

Relative Abundances of Stable Isotopes [%]

Z	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31		
1	H	100	.015																													H	
2	He			.000	100																											He	
3	Li					7.5	92.5																									Li	
4	Be								100																							Be	
5	B									20	80																					B	
6	C											98.9	1.11																			C	
7	N												99.6	.360																		N	
8	O													99.8	.040	.200																O	
9	F																100															F	
10	Ne																		90.5	.270	9.22											Ne	
11	Na																					100										Na	
12	Mg																						79	10	11							Mg	
13	Al																									100							Al
14	Si																										92.2	4.67	3.1				Si
15	P																														100		P

Z	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58					
16 S	95	.760	4.22		.020																											S
17 Cl				75.8		24.2																										Cl
18 Ar					.340		.070		99.6																							Ar
19 K								93.3	.010	6.73																						K
20 Ca									96.9		.647	.135	2.09		.004		.187															Ca
21 Sc														100																		Sc
22 Ti															8	7.5	73.7	5.5	5.3													Ti
23 V																			.250	99.8												V
24 Cr																			4.35		83.8	9.5	2.36									Cr
25 Mn																								100								Mn
26 Fe																							5.8		91.8	2.1	.300					Fe

Z	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82						
26 Fe *	.300																														Fe *
27 Co		100																													Co
28 Ni	68.3		26.1	1.13	3.59		.910																								Ni
29 Cu						69.2		30.8																							Cu
30 Zn							48.6		27.9	4.1	18.8		.600																		Zn
31 Ga												60		40																	Ga
32 Ge													20.5		27.4	7.8	36.5		7.8												Ge
33 As																		100													As
34 Se																	.900		9	7.6	23.5		49.8		9.2						Se

Z	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104				
34 Se *	23.5		49.8		9.2																										Se *
35 Br		50.7		49.3																											Br
36 Kr	.350		2.25		11.6	11.5	56.9		17.4																						Kr
37 Rb								72.2		27.8																					Rb
38 Sr							.500		9.9	7	82.6																				Sr
39 Y												100																			Y
40 Zr													51.4	11.2	17.1		17.5		2.8												Zr
41 Nb																100															Nb
42 Mo															14.8		9.3	15.9	16.7	9.6	24.1		9.6							Mo	
44 Ru																			5.5		1.9	12.7	12.6	17.1	31.6		18.6			Ru	
45 Rh																										100					Rh

Z	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130		
44 Ru *	31.6		18.6																												Ru *
45 Rh		100																													Rh
46 Pd	1		11	22.2	27.3		26.7		11.8																						Pd
47 Ag						51.8		48.2																							Ag
48 Cd					1.2		.900		12.4	12.8	24	12.3	28.8		7.6																Cd
49 In												4.3	95.7																		In
50 Sn											1	.700	.400	14.7	7.7	24.3	8.6	32.4		4.6		5.6									Sn
51 Sb																			57.3		42.7										Sb
52 Te																			.100		2.5	.900	4.6	7	18.7		31.7		34.5		Te
53 I																										100					I

Z	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	
50 Sn *	5.6																															Sn *
52 Te *	4.6	7	18.7		31.7		34.5																									Te *
53 I				100																												I
54 Xe	.100		.100		1.9	26.4	4.1	21.2	26.9		10.4		8.9																			Xe
55 Cs										100																						Cs
56 Ba						.100		.100			2.4	6.6	7.9	11.2	71.7																	Ba
57 La															.090	99.9																La
58 Ce													.200		.300		88.4		11.1													Ce
59 Pr																		100														Pr
60 Nd																			27.2	12.2	23.8	8.3	17.2		5.7		5.6					Nd
62 Sm																					3.1			15.1	11.3	13.9	7.4		26.6		22.6	Sm
63 Eu																											47.8		52.2			Eu

Z	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180		
62 Sm *	26.6		22.6																												Sm *
63 Eu *		52.2																													Eu *
64 Gd	200		2.2	14.8	20.5	15.7	24.8		21.8																						Gd
65 Tb								100																							Tb
66 Dy					.060		.100		2.34	18.9	25.5	24.9	28.2																		Dy
67 Ho														100																	Ho
68 Er											.100		1.6		33.4	22.9	27		15												Er
69 Tm																		100													Tm
70 Yb																	.100		3.1	14.3	21.9	16.2	31.7		12.7						Yb
71 Lu																							97.4	2.6							Lu
72 Hf																							200	5.2	18.5	27.1	13.8	35.2			Hf

Z	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	
72 Hf *	35.2																														Hf *
73 Ta	.012	100																													Ta
74 W	.100		26.3	14.3	30.7		28.6																								W
75 Re						37.4		62.6																							Re
76 Os				.020		1.58	1.6	13.3	16.1	26.4		41																			Os
77 Ir											37.3		62.7																		Ir
78 Pt										.010		.790		32.9	33.8	25.3			7.2												Pt
79 Au																		100													Au
80 Hg																	.200		10.1	16.9	23.1	13.2	29.7		6.8						Hg
81 Tl																								29.5		70.5					Tl
82 Pb																									1.4		24.1	22.1	52.4		Pb
83 Bi																													100		Bi

* = incomplete (not all isotopes are shown in the same line)

FJ Stadermann 07/2010

Ion sources: EI

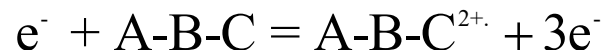
- EI is most common for GC detection
 - Electron ionization (NOT electron impact ionization)
- Many events possible in an electron-neutral collision
 - *excitation* $e^- + A-B-C = A-B-C^* \text{ (not detected)}$
 - *electron capture* $e^- + A-B-C = A-B-C^- \text{ (not detected in positive mode)}$
 - *ionization* $e^- + A-B-C = A-B-C^{+\cdot} + 2e^-$
 - *ionization w/ excitation (w/ or w/out rearrangement)*

$$e^- + A-B-C \rightarrow A-B-C^{+\cdot*} + 2e^- \rightarrow A + (B-C)^{+\cdot}$$

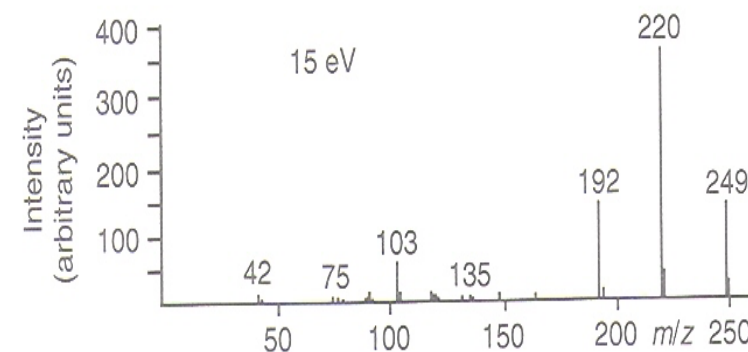
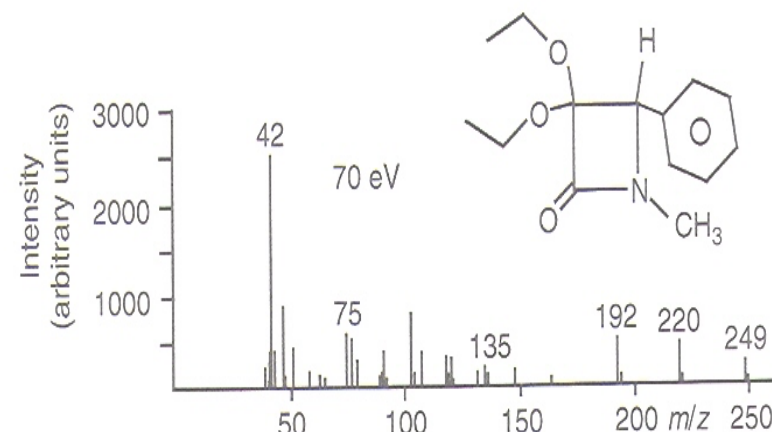
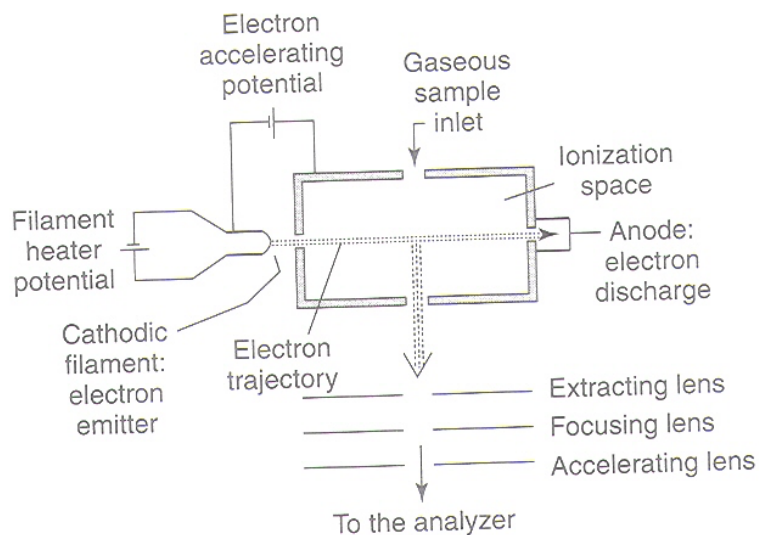
$$\rightarrow A^\cdot + (B-C)^+$$

$$\rightarrow A^{+\cdot} + (B-C)$$

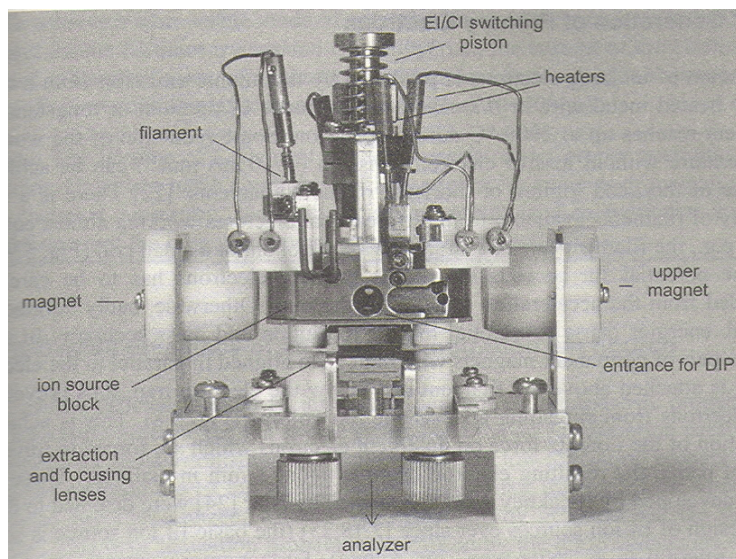
$$\rightarrow (A-C)^{+\cdot} + B \text{ etc.}$$
 - multiple ionization (/ or w/out excitation, dissociation, rearrangement etc.)



Ion sources: EI

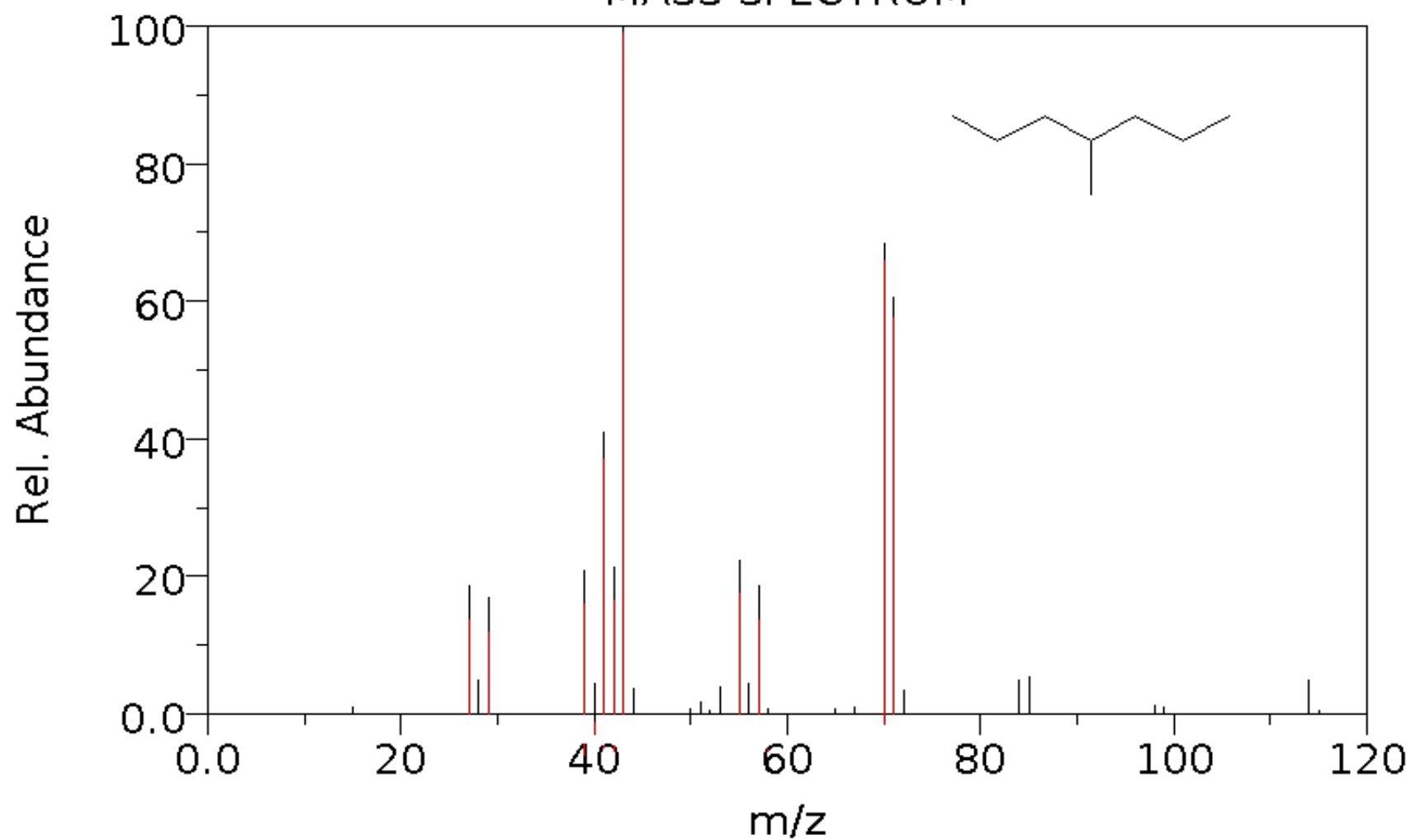


EI spectra of beta lactam at different e^- energies



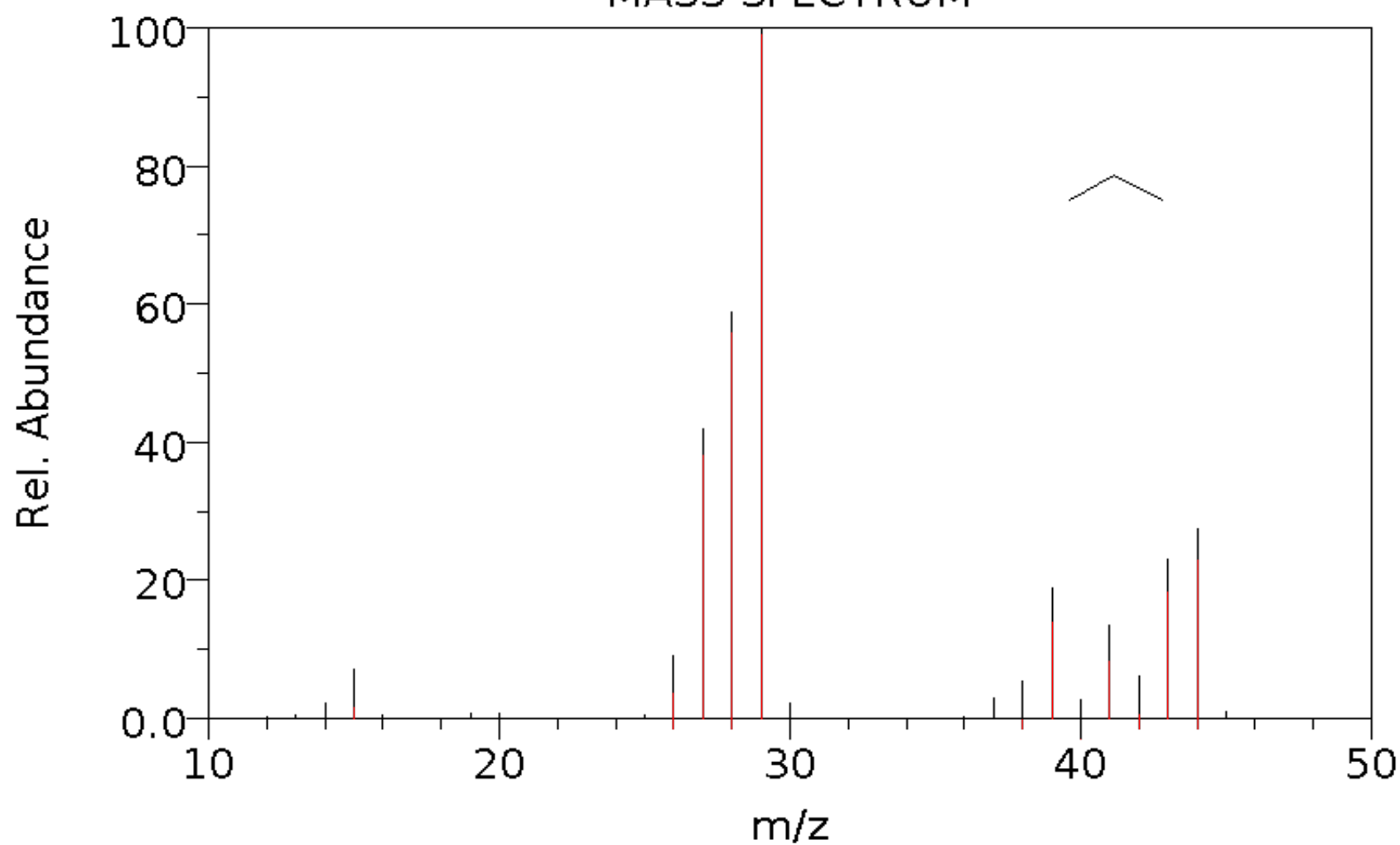
de Hoffmann, E.; Stroobant, V. *Mass Spectrometry: Principles and Applications*, 2nd Ed; Wiley: New York, 2004.

Heptane, 4-methyl-
MASS SPECTRUM



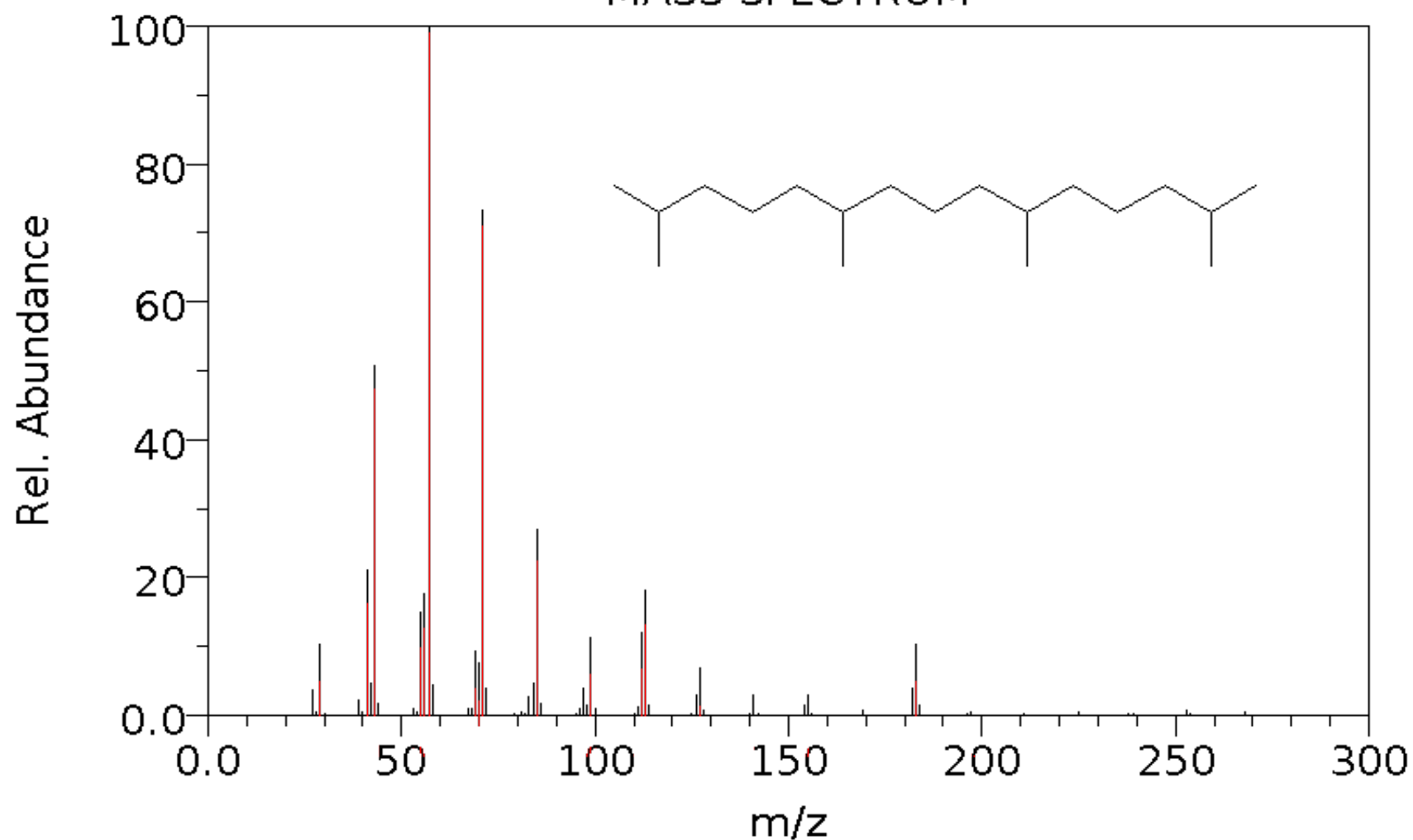
NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Propane
MASS SPECTRUM



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

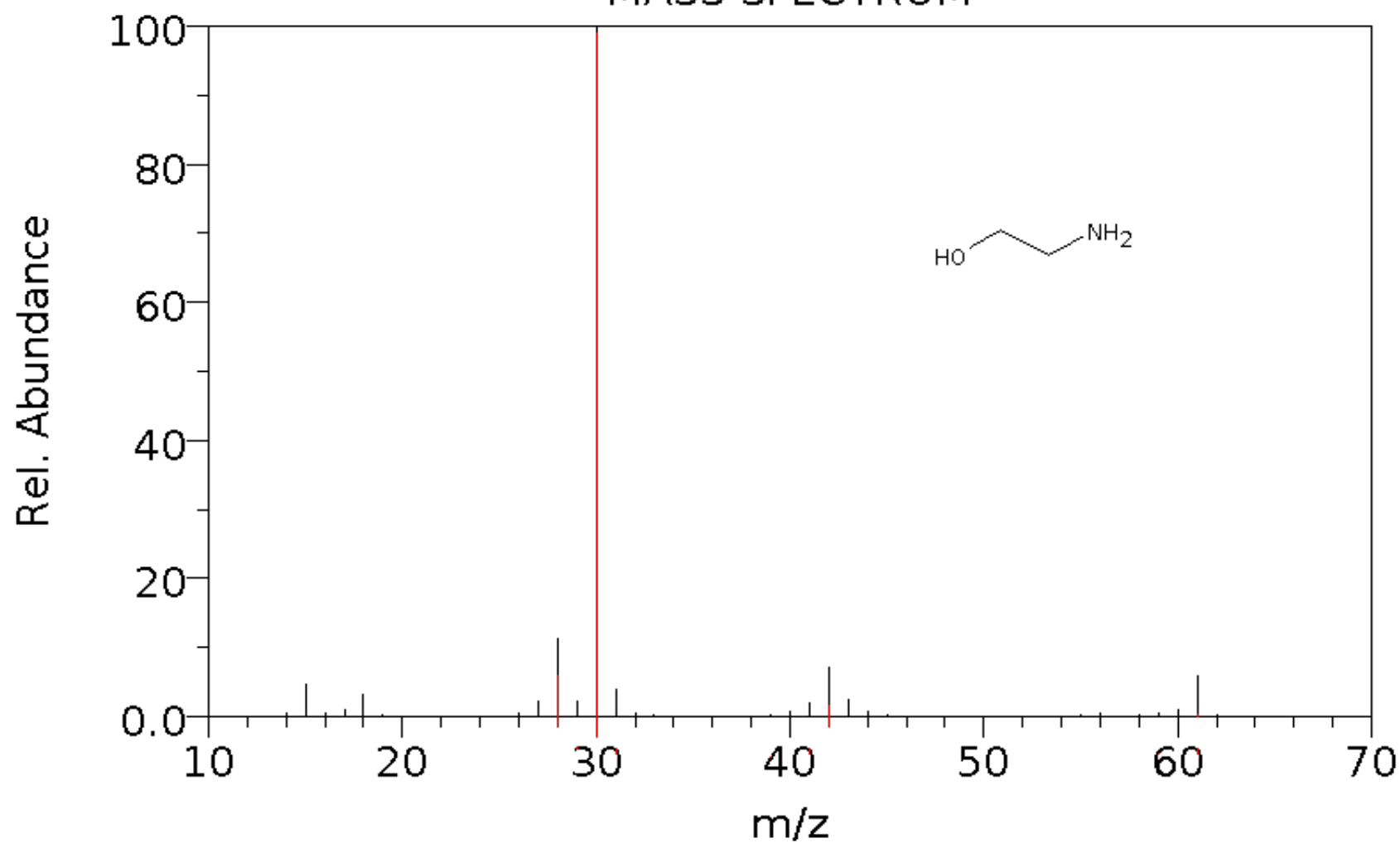
Pentadecane, 2,6,10,14-tetramethyl-
MASS SPECTRUM



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

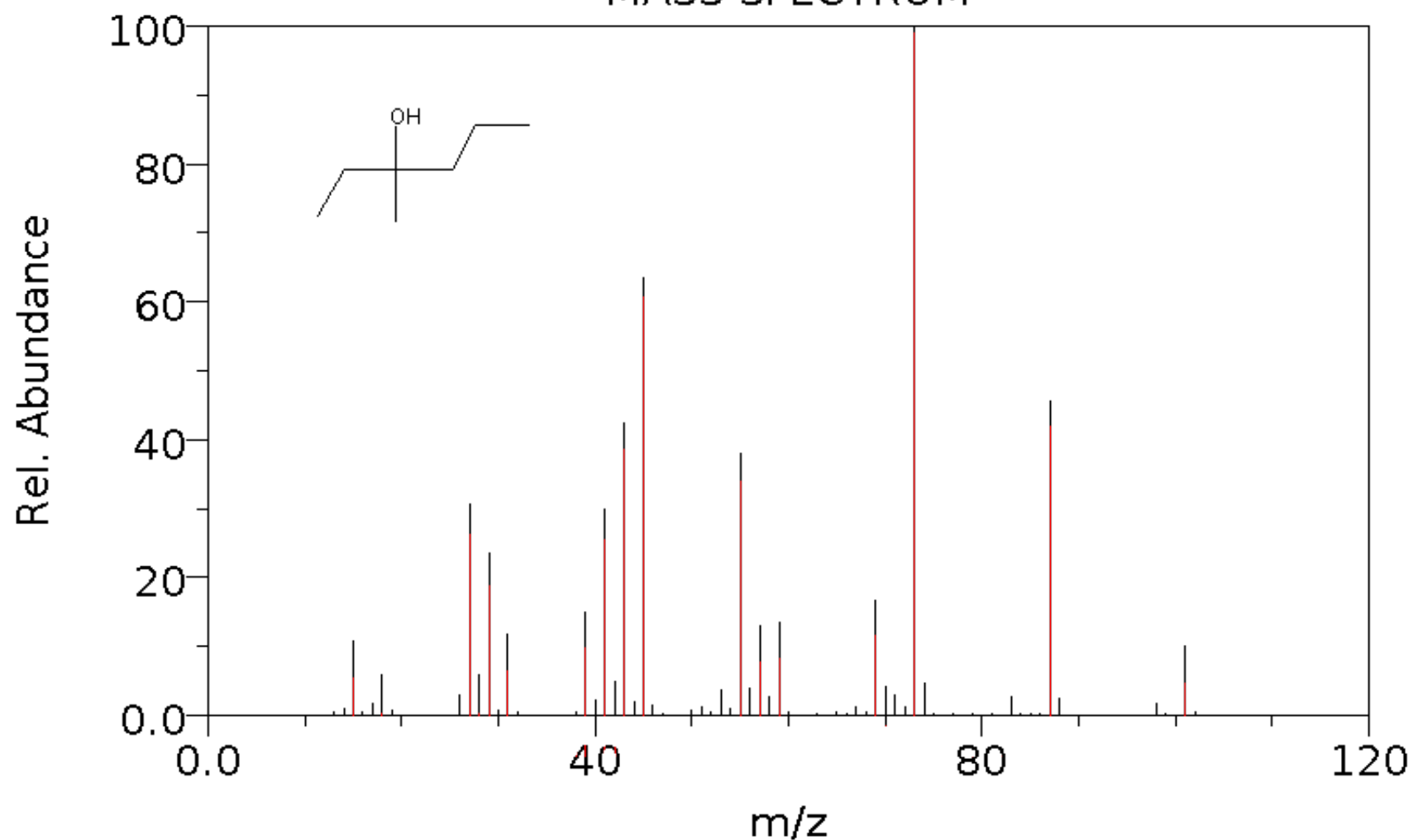
Monoethanolamine

MASS SPECTRUM



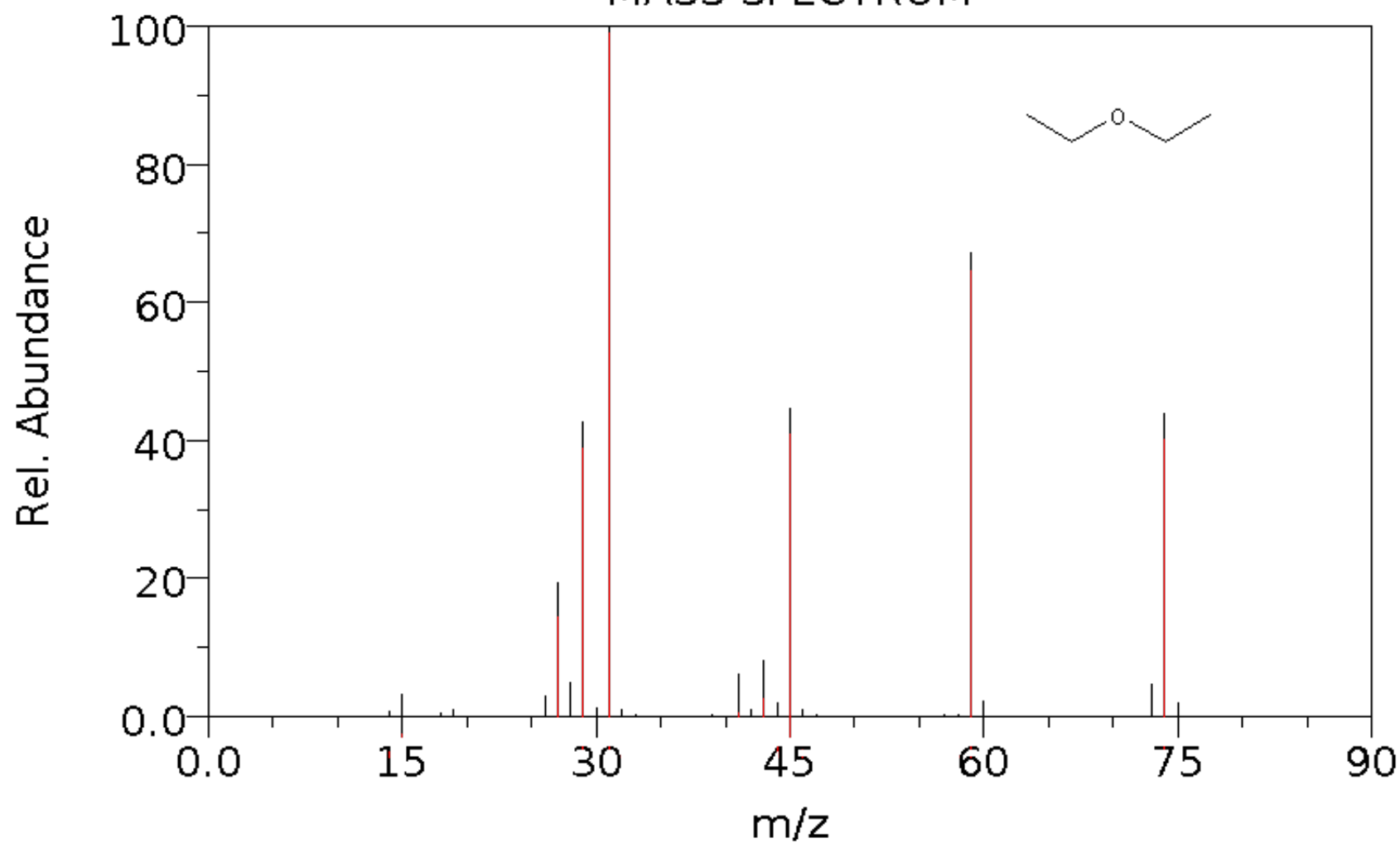
NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

3-Hexanol, 3-methyl-
MASS SPECTRUM



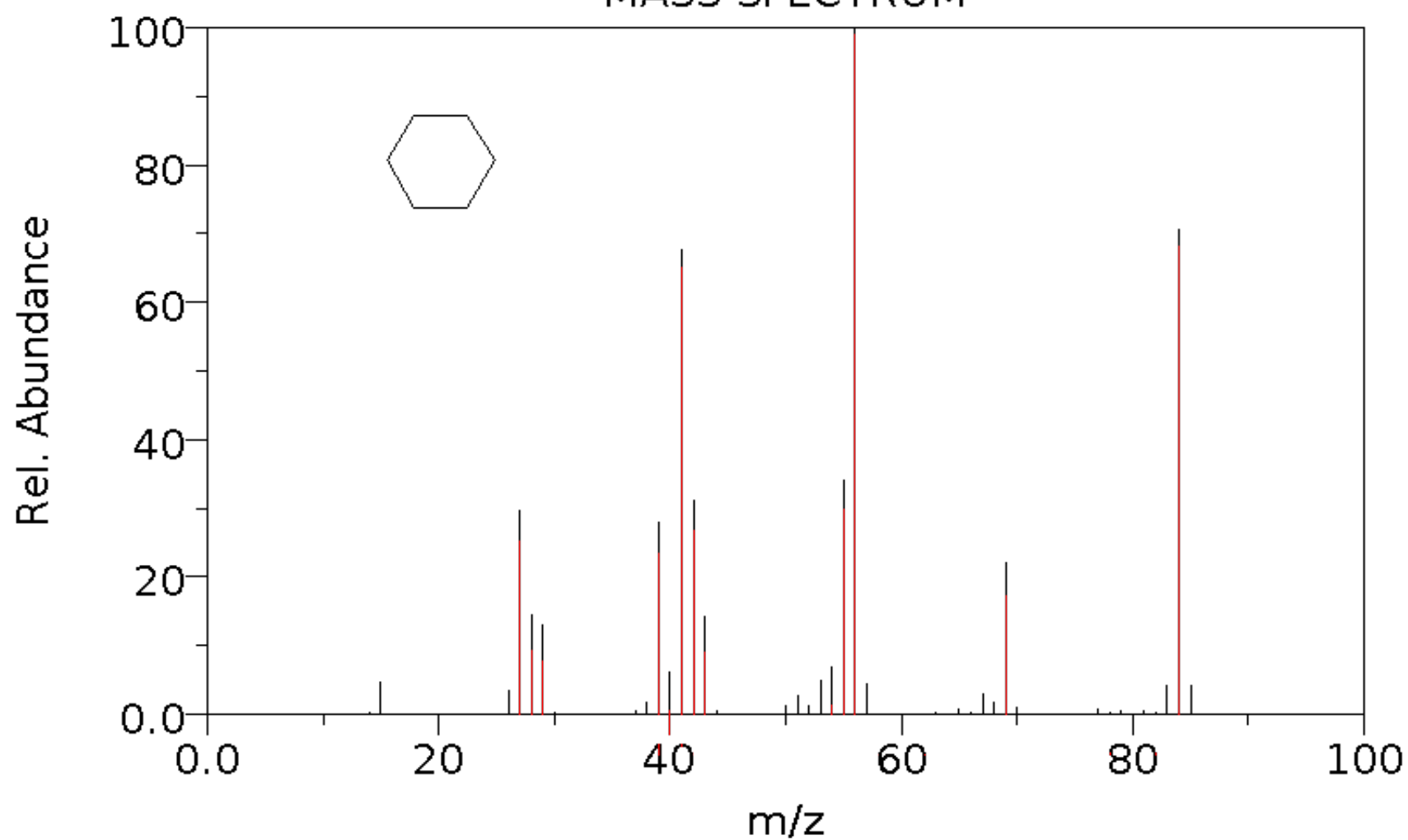
NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Ethyl ether
MASS SPECTRUM



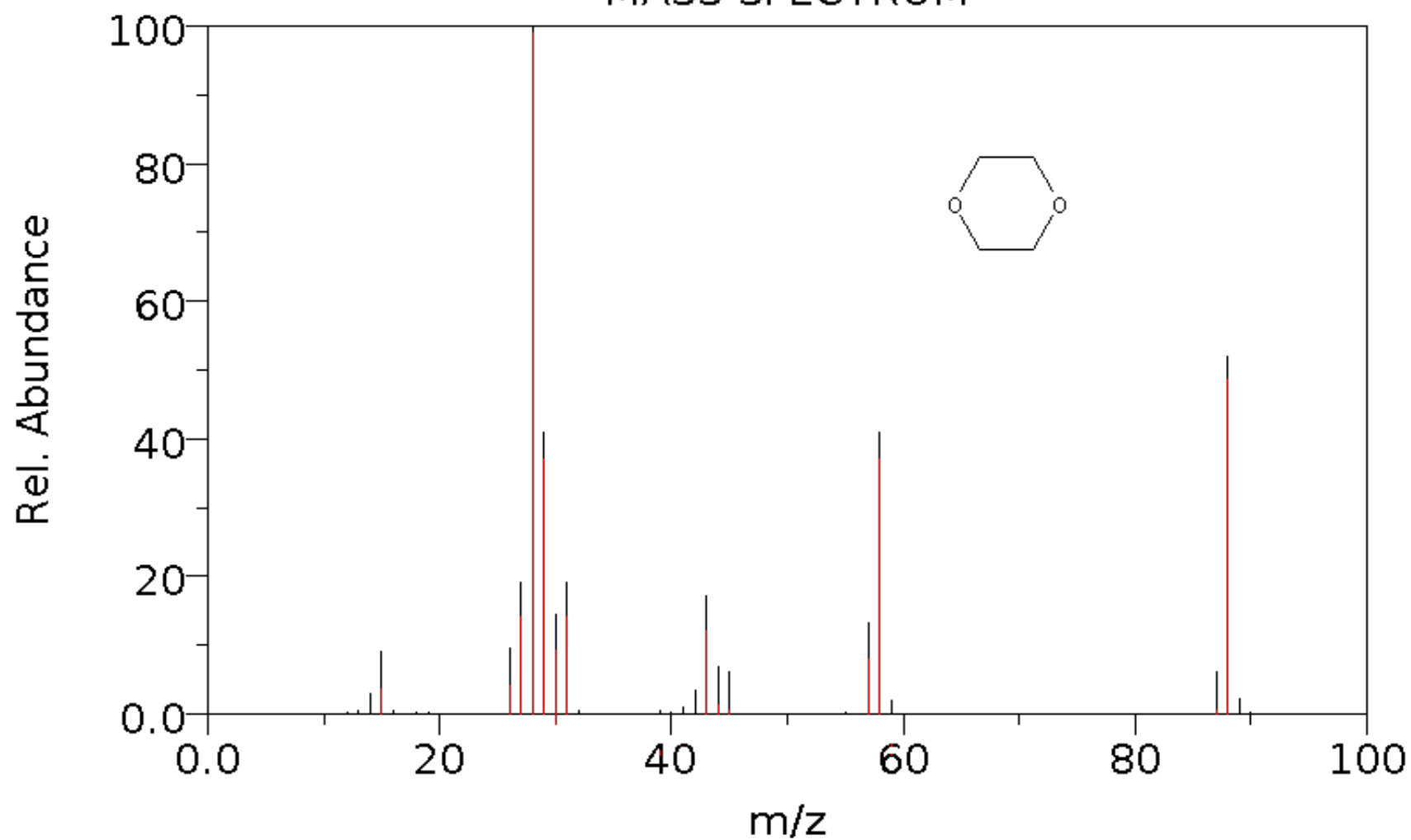
NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Cyclohexane
MASS SPECTRUM



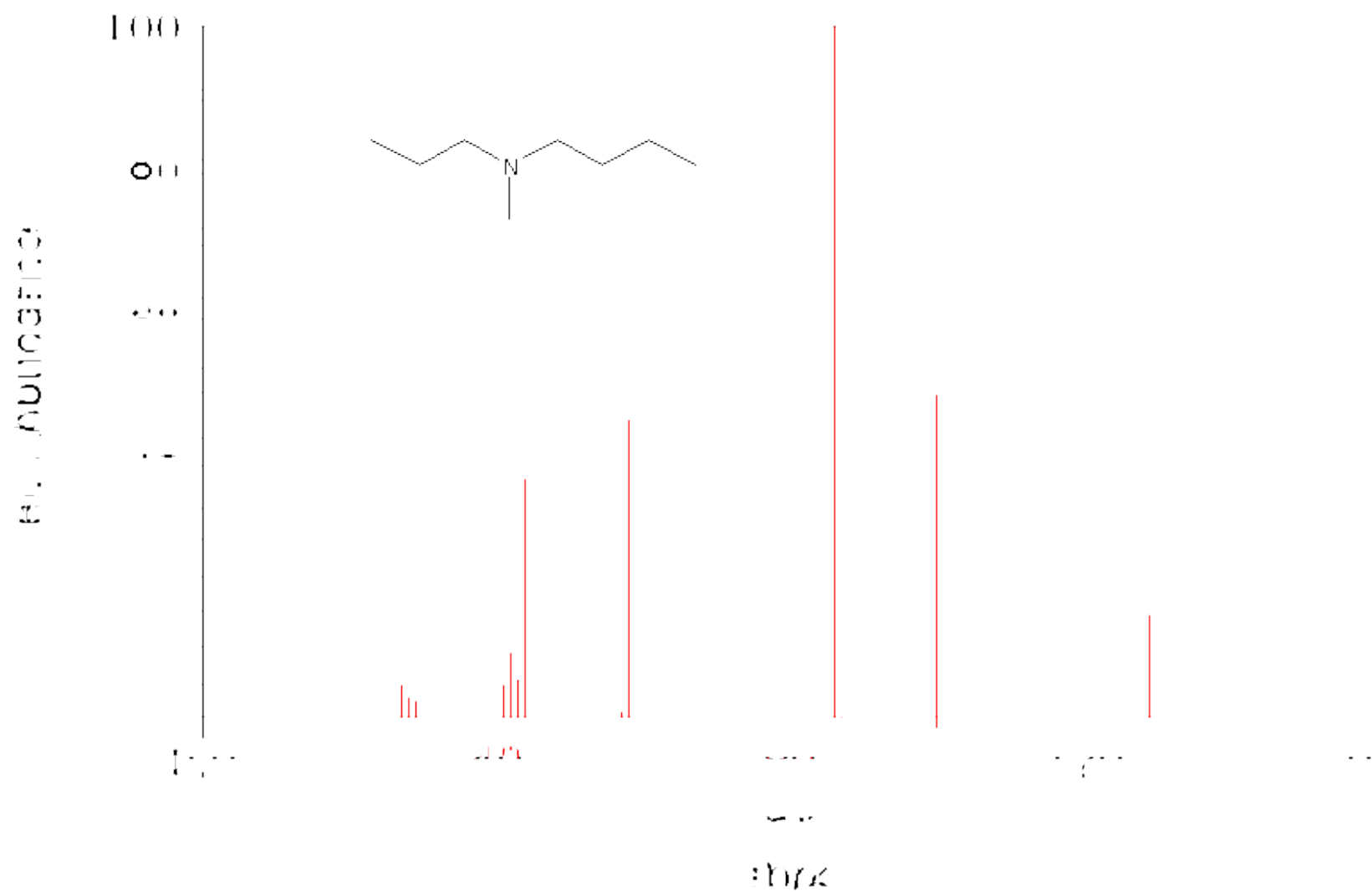
NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

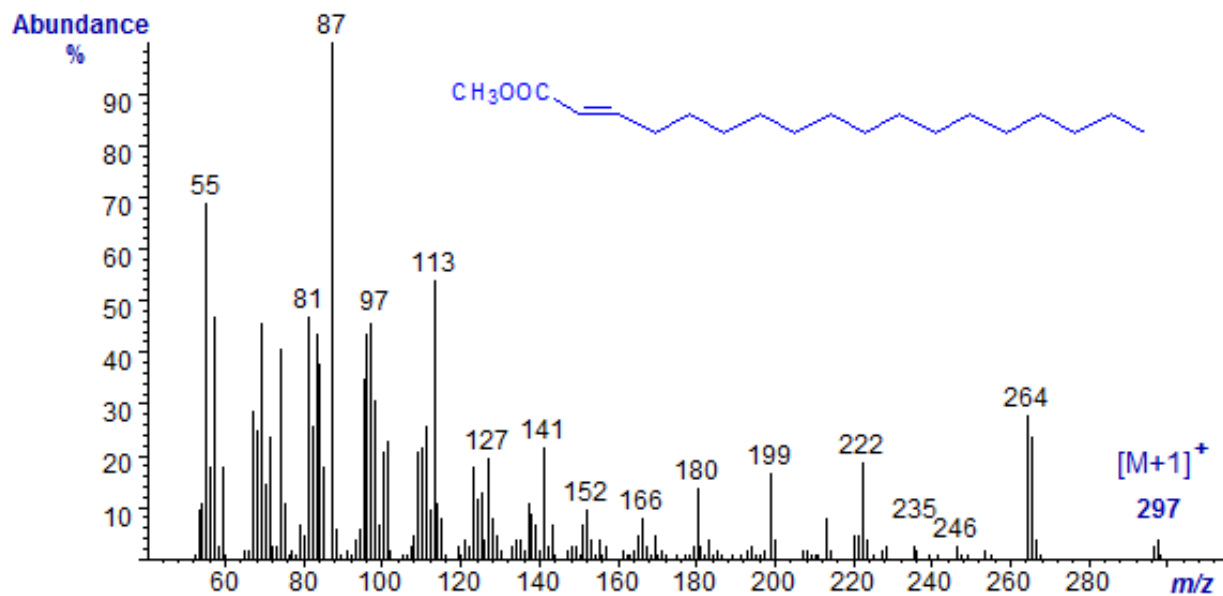
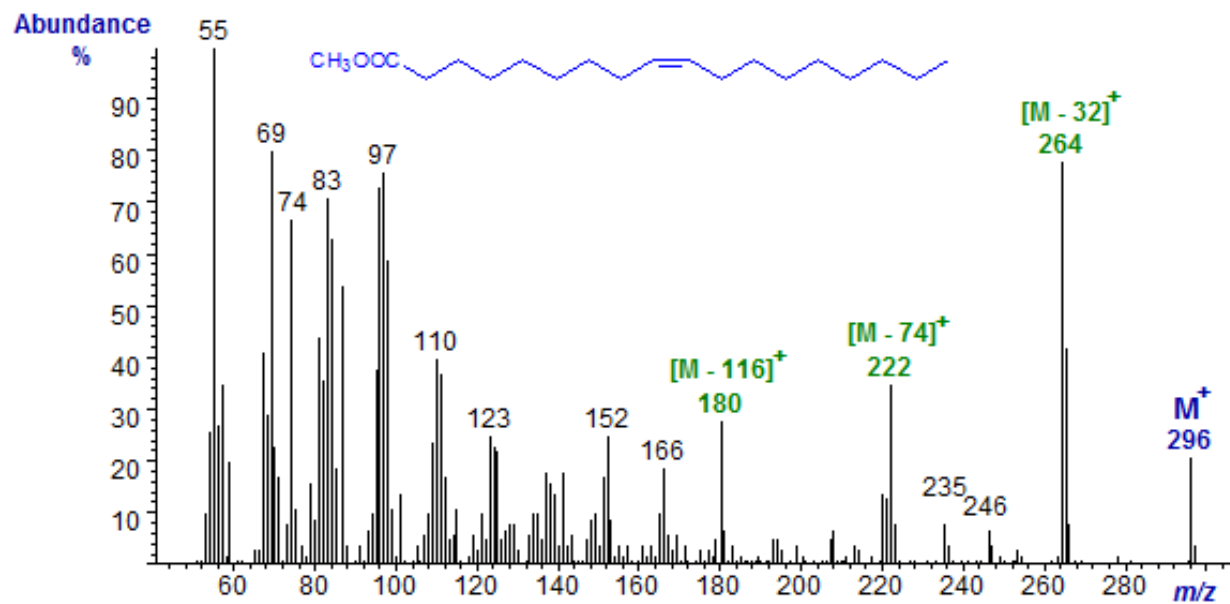
1,4-Dioxane
MASS SPECTRUM



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Butylamine, N-methyl-N-propyl- MASS SPECTRUM





Electrospray/Nanospray Ionization

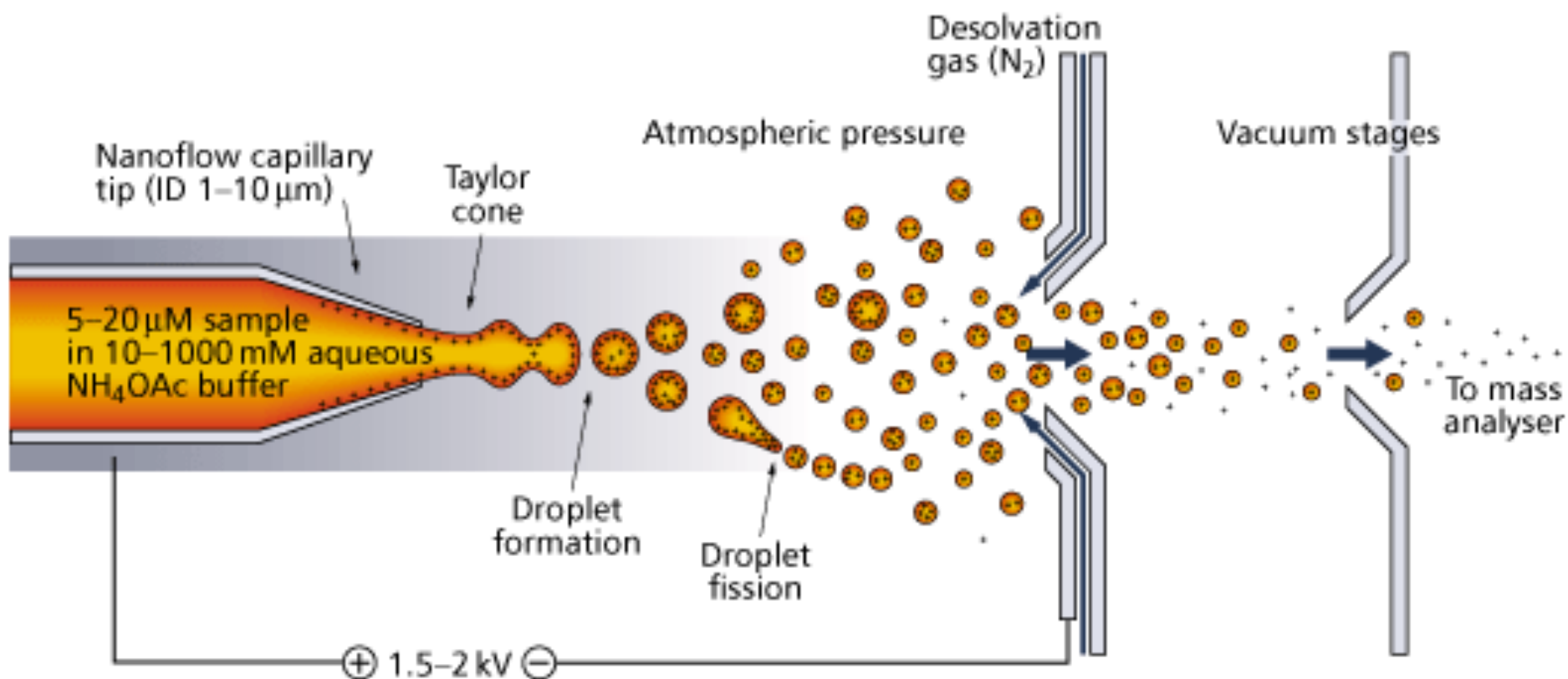
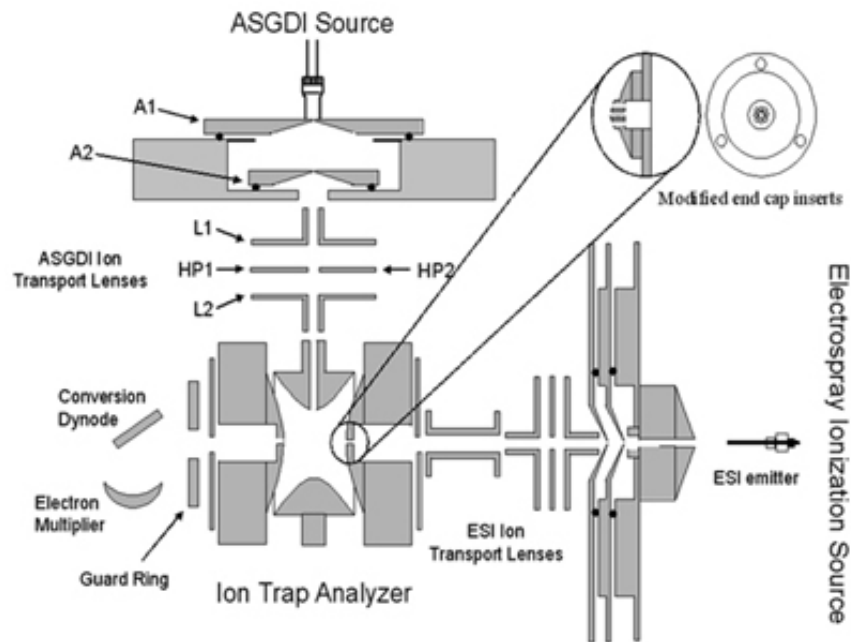


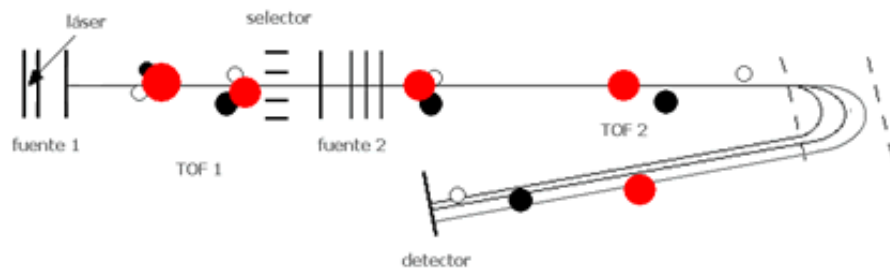
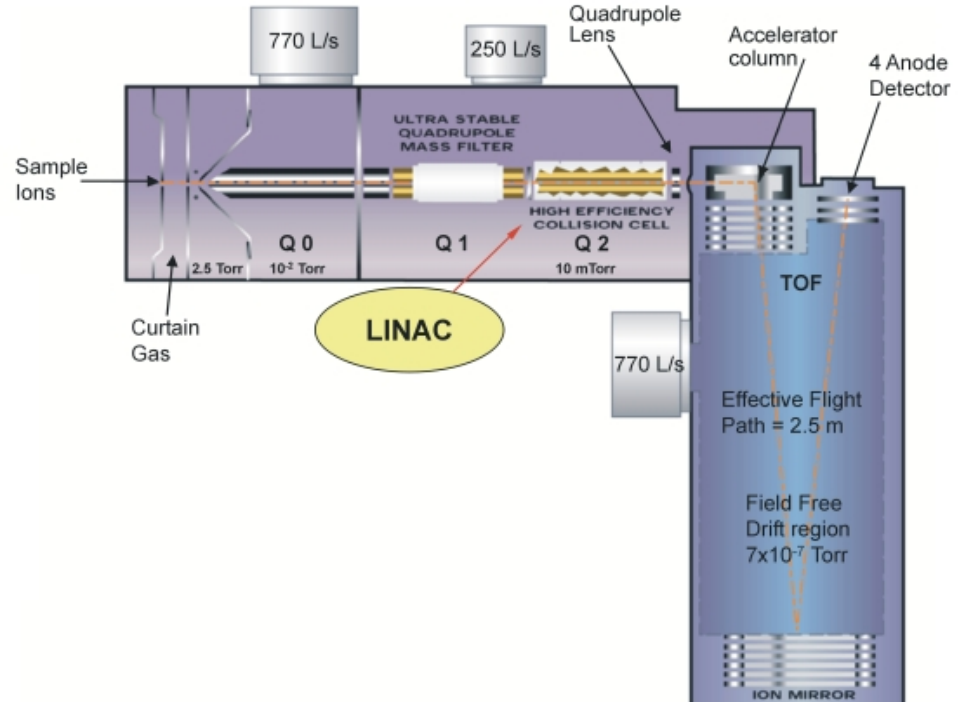
Image from: http://www.uab.edu/botanicals/pdfs/08_Sam090902.pdf

Hitachi M8000 LC/MSn



ESI

QStar



ESI

hen egg lysozyme

Platform II, BMB, The University of Leeds

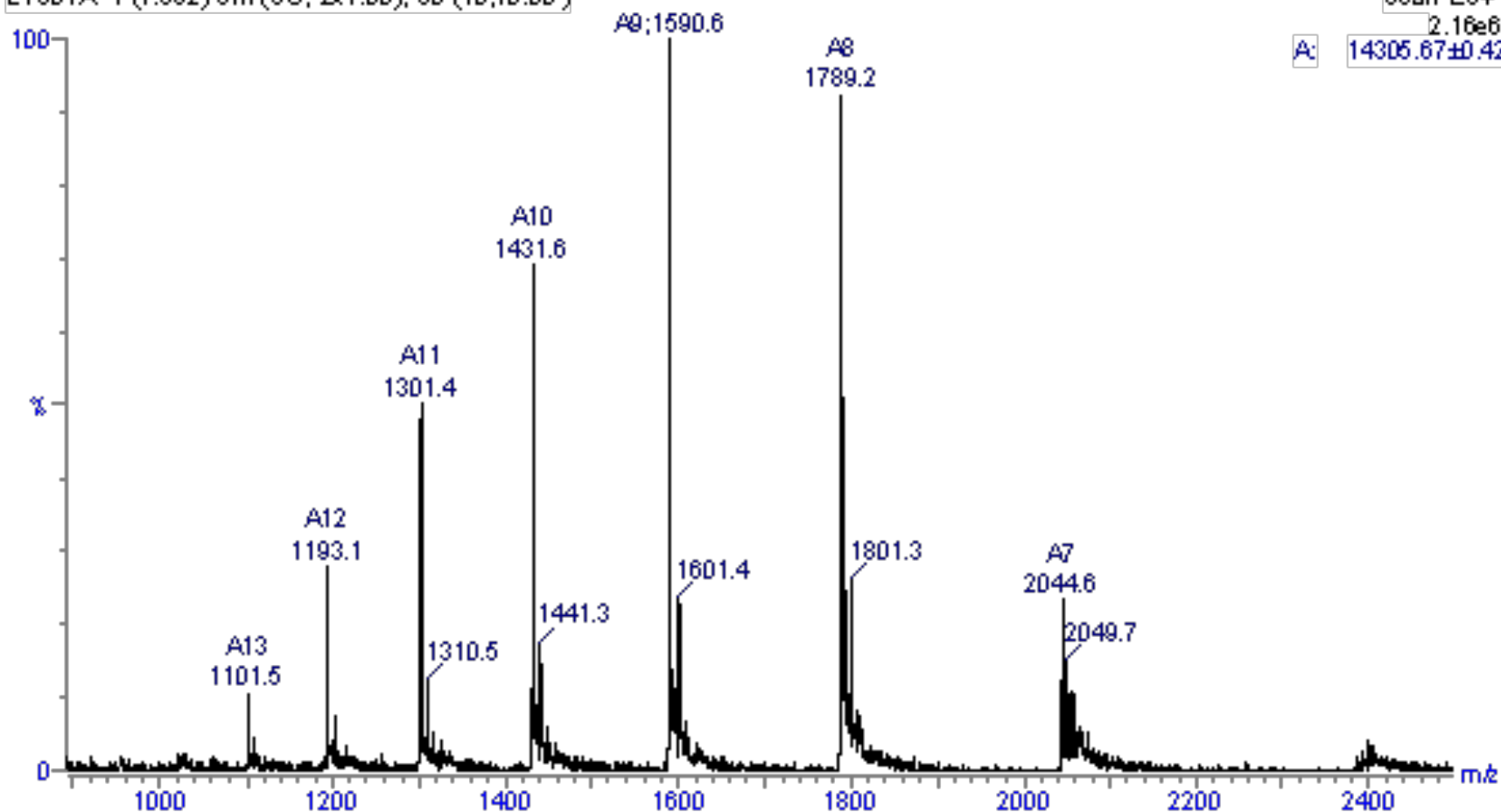
25-Jan-2000 10:00:37

LYS01A 1 (1.392) Sm (SG, 2x1.00); Sb (10,10.00)

Scan ES+

2.16e6

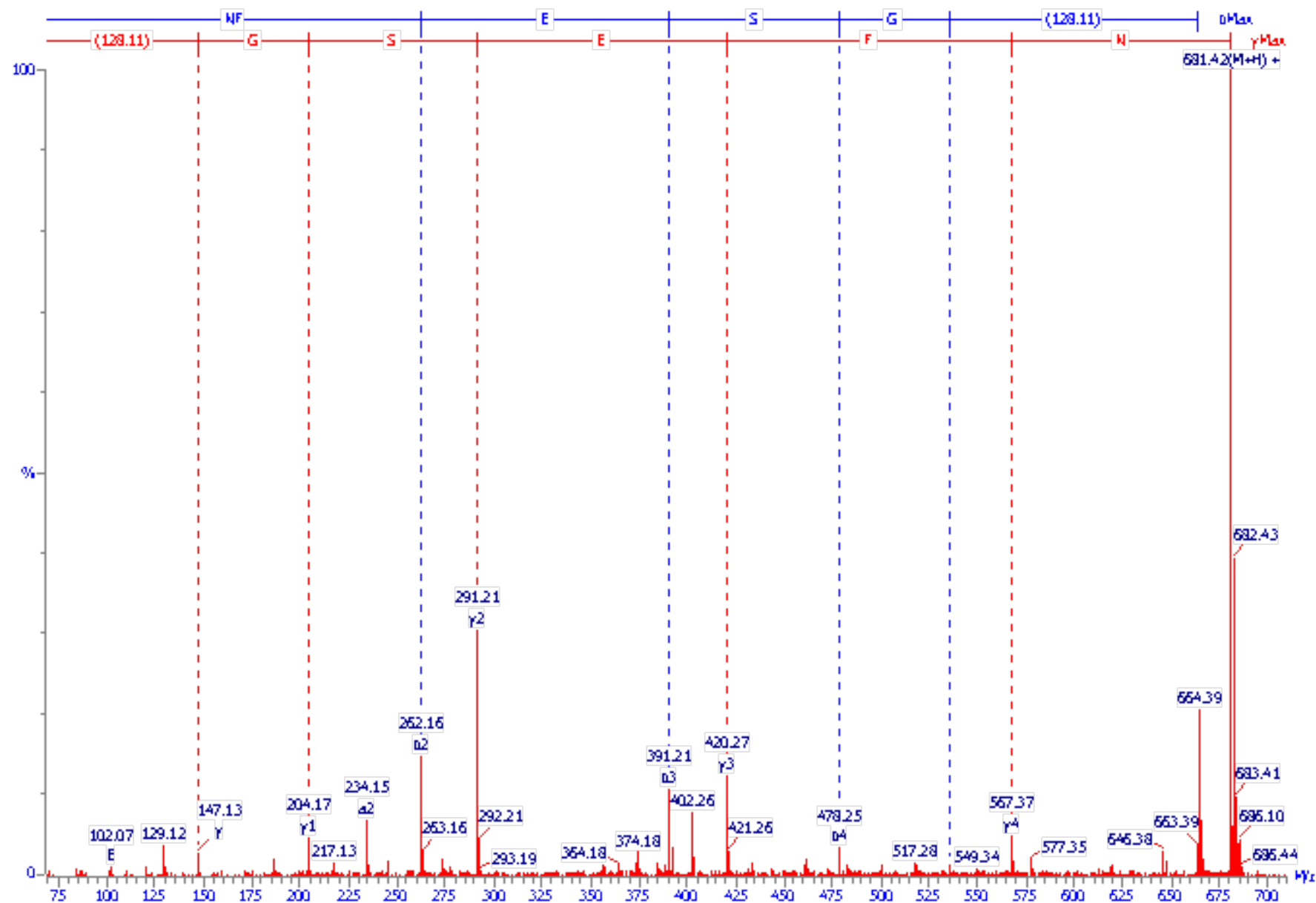
A: 14305.67±0.42



1:1000; 0 of 681.3

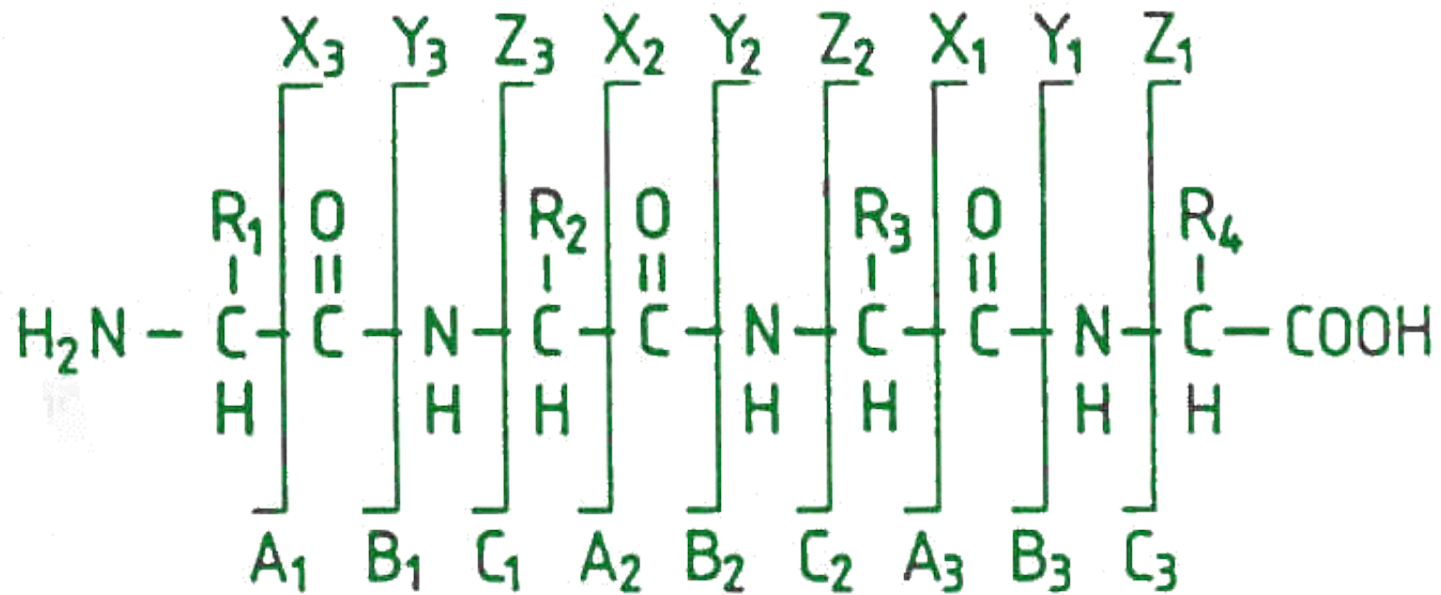
snsp09 AccMass 3 (Top2, H₂5000.0,0.00)

1: TO F MSMS 681.30ES+

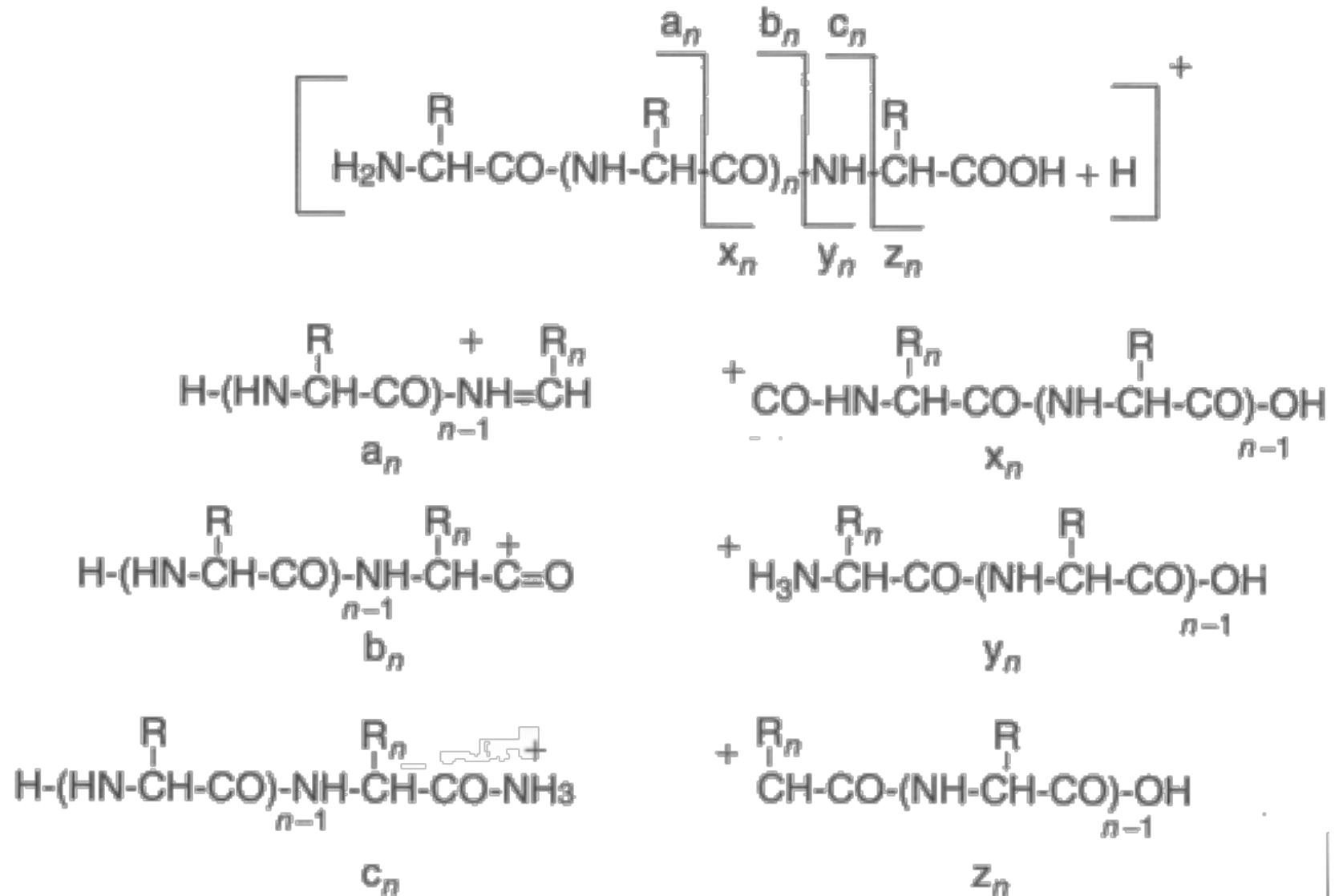


<i>Amino Acid</i>	<i>3 Letter Code</i>	<i>Single Letter Code</i>		<i>Residue Mass</i>	
				Monoisotopic	Average
Glycine	Gly	G		57.02147	57.052
Alanine	Ala	A		71.03712	71.079
Serine	Ser	S		87.03203	87.078
Proline	Pro	P		97.05277	97.117
Valine	Val	V		99.06842	99.133
Threonine	Thr	T		101.04768	101.105
Cysteine	Cys	C		103.00919	103.144
Isoleucine	Ile	I		113.08407	113.160
Leucine	Leu	L		113.08407	113.160
Asparagine	Asn	N		114.04293	114.104
Aspartic Acid	Asp	D		115.02695	115.089
Glutamine	Gln	Q		128.05858	128.131
Lysine	Lys	K		128.09497	128.174
Glutamic Acid	Glu	E		129.04260	129.116
Methionine	Met	M		131.04049	131.198
Histidine	His	H		137.05891	137.142
Phenylalanine	Phe	F		147.06842	147.177
Arginine	Arg	R		156.10112	156.188
Tyrosine	Tyr	Y		163.06333	163.170
Tryptophan	Try	W		186.07932	186.213
Homoserine Lactone				83.03712	83.090
Homoserine				101.04768	101.105
Pyroglutamic acid				111.03203	111.100
Carboxyamidomethyl Cysteine				160.03065	160.197
Carboxymethylcysteine				161.01466	161.181
Pyridylethylcysteine				208.06703	208.284

Peptide Fragmentation

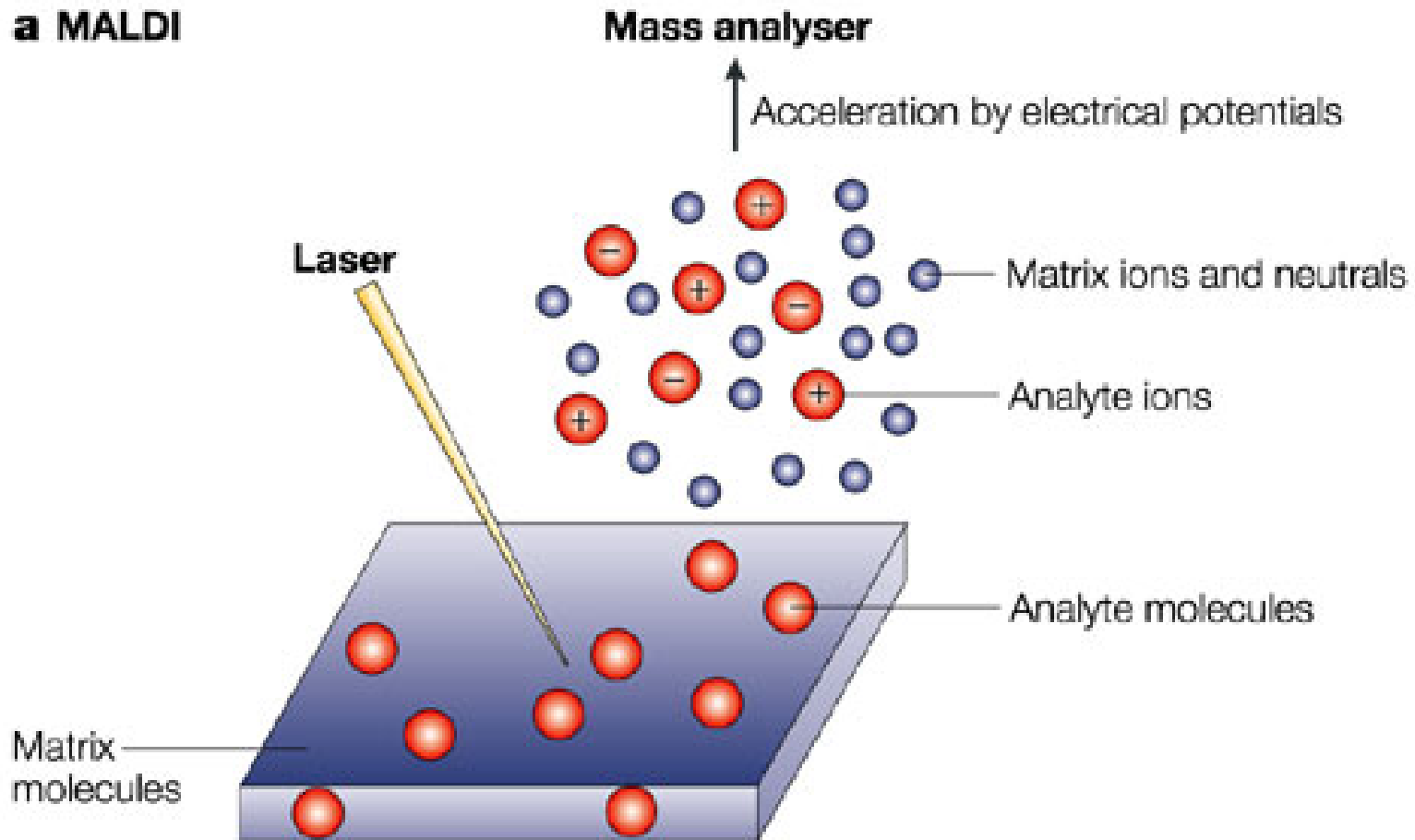


Peptide Fragmentation

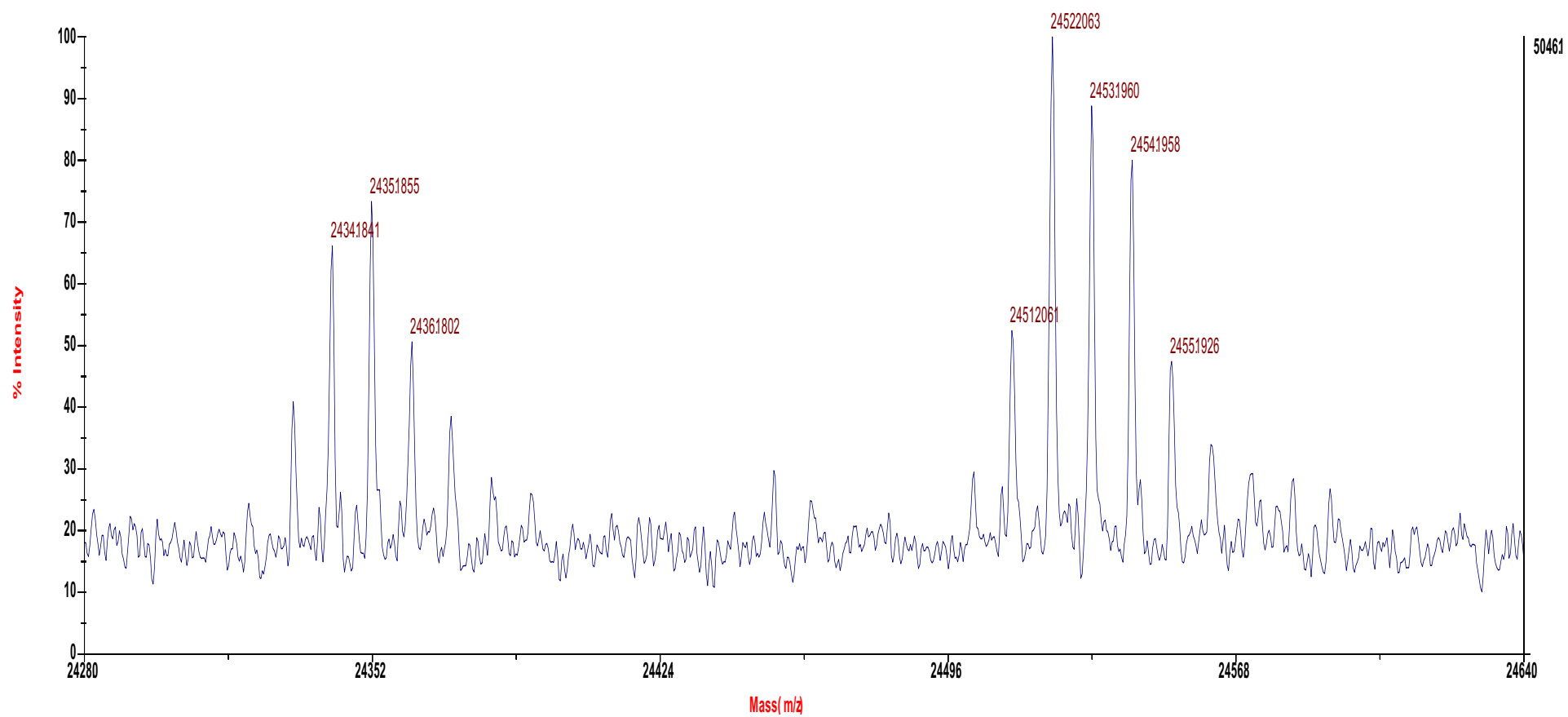


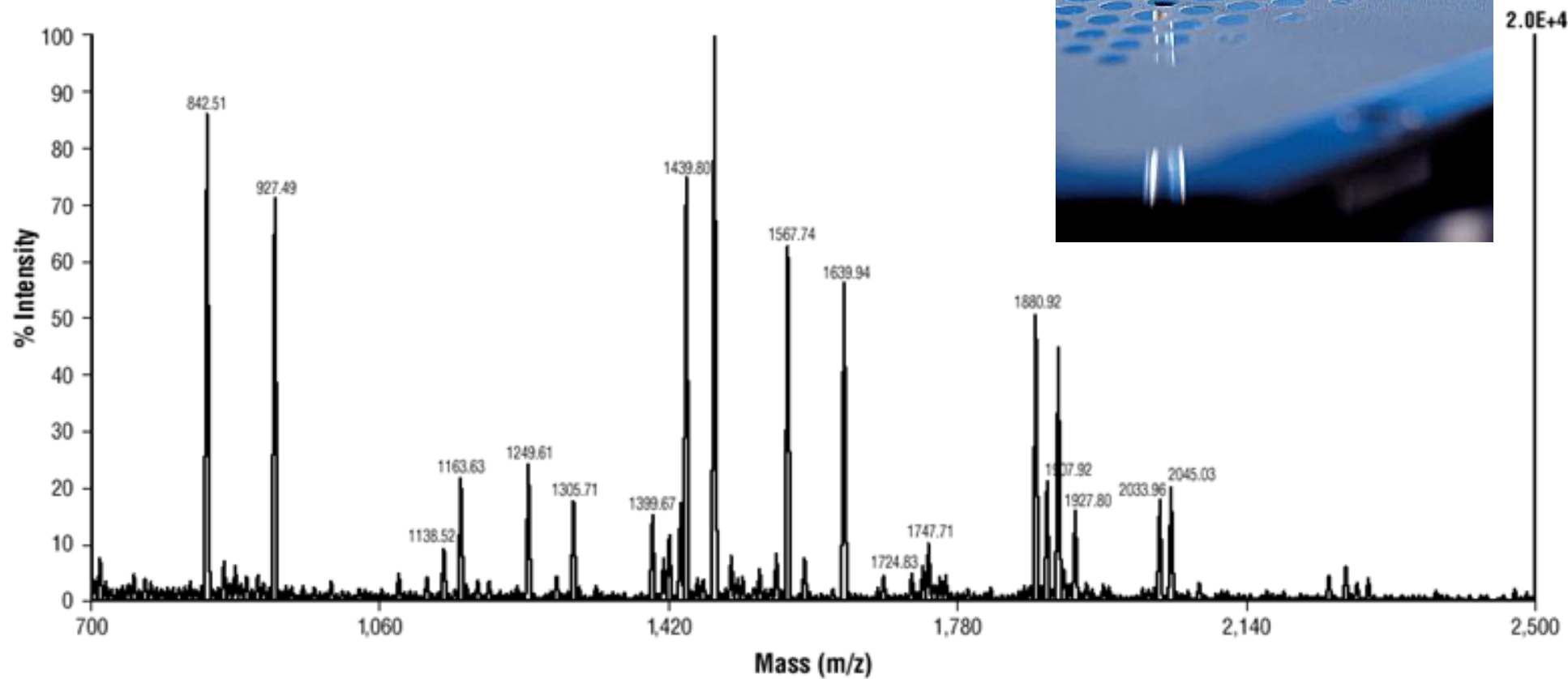
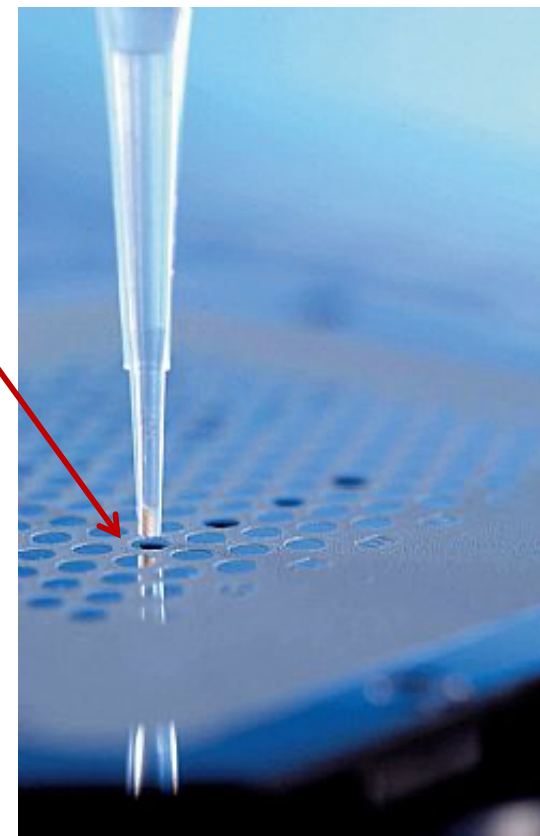
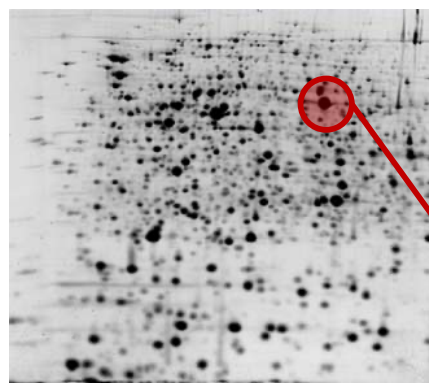
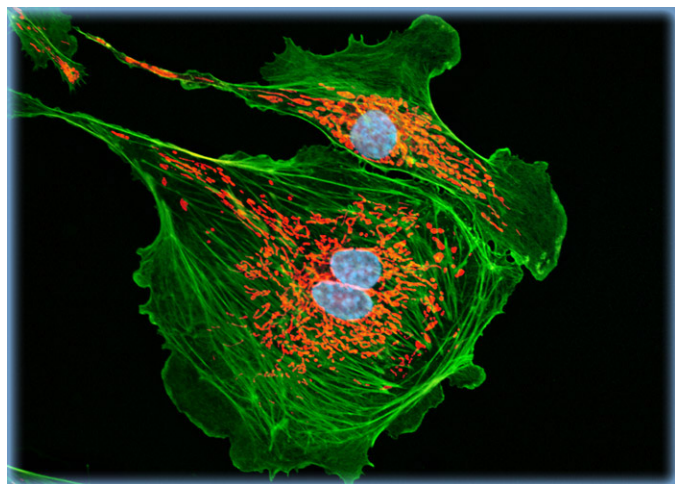
MALDI Ionization

a MALDI



Voyager Spec #1 [BP = 139.5.8, 590.7]







ProteinProspector

v 5.10.0

*Proteomics tools for mining sequence databases
in conjunction with Mass Spectrometry experiments.*

[Click here to see the latest new features.](#)

[The iPRG2012 study on detecting modified peptides in a complex mixture has been launched!](#)

[Click for more details.](#)

[ProteinProspector Asia Pacific](#)

ProteinProspector Tools

Administration/Help

Batch MSMS Database Searching [Instructions](#)

[Search Compare](#) [Batch-Tag Web](#) [Batch-Tag](#)

[Results Management](#) [Search Table](#)

Database Search Programs

[MS-Fit](#) [MS-Tag](#) [MS-Homology](#) [MS-Bridge](#)

[MS-Fit Upload](#) [MS-Seq](#) [MS-Pattern](#) [MS-NonSpecific](#)

Peptide / Protein MS Utility Programs

[MS-Digest](#) [MS-Product](#) [MS-Viewer](#) [\(Video\)](#)

[MS-Isotope](#) [MS-Comp](#)

Database Management

[DB-Stat](#)

[Video Tutorials](#) ^{NEW!}

[Administering ProteinProspector](#)

[User's Manual](#)

[FAQ](#)

[Bug Listing](#)

[ProteinProspector Revision History](#)

[ProteinProspector Automation Guidance](#)

Useful Tables

- [Mutation Mass Shifts](#)
- [Dipeptide Masses](#)
- [Trypsin Autolysis Products](#)

[Publications](#)

[Useful Links](#)

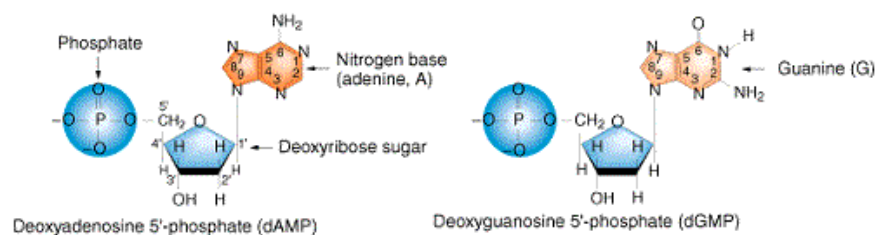
Questions/comments email: ppadmin@cgl.ucsf.edu

These programs were developed in the [UCSF Mass Spectrometry Facility](#), which is directed by Dr. Alma Burlingame, Professor of Chemistry and funded by the [NIH National Center for Research Resources](#).

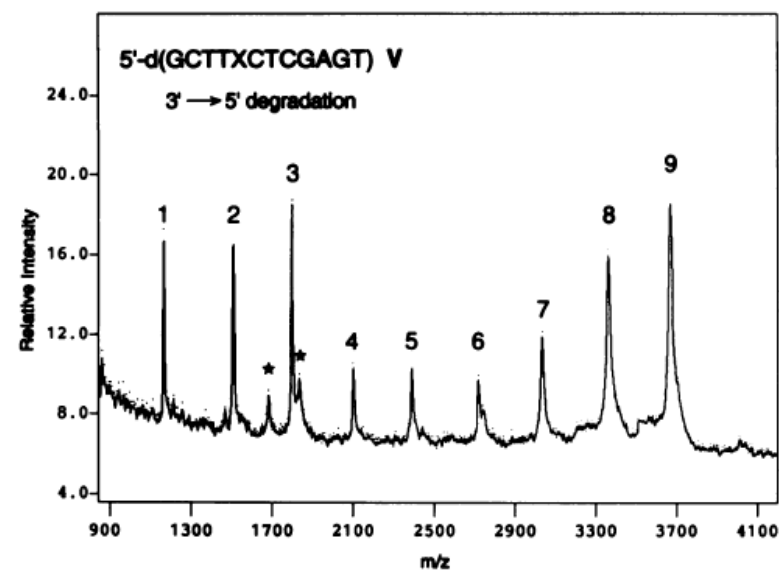
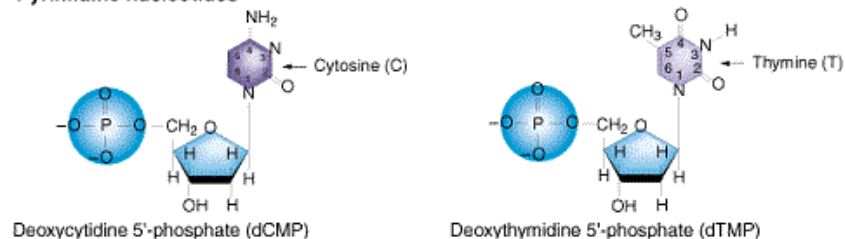
MS-Fit

Database User Protein NCBI nr.2011.10.10 NCBI nr.2011.10.10.random NCBI nr.2011.10.10.random.concat [+] User Protein Sequence DNA Frame Translation 3 Taxonomy All HUMAN MOUSE HUMAN RODENT MODEL PLANTS RODENT ROACH LOCUST BEETLE Output HTML ☐ Hits to file ☐ Name lastres	Digest Trypsin Max. Missed Cleavages 1 Constant Mods Acetohydrazide (C-term) Acetohydrazide (DE) Acetyl (K) Acetyl (N-term) Acetyl:2H(3) (K) Acetyl:2H(3) (N-term)
[+] Pre-Search Parameters	
Start Search	Sample ID (comment) Display Graph ☐
Maximum Reported Hits 5 Sort By Score Sort Report Homologous Proteins Interesting Min. # peptides required to match 4 Report MOWSE Scores ☒ Pfactor 0.4 Masses are monoisotopic Tol 20 ppm Sys Err 0 Contaminant Masses	Possible Modifications Peptide N-terminal Gln to pyroGlu Oxidation of M Protein N-terminus Acetylated Acrylamide Modified Cys User Def Mod 1 Acetyl (K) User Def Mod 2 Acetyl (K) User Def Mod 3 Acetyl (K) User Def Mod 4 Acetyl (K) OR Unknown Amino Acid ☐ Single Base Change ☐ Homology ☐ Max Mods 1 Min. # match with NO AA subs 1
Instrument ESI-Q-TOF Data Format PP M/Z Charge	
Data Paste Area 842.5100 856.5220 864.4733 870.5317 940.4754 943.4885 959.4934 970.4308	

Purine nucleotides



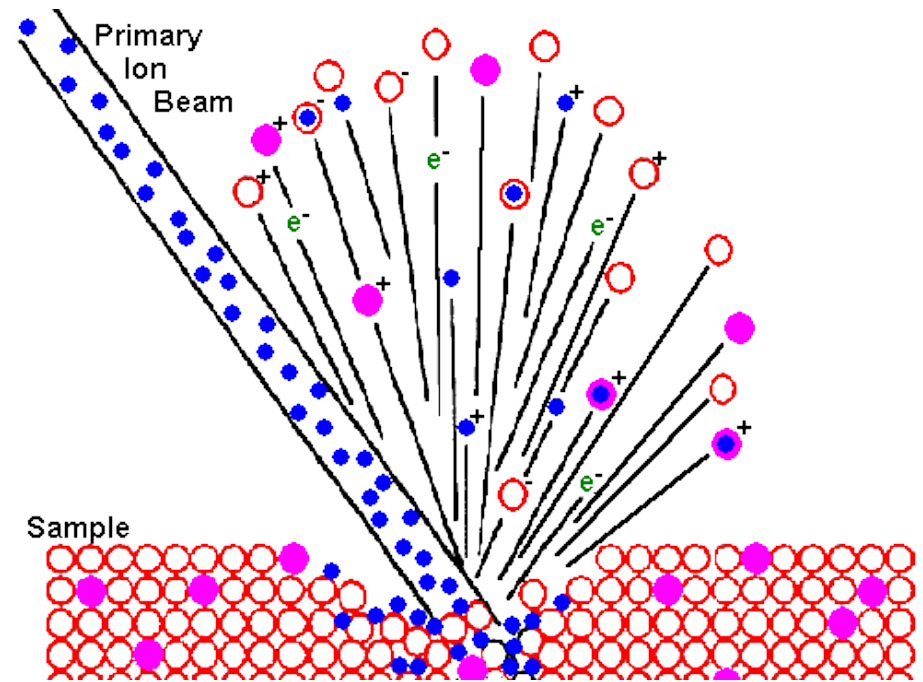
Pyrimidine nucleotides



Peak	Sequence	Mass calc.	Mass found	Δm
1	5'-d(GCTT)	1163.8	1163.9	-0.1
2	5'-d(GCTTX)	1507.1	1506.9	0.2
3	5'-d(GCTTXC)	1796.2	1796.2	0
4	5'-d(GCTTXCT)	2100.4	2100.5	-0.1
5	5'-d(GCTTXCTC)	2389.6	2389.8	-0.2
6	5'-d(GCTTXCTCG)	2718.9	2719.3	-0.4
7	5'-d(GCTTXCTCGA)	3032.1	3032.8	-0.7
8	5'-d(GCTTXCTCGAG)	3361.3	3362.0	-0.7
9	5'-d(GCTTXCTCGAGT)	3665.5	3666.0	-0.5

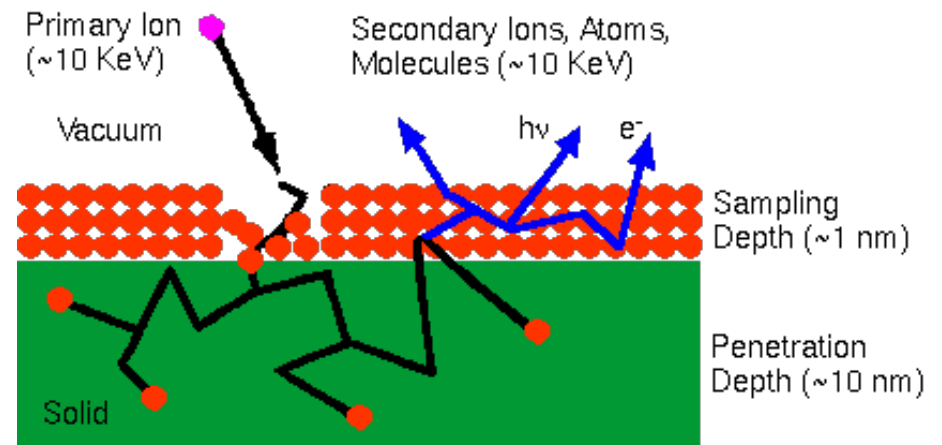
Ion Beam Sputtering

- The bombarding primary ion beam produces monatomic and polyatomic particles of sample material and resputtered primary ions, along with electrons and photons.
- The secondary particles carry negative, positive, and neutral charges and they have kinetic energies that range from zero to several hundred eV.
- Primary beam: Cs^+ , O_2^+ , O , Ar^+ , and Ga^+ with depths of depths 1 to 10 nm between 1 and 30 keV.



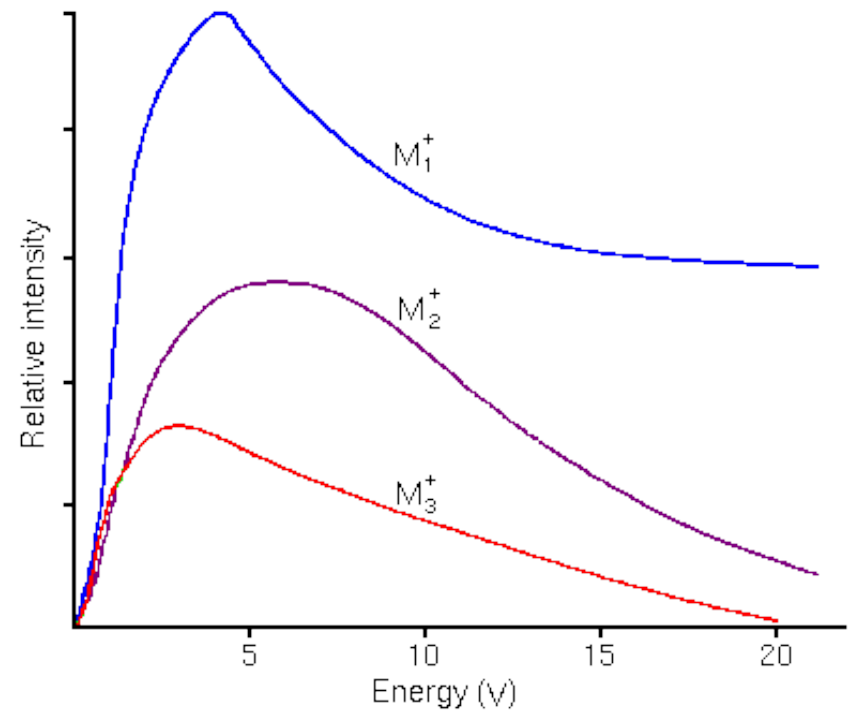
Sputtering Effects

- The collision cascade model has the best success at quantitatively explaining how the primary beam interacts with the sample atoms.
- Sputtering leads to surface roughness in the sputter craters.



Secondary Ion Energy Distributions

- The sputtering process produces secondary ions with a range of (translational) kinetic energies.
- Molecular Ions (internal vibrational and rotational modes)
- Atomic Ions (only in translational modes)



Secondary Ion Yields

Primary Beam Effects

- The variability in ionization efficiencies leads to different analysis conditions for different elements as indicated on the periodic table.

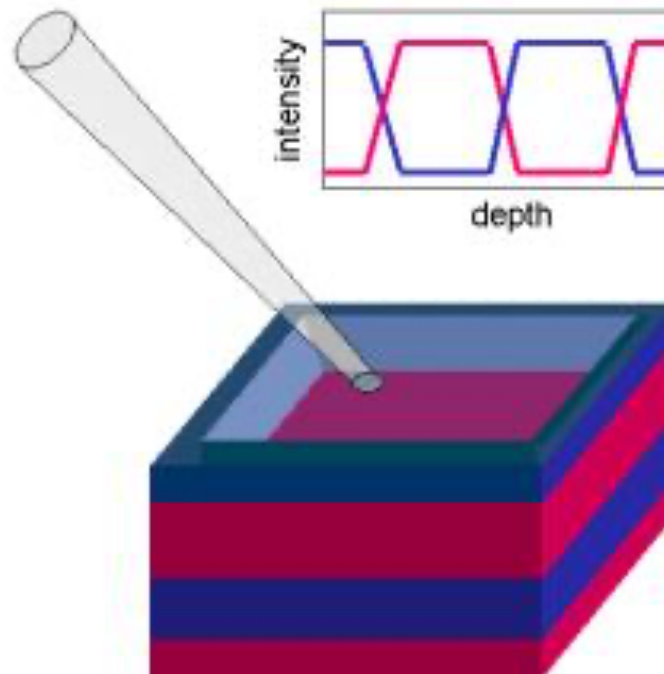
H																	He				
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac																			
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu								
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr								

Sensitivity and Detection Limits

- The SIMS detection limits for most trace elements are between 1×10^{12} and 1×10^{16} atoms/cc.
- Dark Current : The output of an electron multiplier if no secondary ions are striking it.
- Oxygen present in vacuum systems or analyte atoms sputtered from mass spectrometer parts.

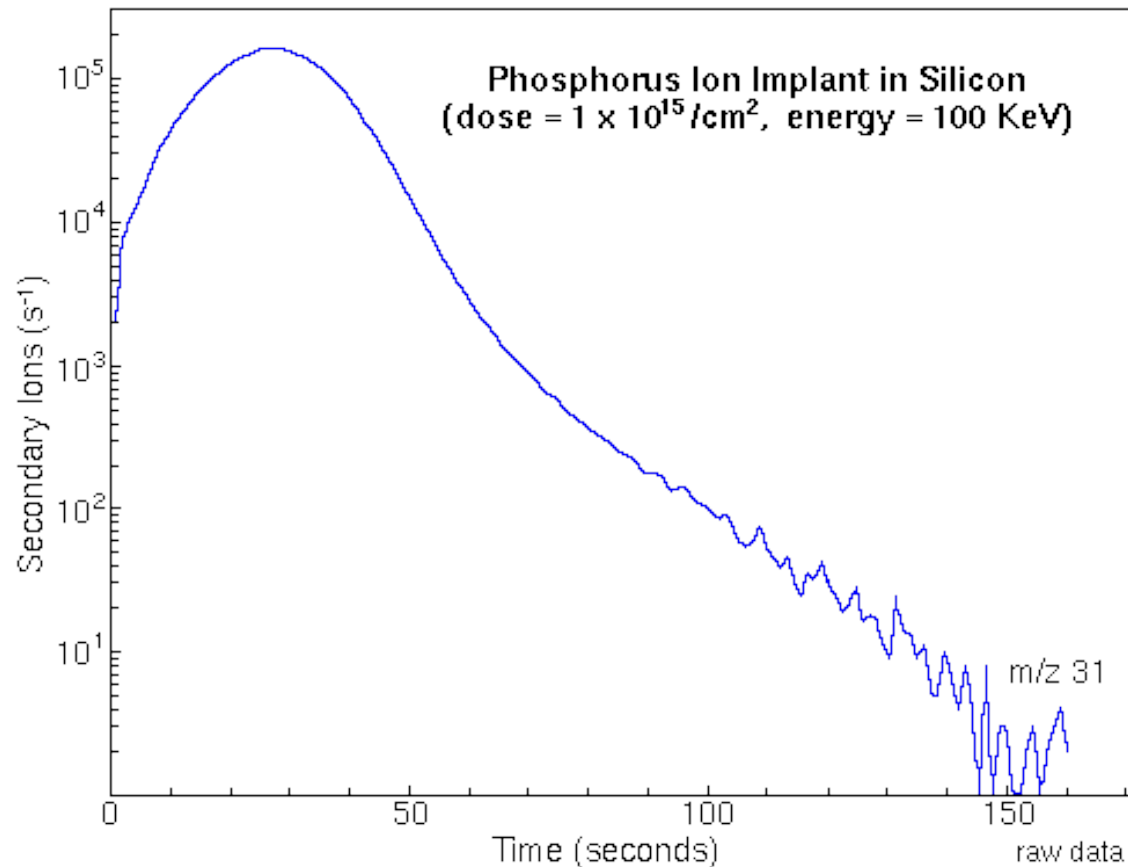
(3) Depth Profiling

- In contrast to a static SIMS experiment, high primary ion dose densities are applied giving a successive removal (sputtering) of the respective top surface layers. By acquiring spectra during the sputtering the in-depth distribution of elements and small clusters (e.g. oxides) can be monitored.



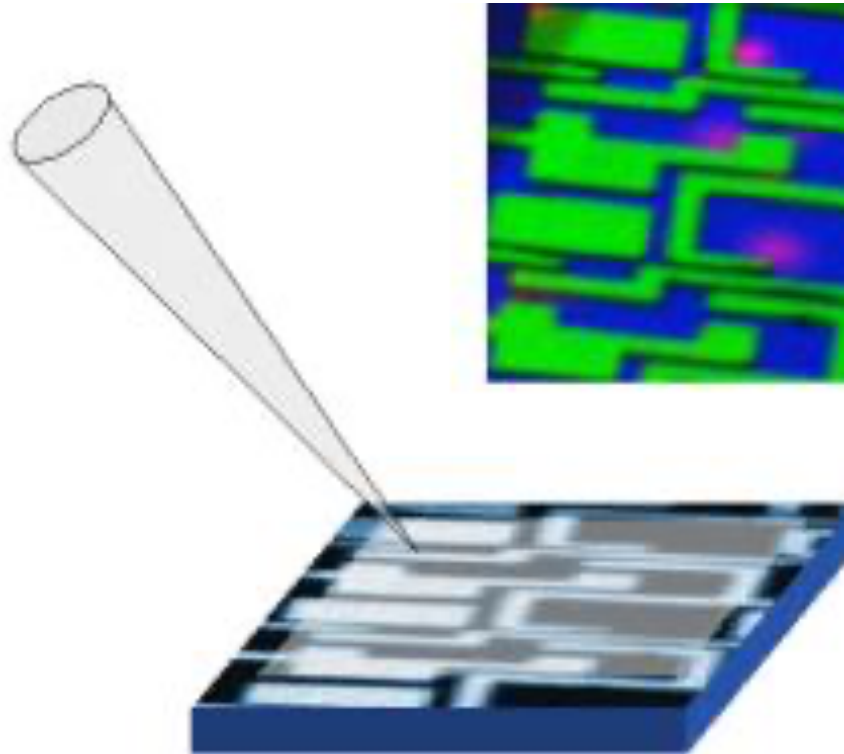
Depth Profiling

- Monitoring the secondary ion count rate of selected elements as a function of time leads to depth profiles.



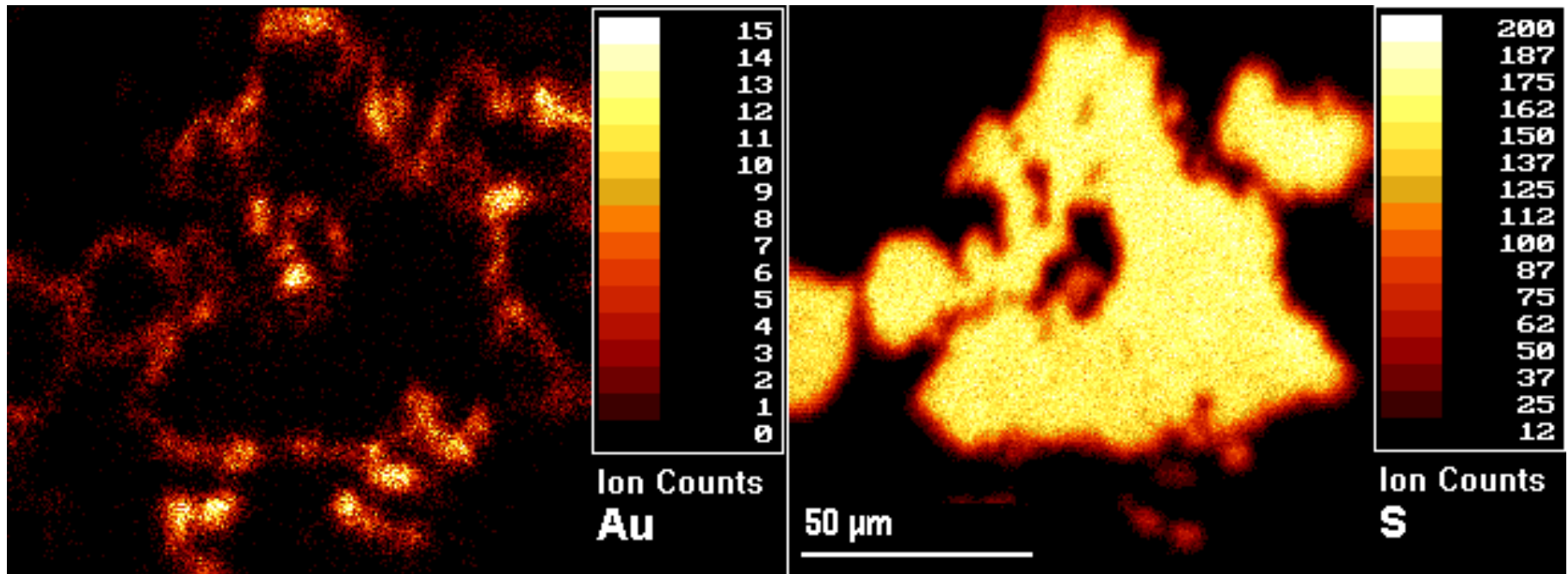
(2) Surface Imaging

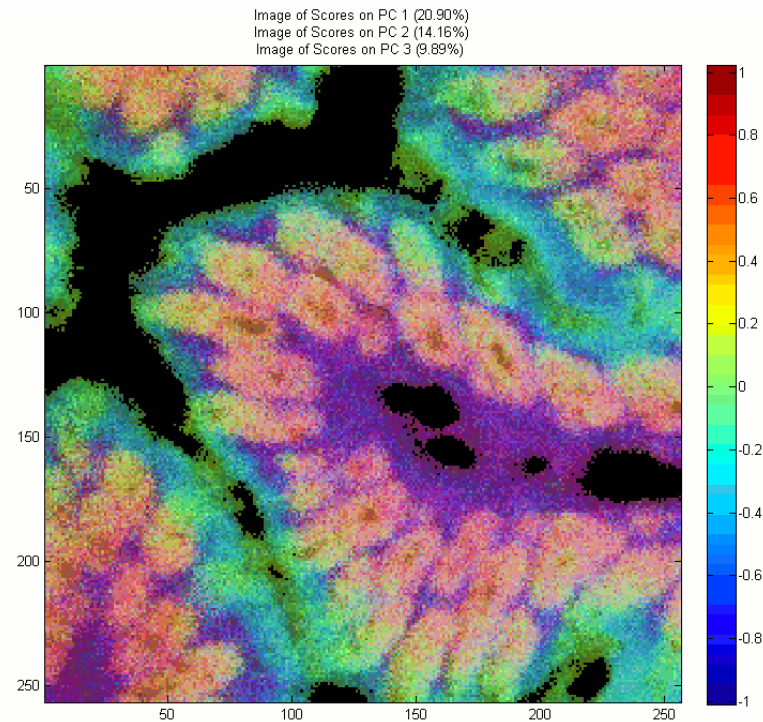
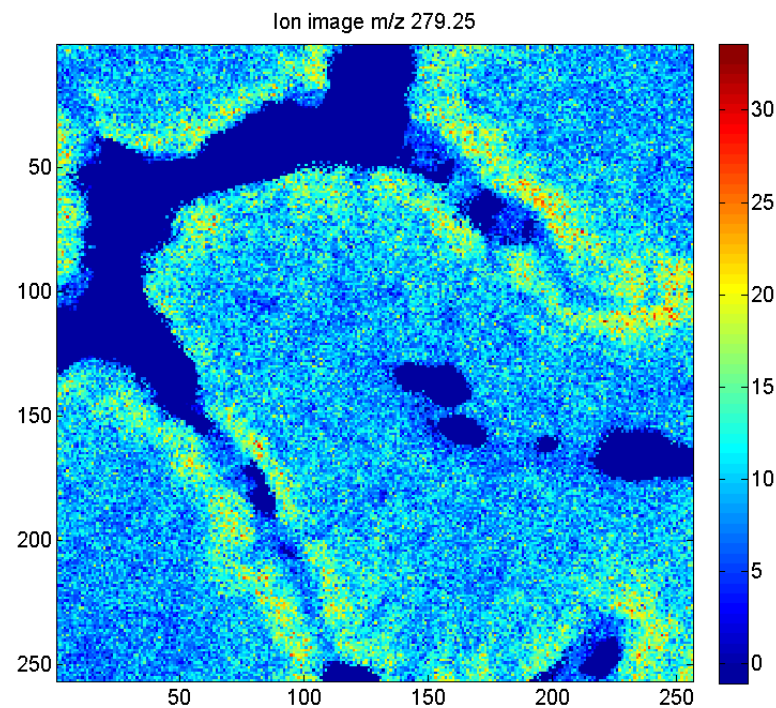
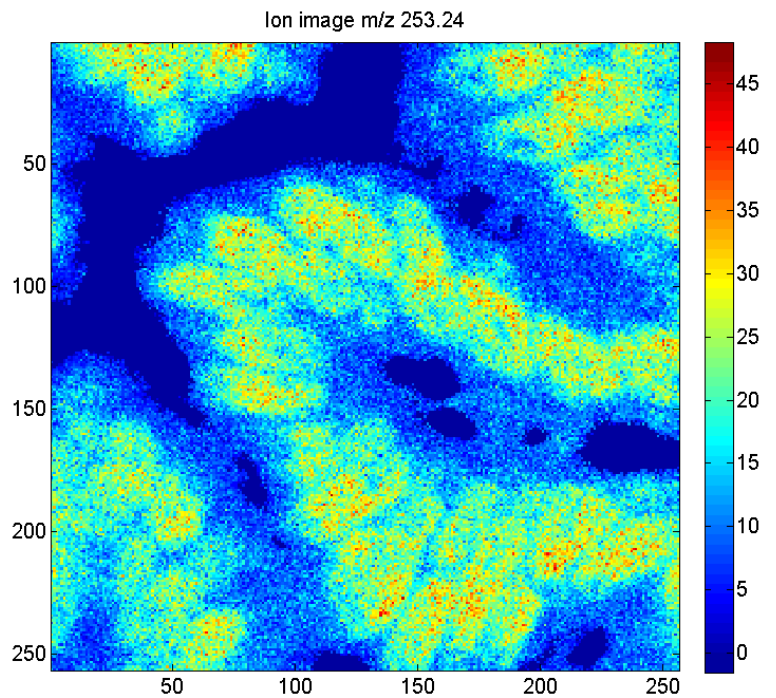
- By rastering a finely focussed ion beam over the surface, like an electron beam in an electron microprobe, mass resolved secondary ion images (chemical maps) can be obtained simultaneously.



Microbeam Imaging

- For ion microbeam imaging, a finely focused primary ion beam sweeps the sample in a raster pattern and software saves secondary ion intensities as a function of beam position.





Lipid mapping of colonic mucosa by cluster TOF-SIMS imaging and multivariate analysis in *cftr*

knockout mice. Marc Brulet , 1, * Alexandre Seyer , 1, * Aleksander Edelman , † Alain Brunelle , * Janine Fritsch , † Mario Ollero , 2, * , † and Olivier Laprévote * , § *Journal of Lipid Research*, 51 (2010) 3034.

Building Blocks of An ICP - MS

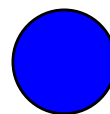
- Atmospheric pressure

- Sample introduction
- Desolvation
- Atomization
- Ionization > 90%

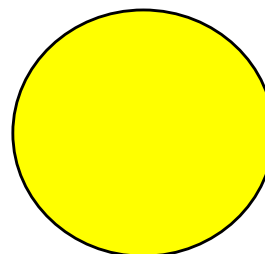
• -----

- Vacuum

- Ion focusing
- Mass separation
- Isotope detection

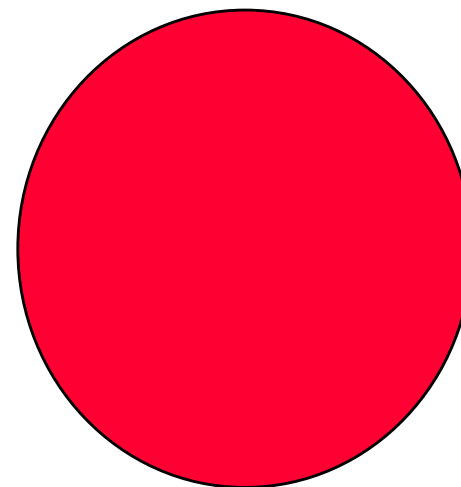


${}^7\text{Li}^+$



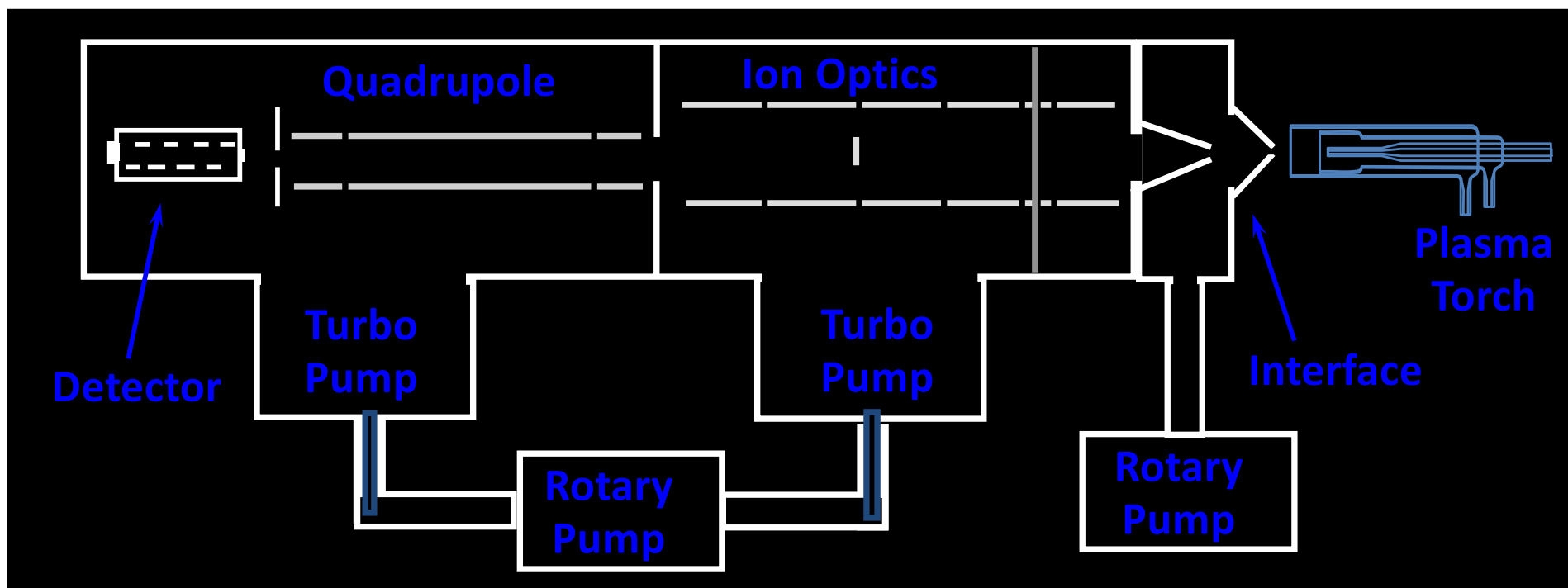
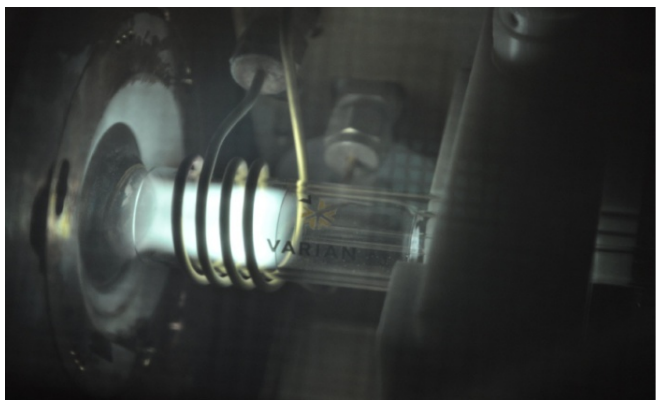
${}^{114}\text{Cd}^+$

${}^{208}\text{Pb}^+$





Generic ICP-MS System Hardware

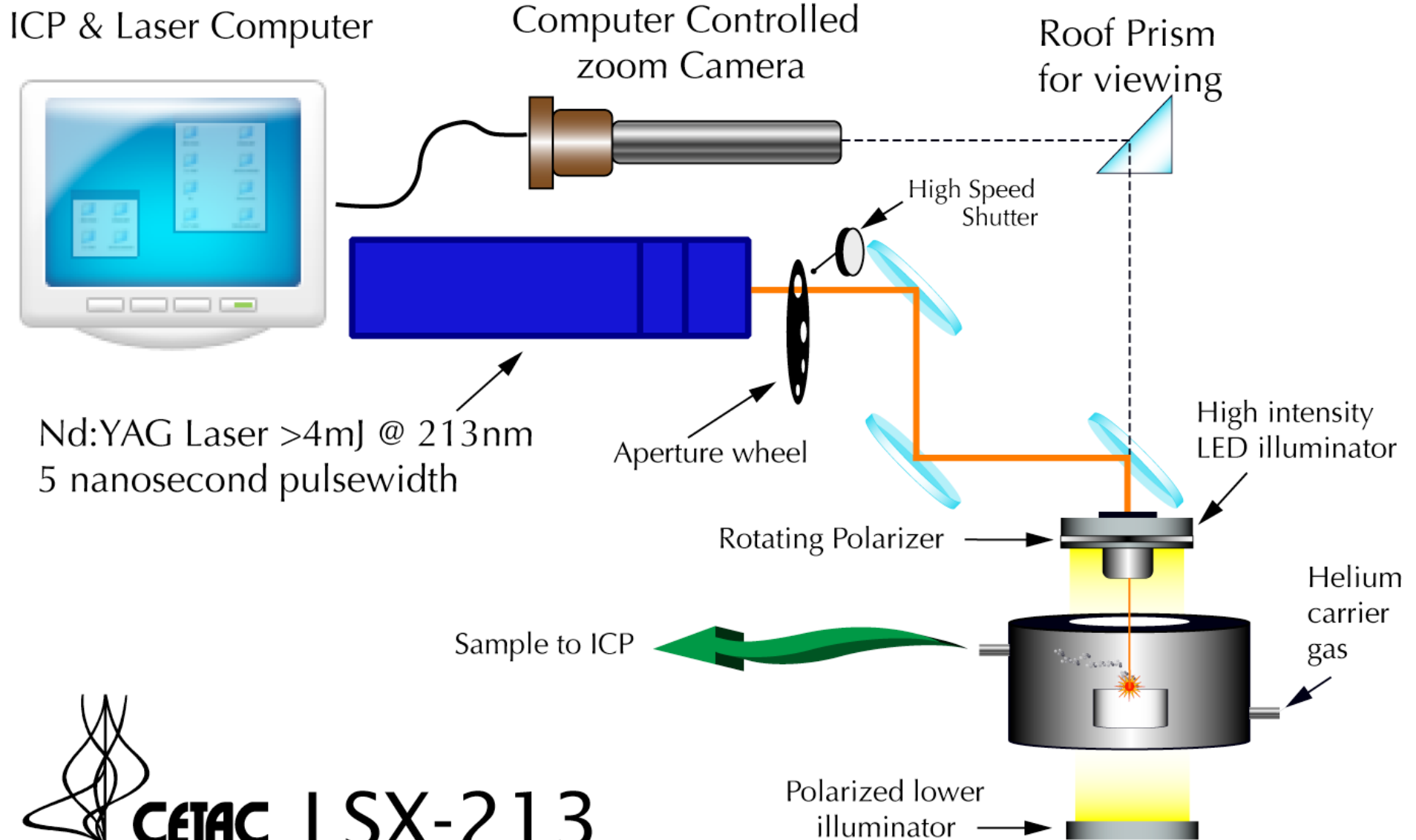


Applications: Forensic Analysis

- **Sample Preparation: Laser Ablation**
- Direct Solid Sampling
- Very Little Sample Prep
- Spatially Resolved In Situ Analysis
- Integrated software control

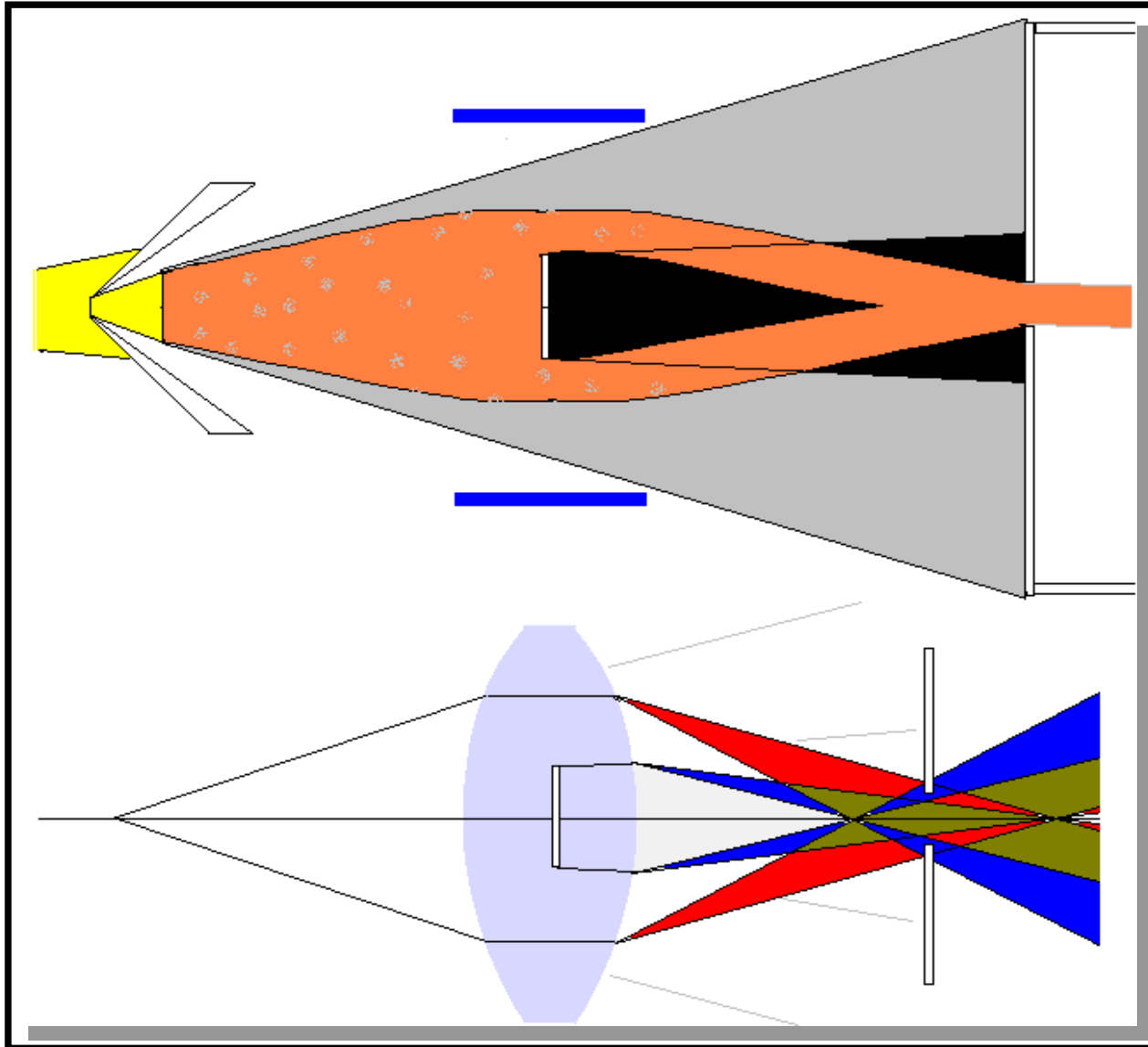


LSX-213 schematic



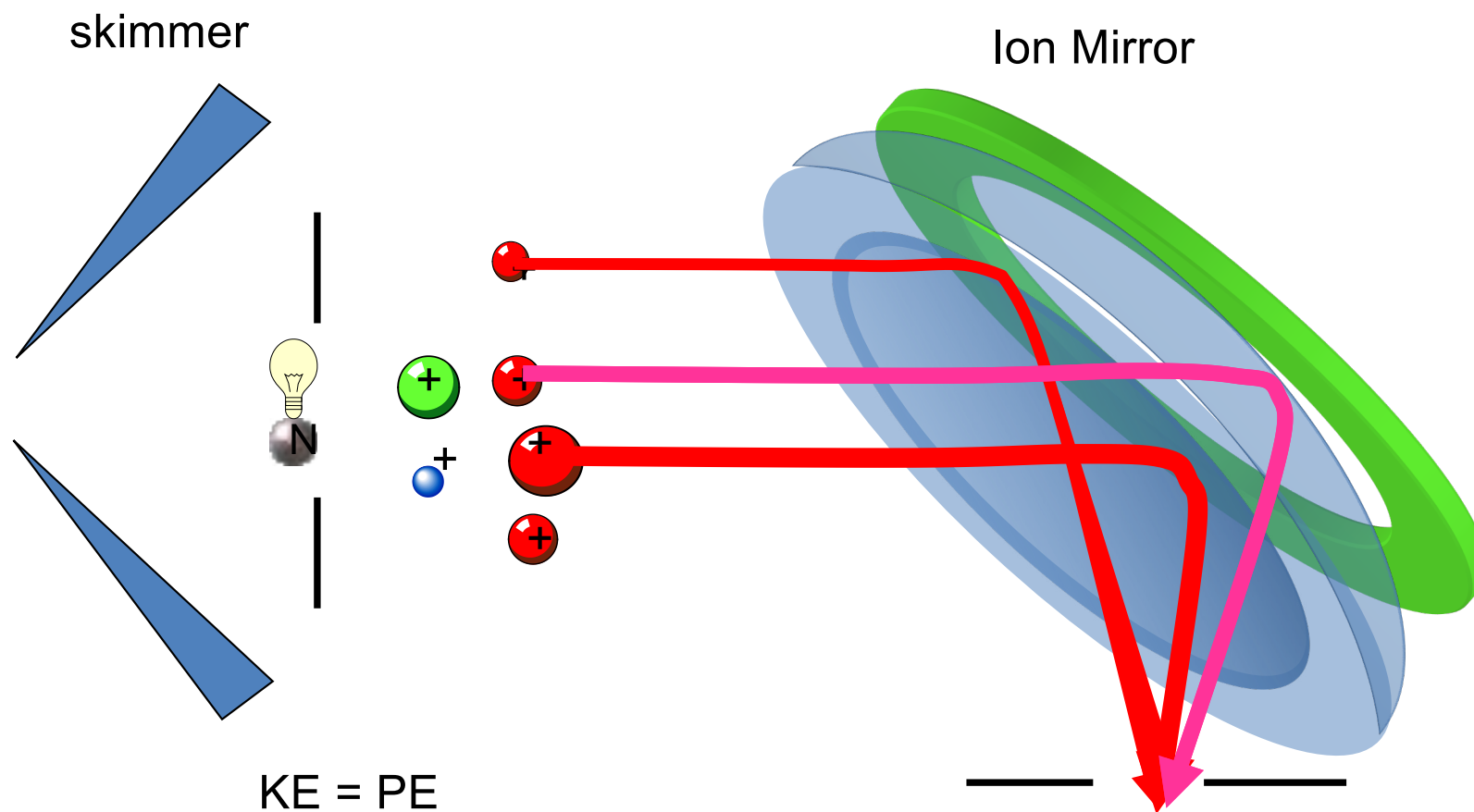
CETAC LSX-213

Ion Optics - Photon Stop Design



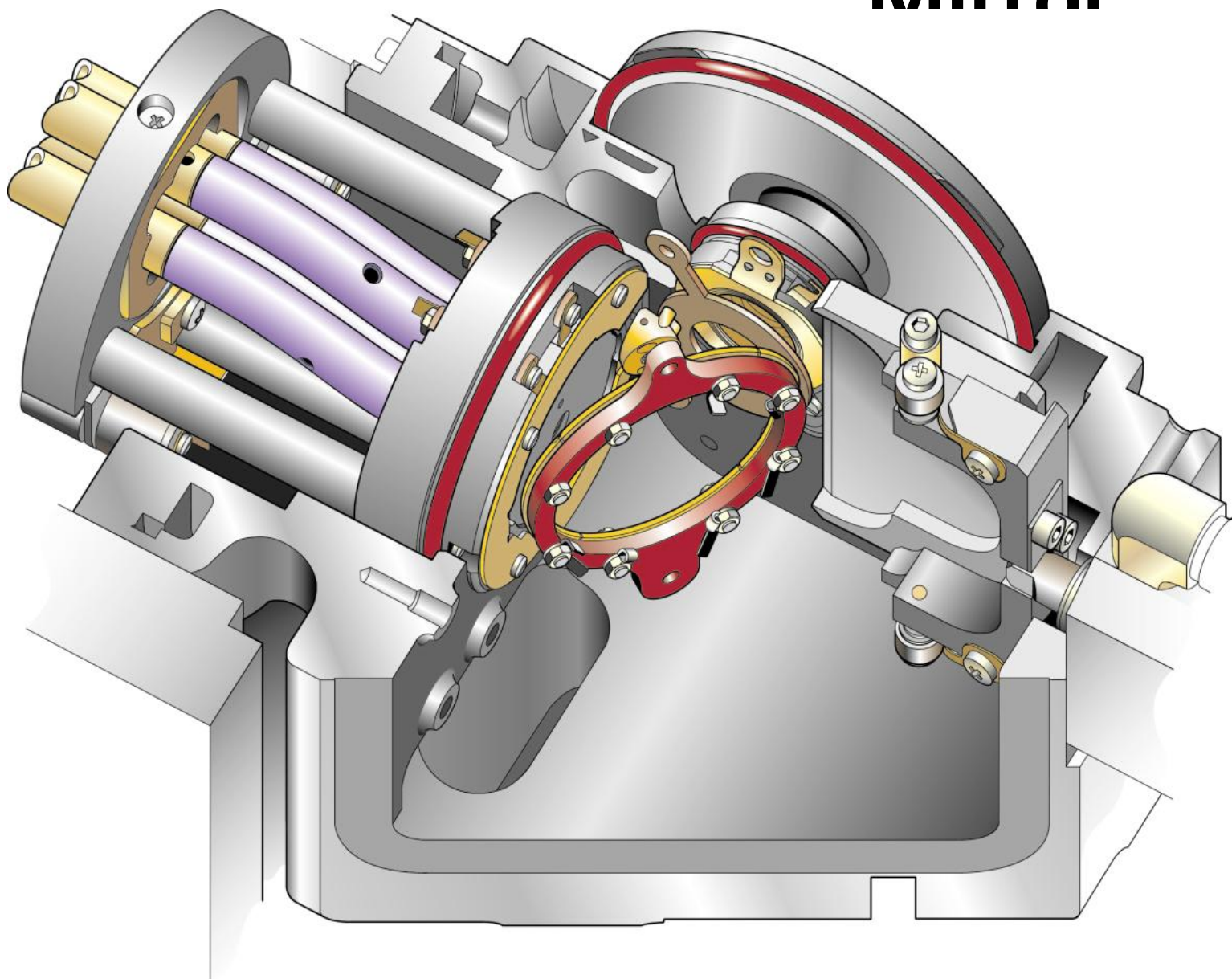
- Ion beam aberrations present
- Optical analogy – note different focal points
- (still used by one competitor)
- **About 10-15% efficient**

4 D Focusing of the Ion Mirror





varianS ion Optics Design – the 90 Degree Ion Mirror





Fractionation

- Fractionation is defined as non-stoichiometric sampling
- It was originally believed that the laser was causing fractionation at the ablation site
 - This may still happen to some degree with all lasers in metal samples...melting
- Elemental fractionation can occur in three parts of the LA sampling process
 - At the ablation site
 - During transport
 - In the ICP
- Elemental fractionation has been shown to be reduced using lower wavelength lasers as compared to 266 nm system (smaller more easily ionized particles)



Fractionation

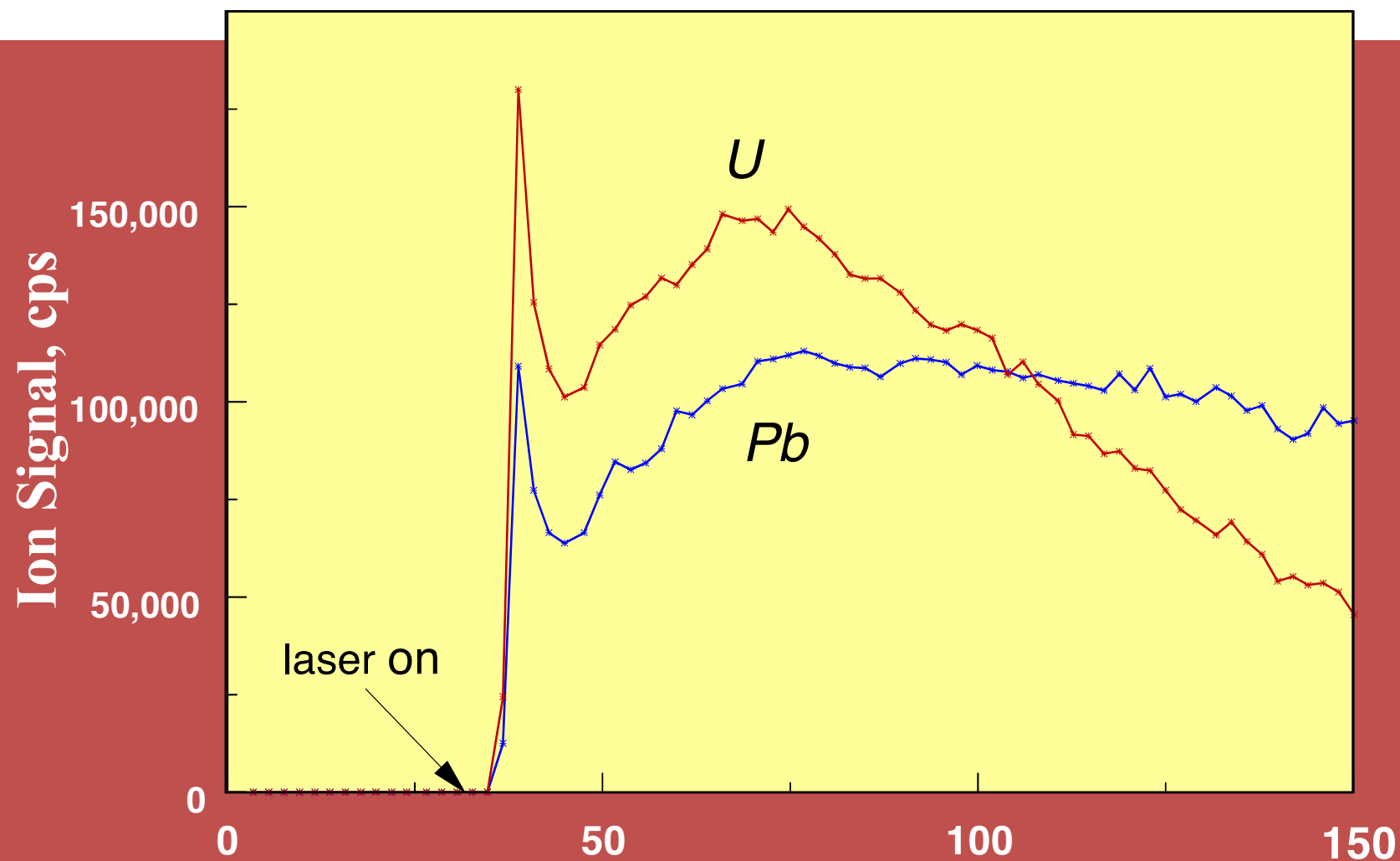


Figure 4- (A) Image of spotted gar liver showing ablations in a macrophage aggregate and normal tissue . ^{202}Hg signal in (B) normal tissue and a (C) macrophage aggregate.

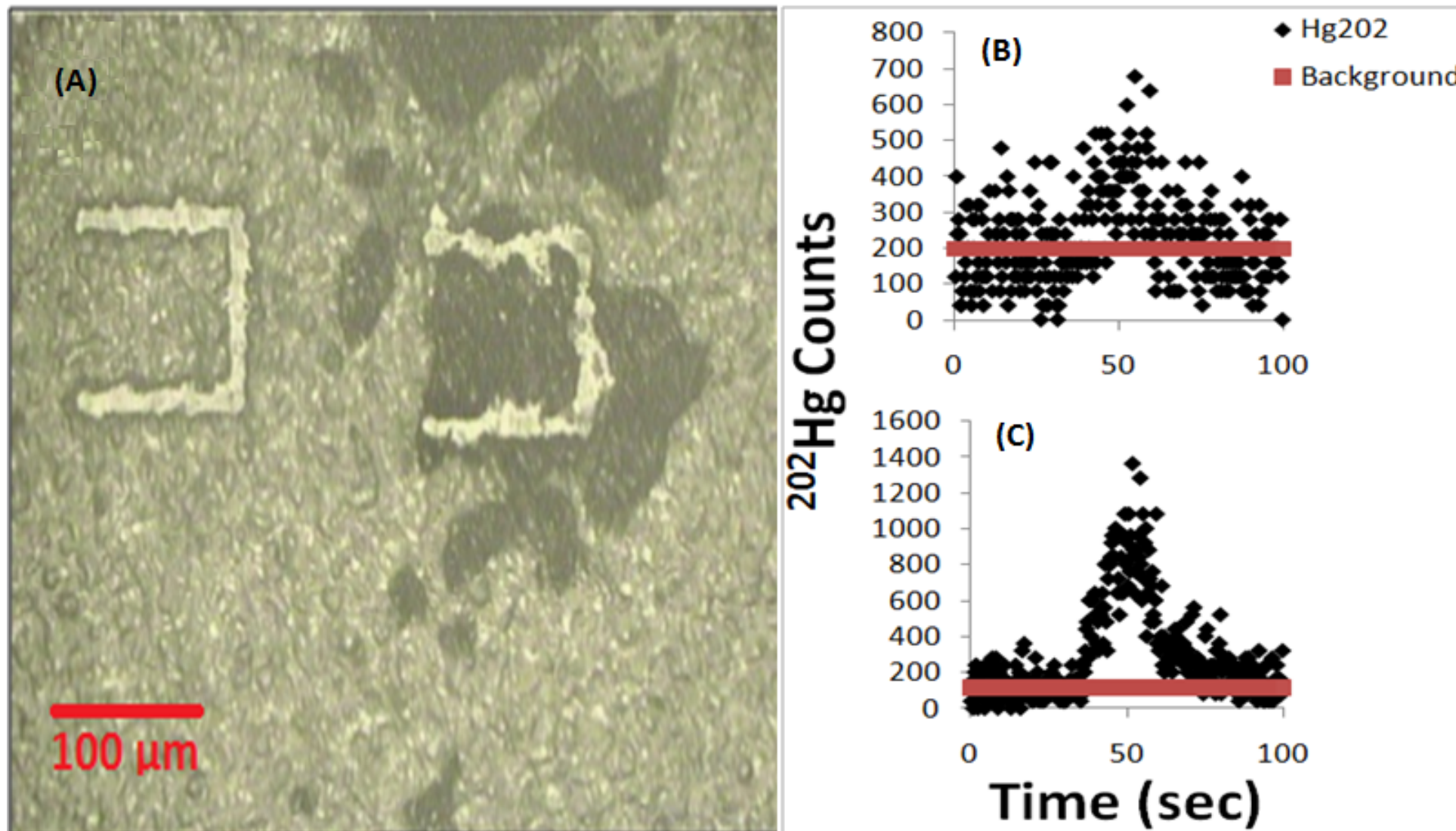
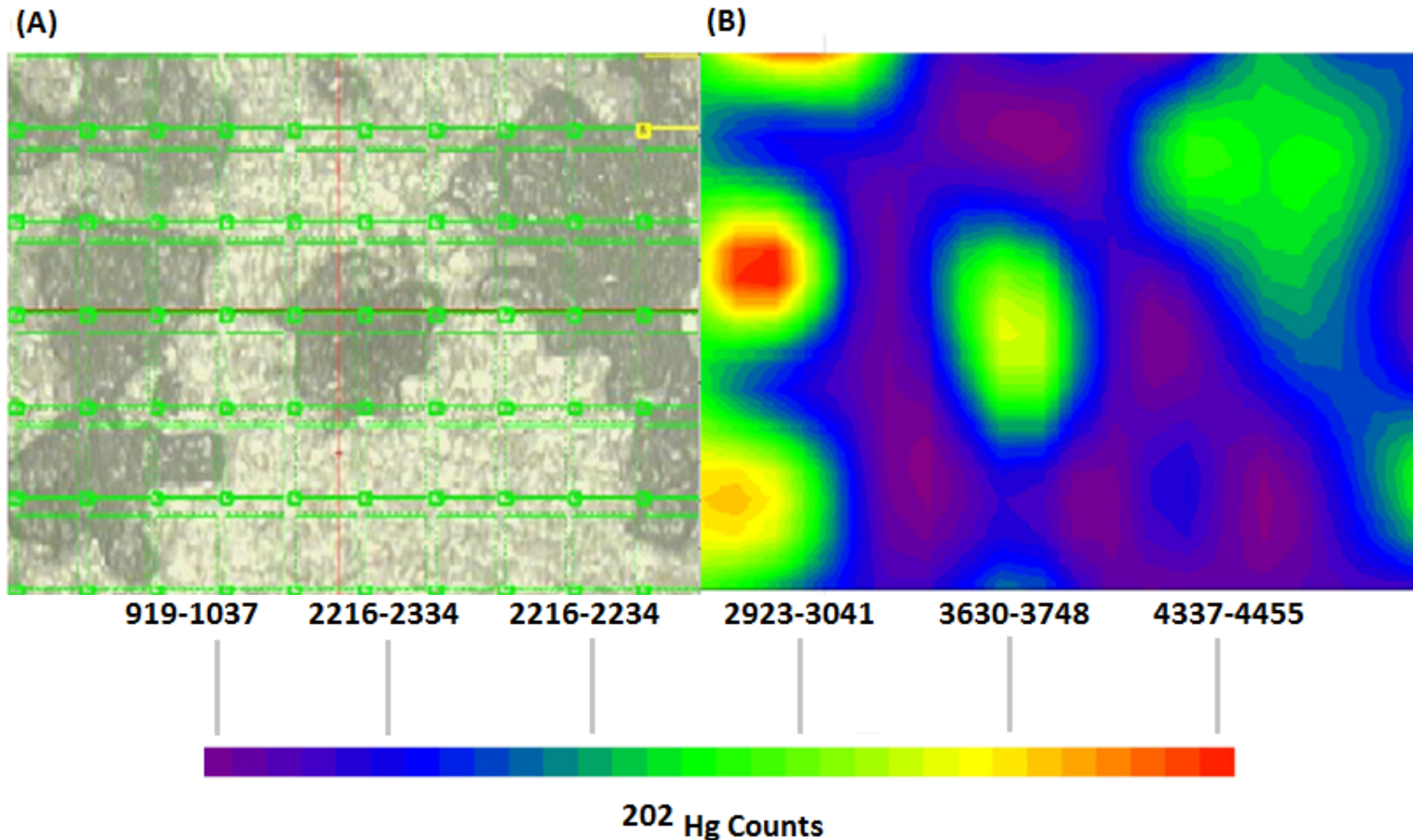
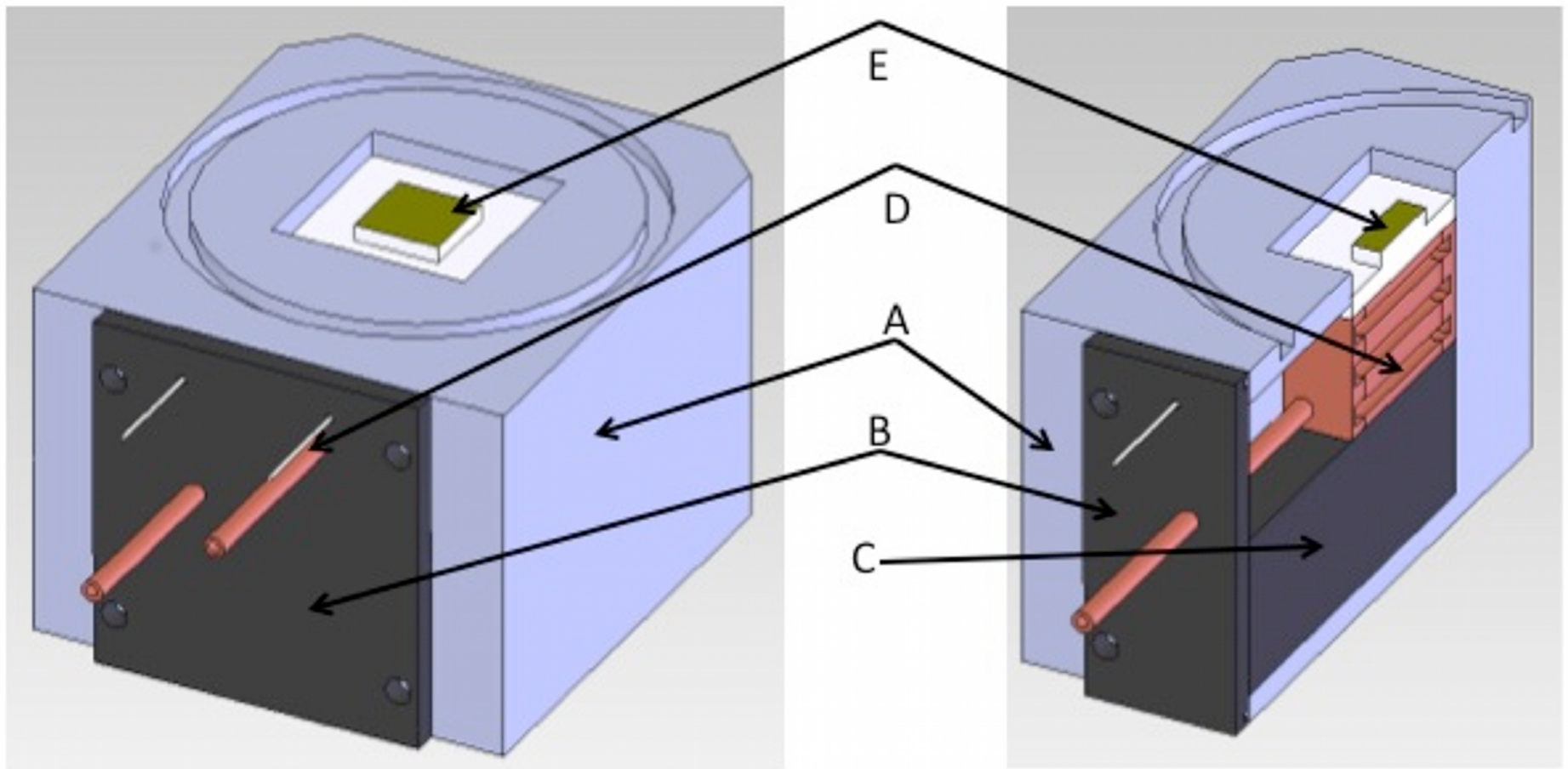


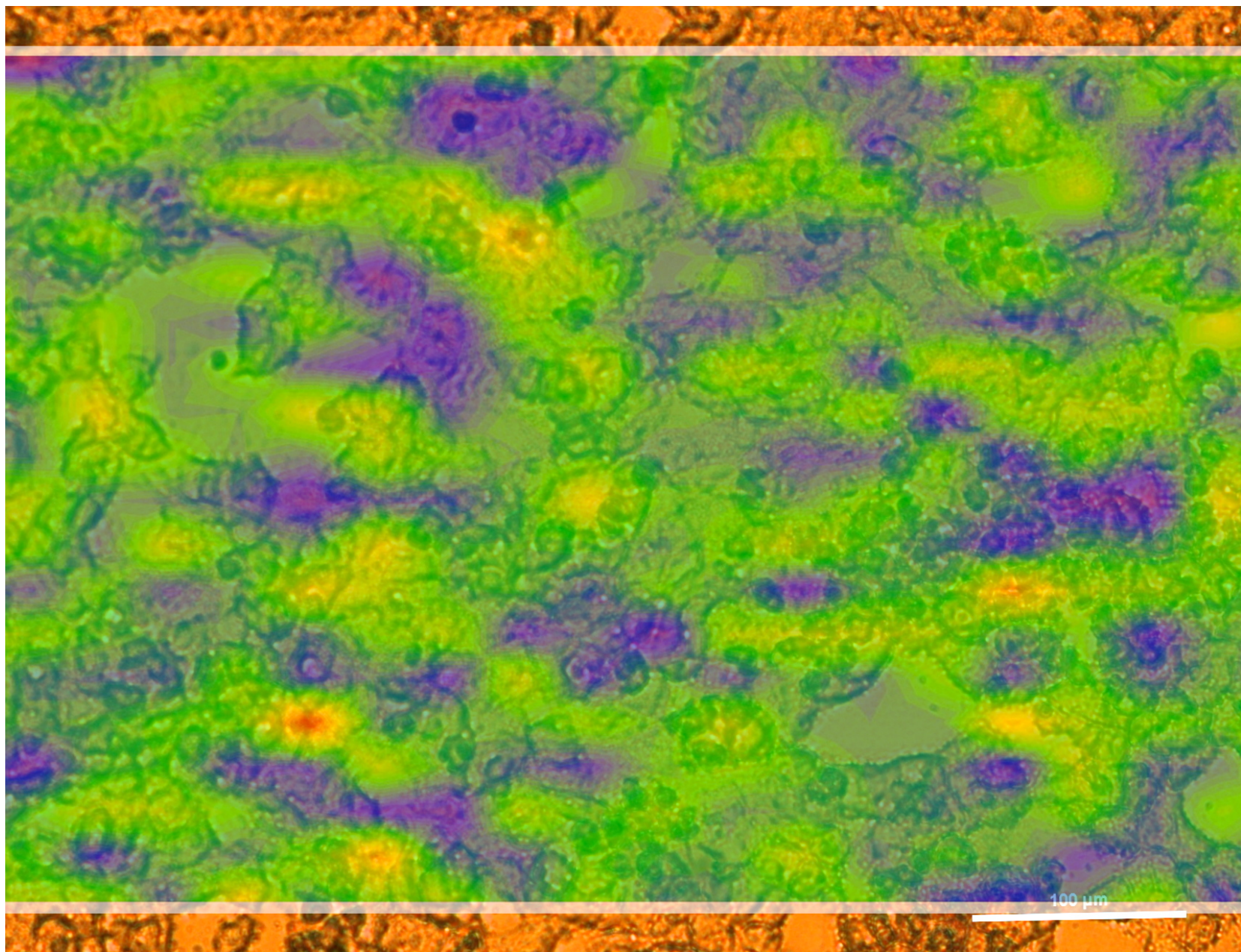
Figure 5- (A) A pre-ablation image of a spotted gar liver section with a superimposed raster pattern . Dark patches are macrophage aggregates. Lighter patches are normal parenchyma. (B) 3D contour image showing the relative distribution of ^{202}Hg after laser ablation of the section shown in (A).



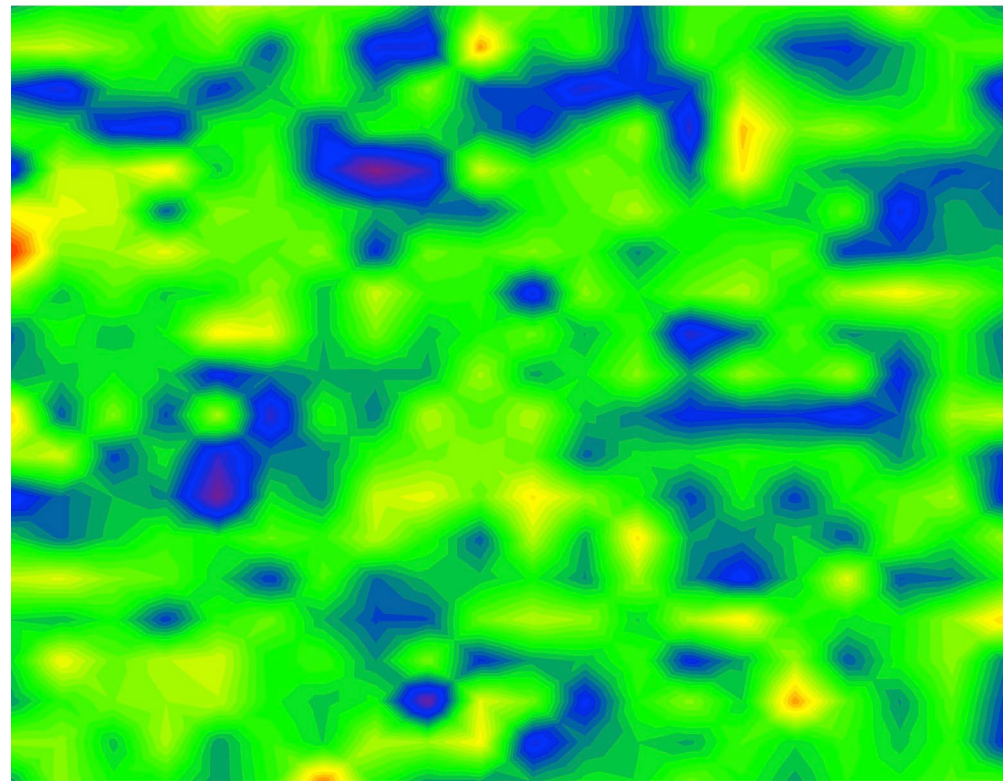
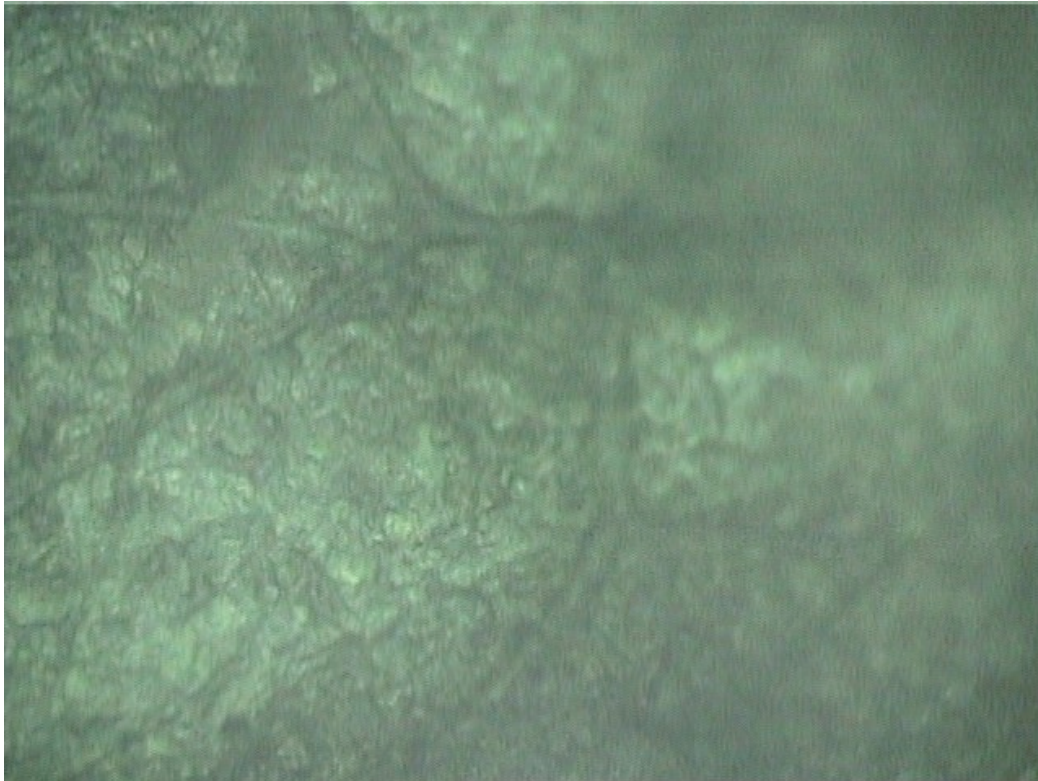
Barst, B.D.; Gevertz, A.K.; Chumchal, M.M.; Smith, J.D.; Rainmater, T.R.; Drevnick, P.E.; Hudelson, Hart, A.; Verbeck, G.F.; Roberts, A.P., “Mercury accumulates in melanomacrophage aggregates in wild fish livers: Evidence of link between mercury exposure and negative effects on the health of wild fish”, Science, 2011. *Submitted, In Review*



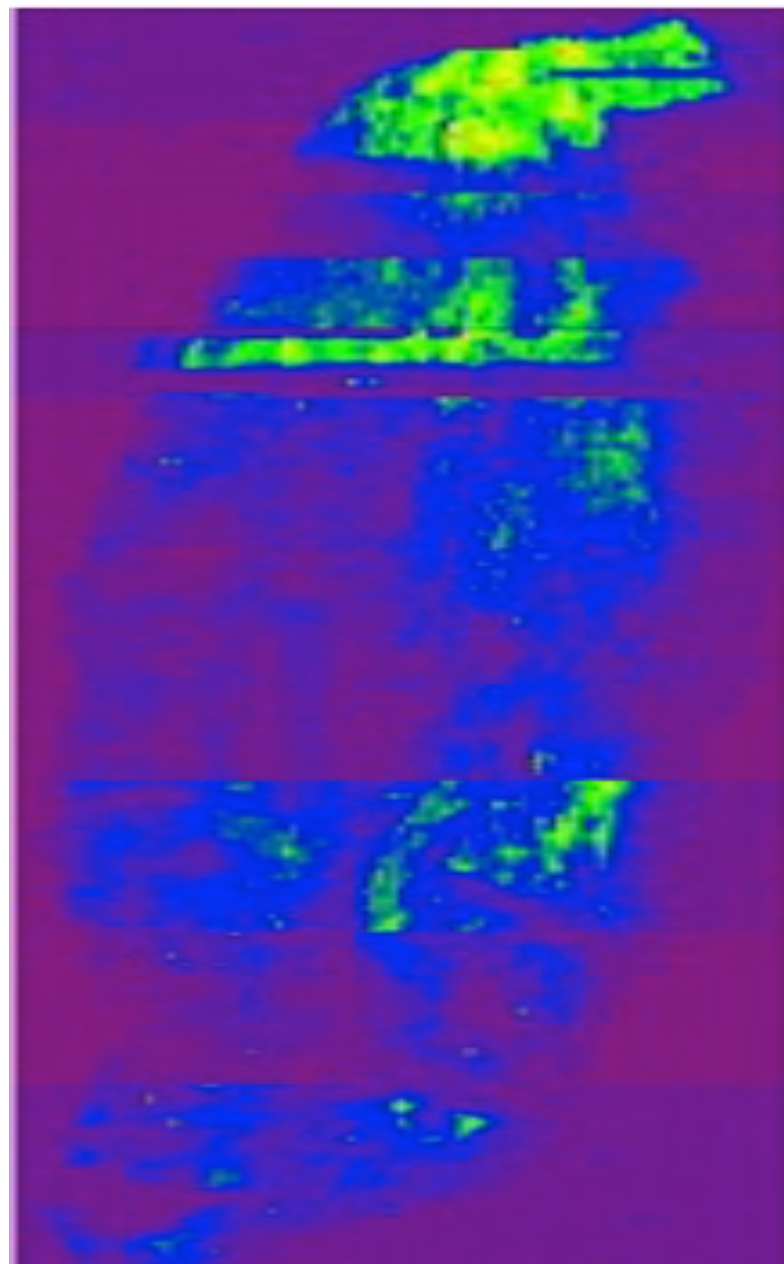
Cold Cell Block



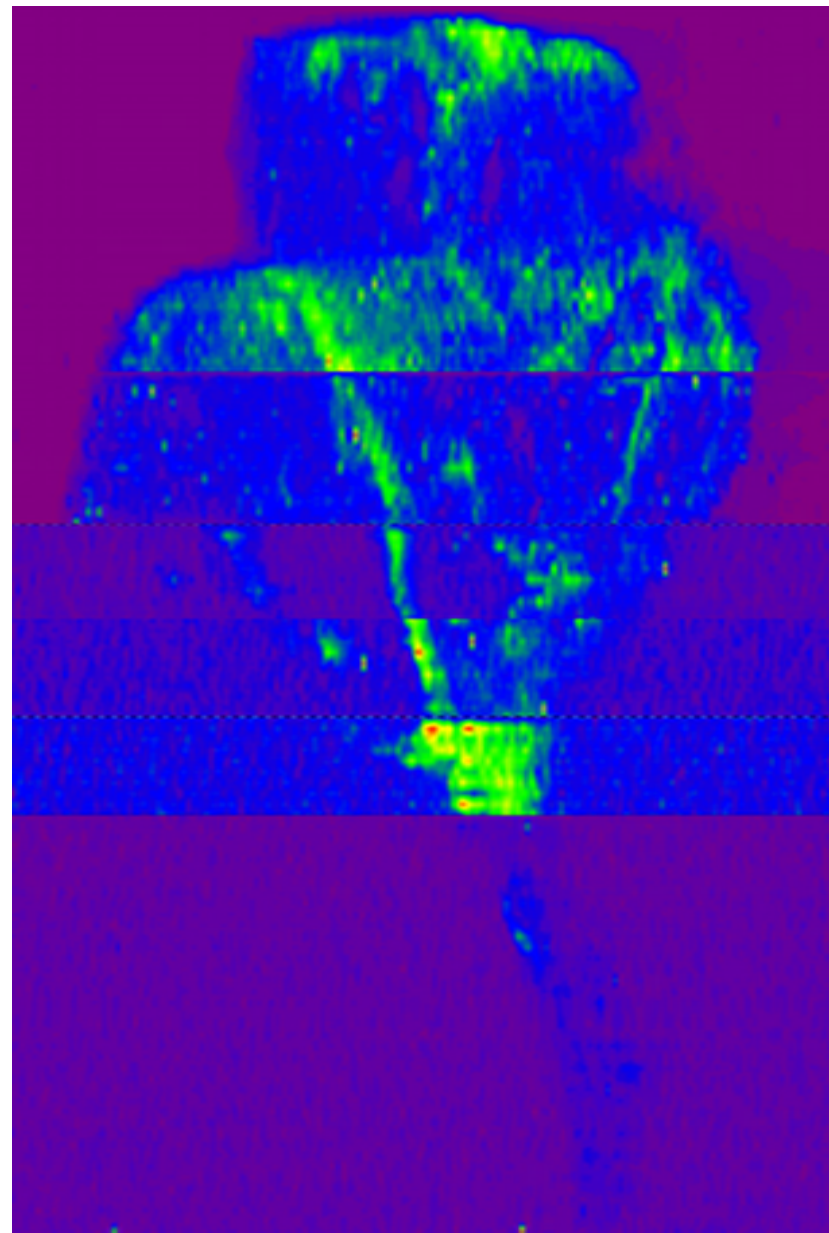
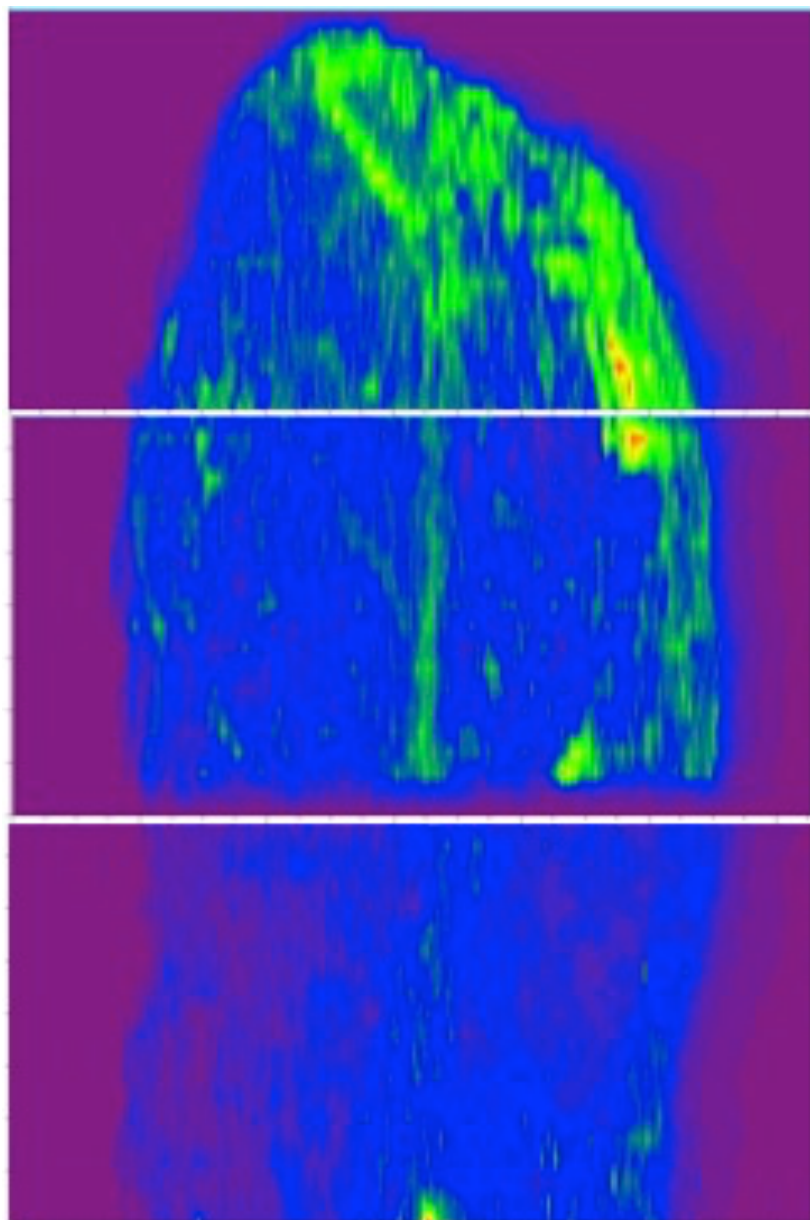
^{102}Ru image mapping in HeLa Cells



^{39}K Mapping Image of Arabidopsis leaf section
with cold cell LA-ICPMS



^{23}Na mapping image of Arabidopsis Leaf
cold cell LA-ICPMS



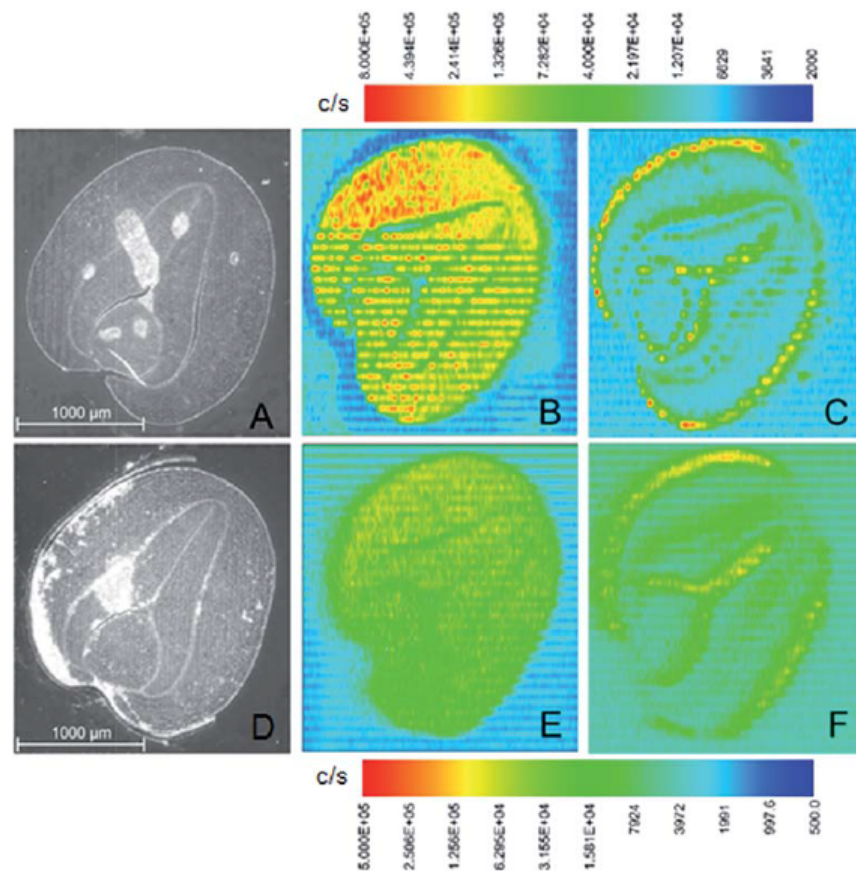


Fig. 3 Top: (A) CCD pre-ablation image of *B. napus* seed section, cooled ablation of ^{31}P (B) and ^{55}Mn (C). Bottom: (D) CCD pre-ablation image of *B. napus* seed section, normal ablation of ^{31}P (E) and ^{55}Mn (F) differences in orientation between the CCD images and elemental images are due to shifts in placement when moving the seed to microscope after ablation. Artefacts in the images are due to the line scan method.

Evaluation of a custom single Peltier-cooled ablation cell for elemental imaging of biological samples in laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)

J. S. Hamilton,^a E. L. Gorishek,^a P. M. Mach,^a D. Sturtevant,^b M. L. Ladage,^b N. Suzuki, P. A. Padilla,^b R. Mittler,^b K. D. Chapman^b and G. F. Verbeck

Evaluation of a custom single Peltier-cooled ablation cell for elemental imaging of biological samples in laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)

J. S. Hamilton,^a E. L. Gorishek,^a P. M. Mach,^a D. Sturtevant,^b M. L. Ladage,^b N. Suzuki, P. A. Padilla,^b R. Mittler,^b K. D. Chapman^b and G. F. Verbeck

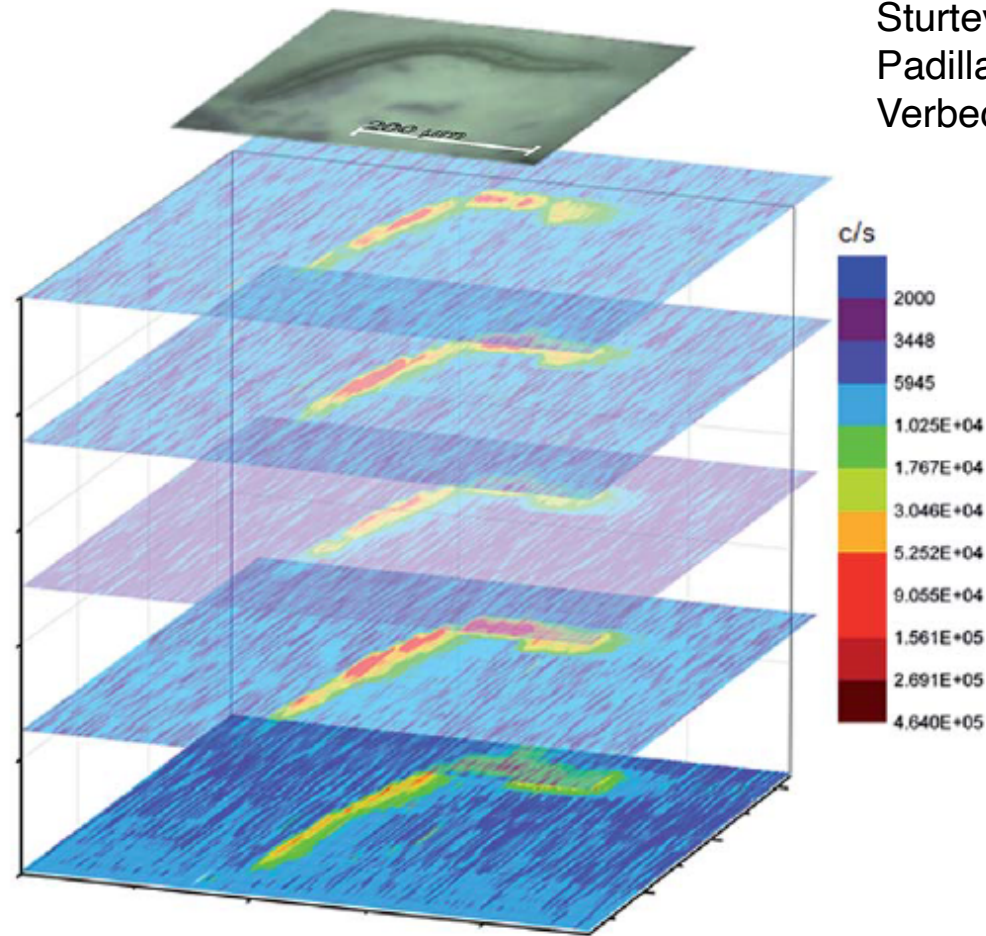


Fig. 4 Stacked 2D measured intensities elemental maps of ^{31}P in a wild type *C. elegans* worm at depth increments of 1.04 μm with an overlaid CCD image of the worm before ablation.