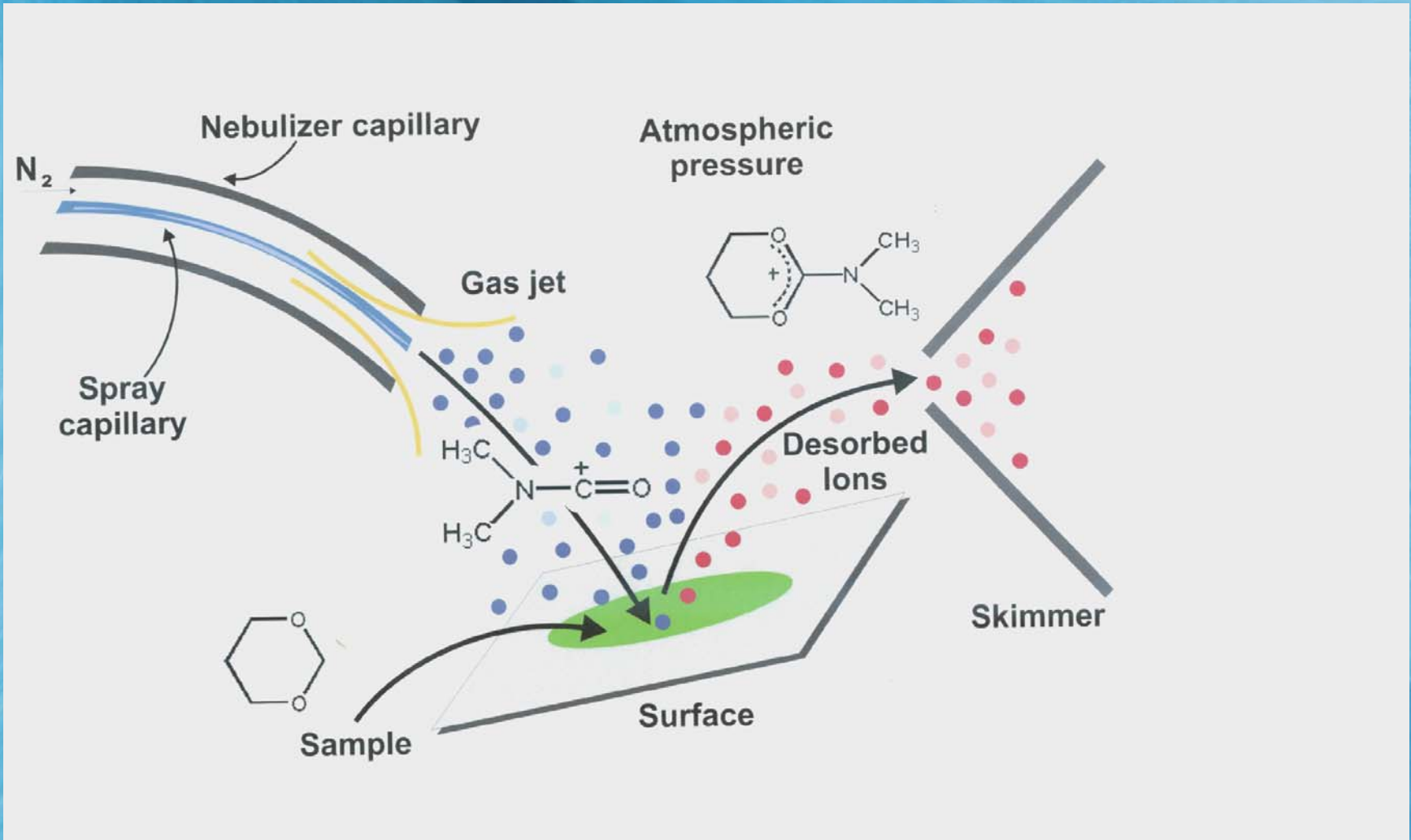
DESI

ESSI

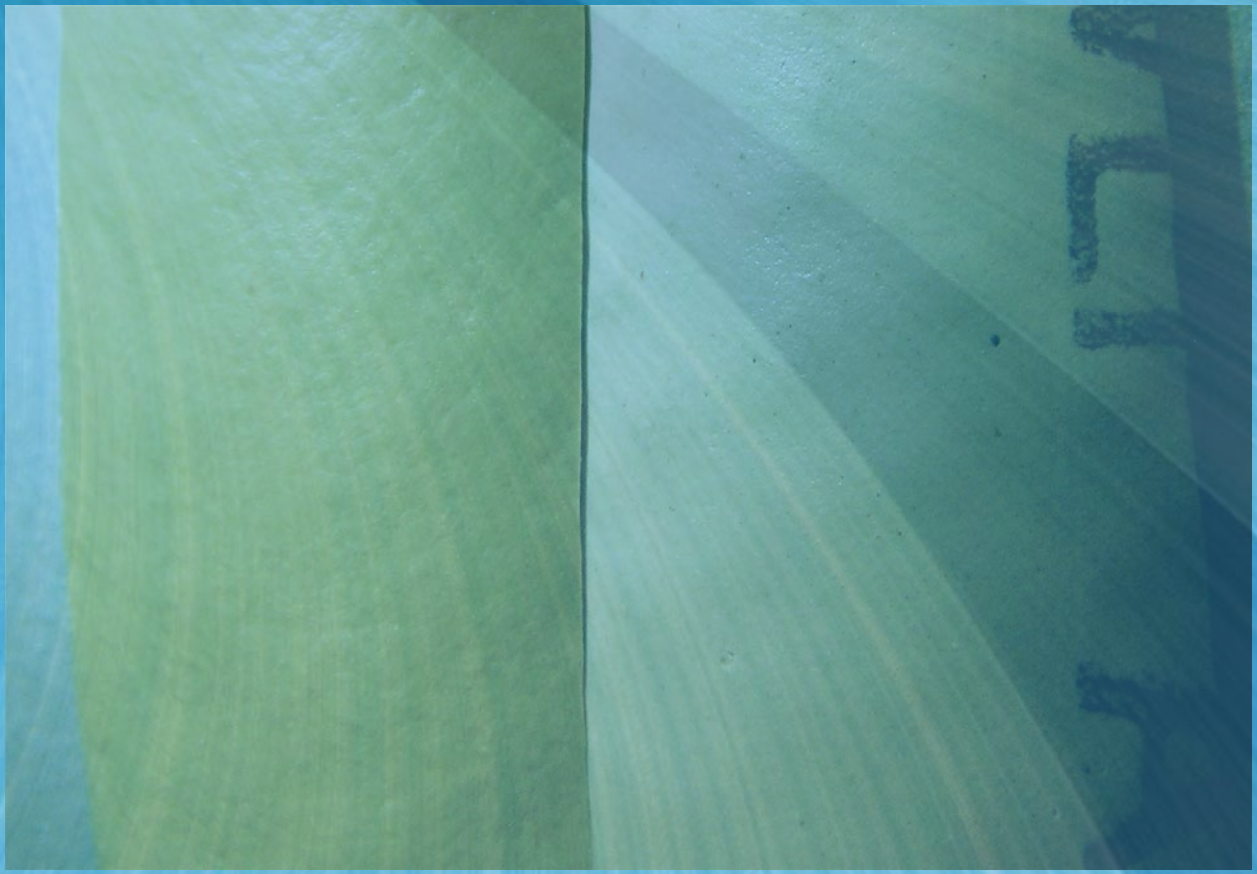
Reactive DESI

- Proton bound dimers
- Cu complex of amino acids
- Eberlin reaction
- Oxidation reduction
- Small molecules from polymers

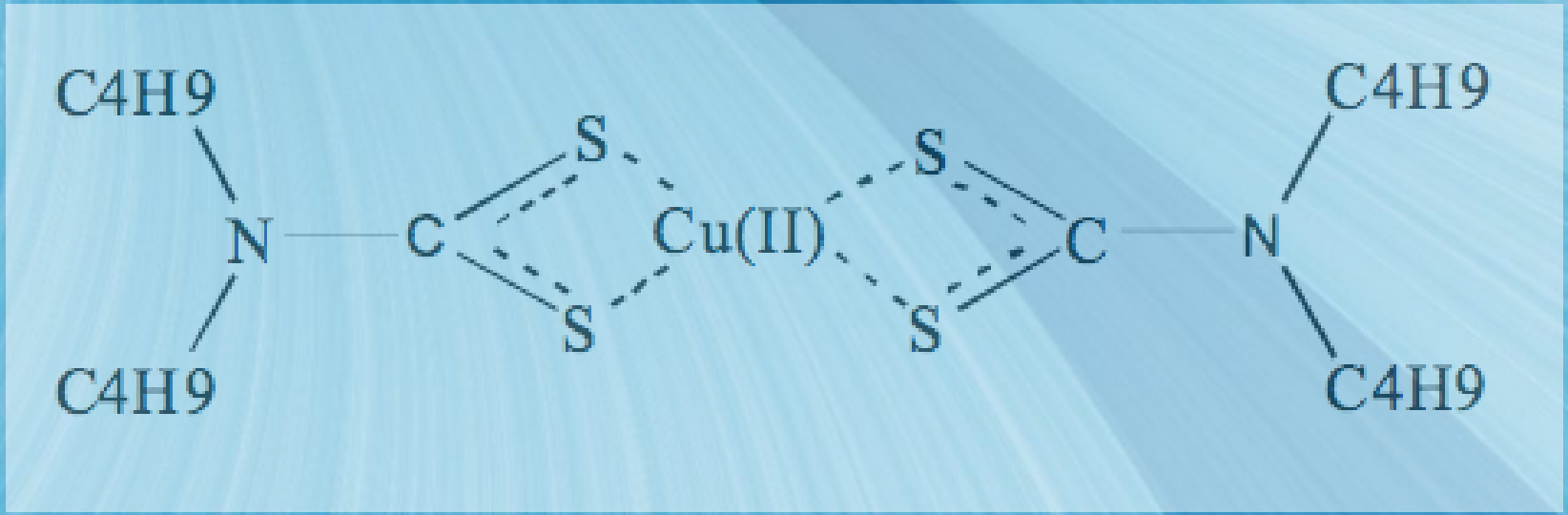
Eberlin reaction



Discoloration Problem

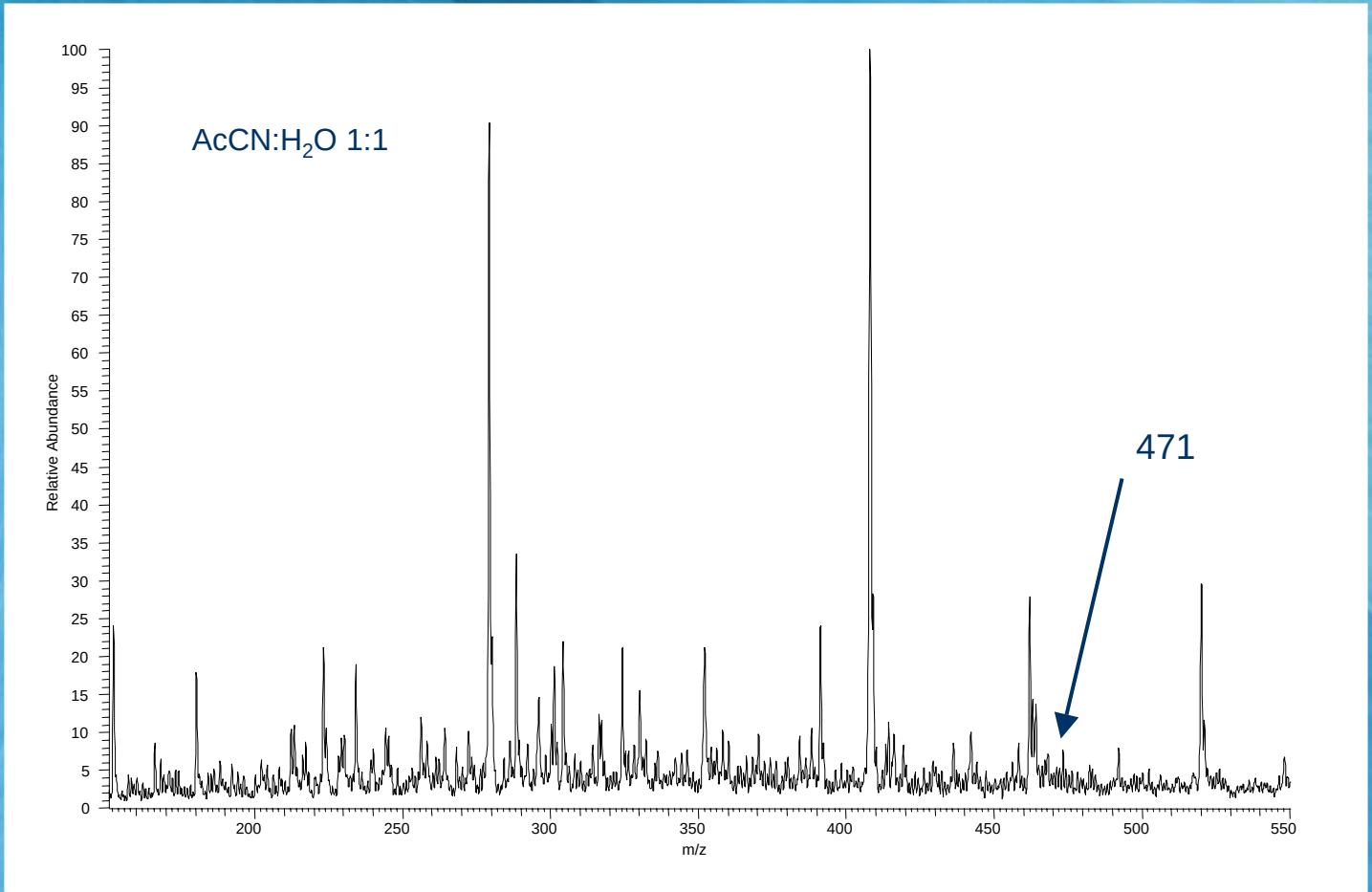


Cu(II) dimer of tetrabutyl thiuram disulfide (TBTD)



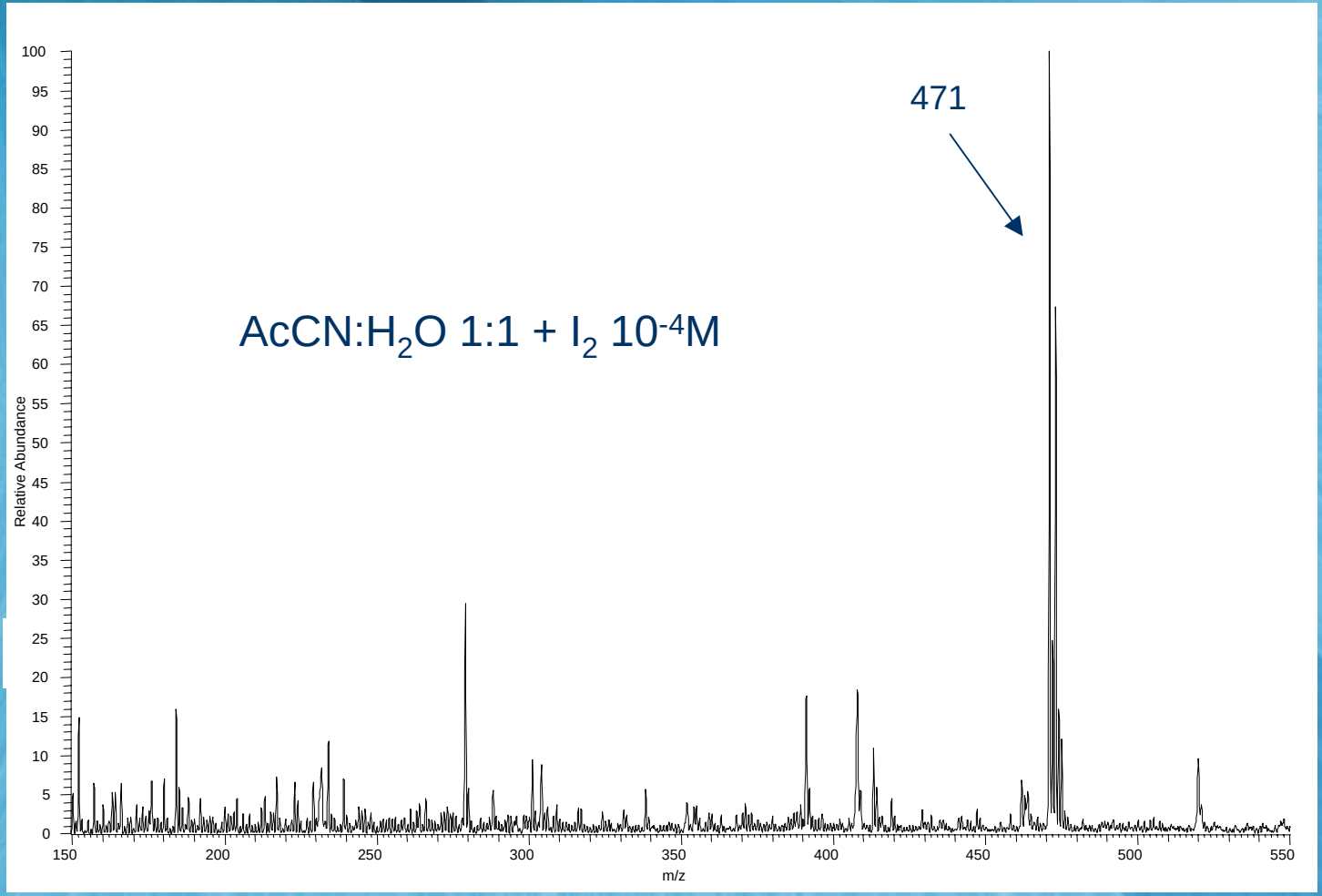
Moore, McKeown, JASMS (2005) 16, 295-301

DESI on polymer surface



Nefliu, Moore, McKeown,Cooks, Paper In preparation

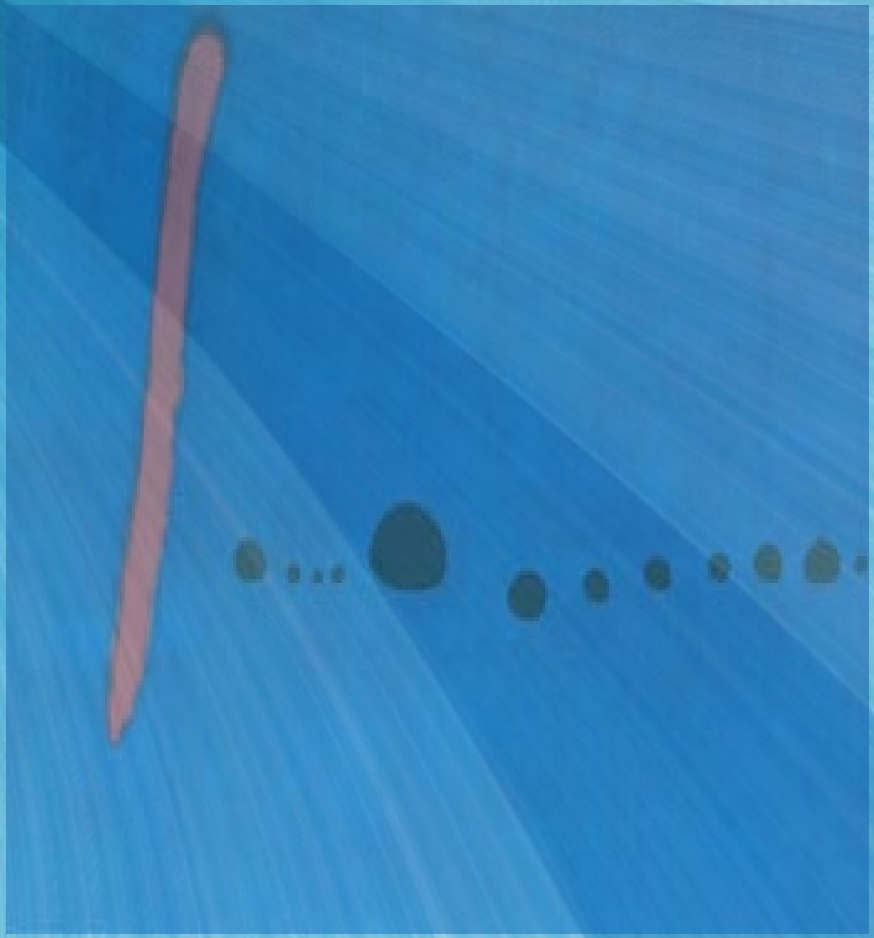
Reactive DESI
Iodine mediated oxidation



Nefliu, Moore, McKeown,Cooks, In preparation

Conclusions

- polymers can be analyzed by DESI
- There are issues with some polymers DESI that need to be addressed
- Reactive DESI
- DESI ideal for polymer additives

Acknowledgements

- Co-authors
- Cooks Group
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