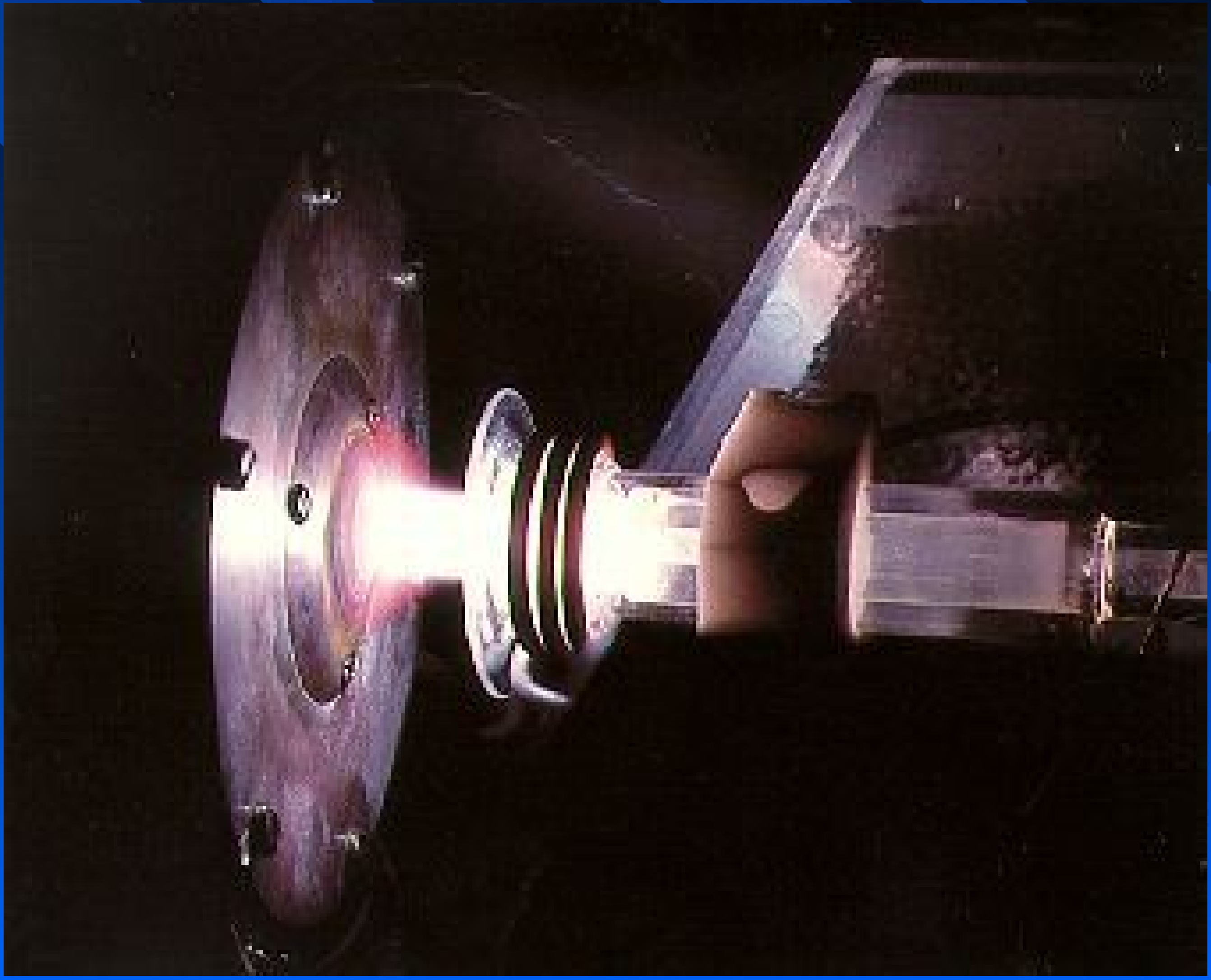
ICP-Mass Spectrometer



New Mass Spectrometers

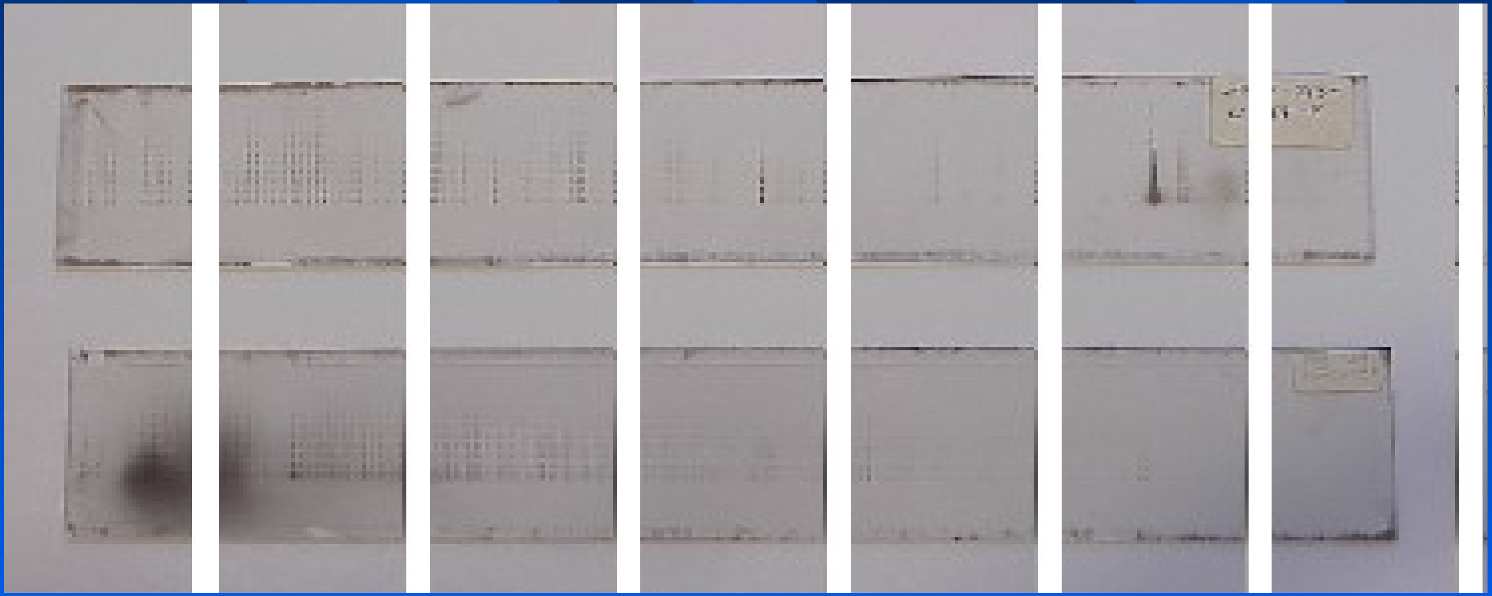
Simultaneous

The main issue: sequential *vs.* simultaneous

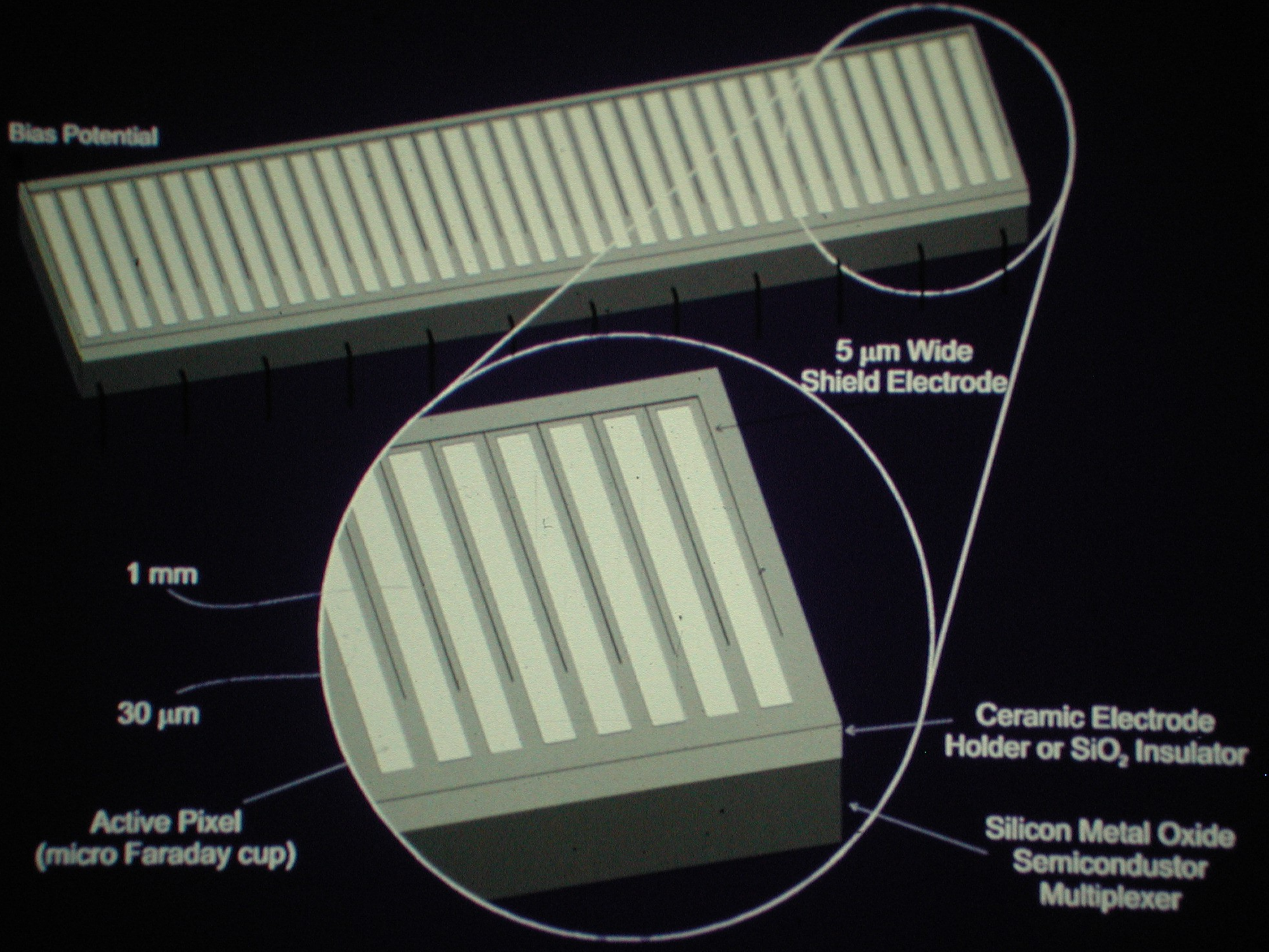
- Scanning, peak hopping are sequential
- Like viewing a photo through a peephole
  - One pixel at a time
  - Other parts of photo are invisible
- Even worse: viewing a <u>movie</u> through a peephole
  - The most important parts always seem to be where you are NOT looking!

Concept: Electronic Photoplate

- Truly simultaneous
- High spatial resolution
- Fast recording
- Direct integration
- Broad dynamic range
- ~~Linear~~
- ~~Stable; simple storage~~
- ~~Immediate readout~~

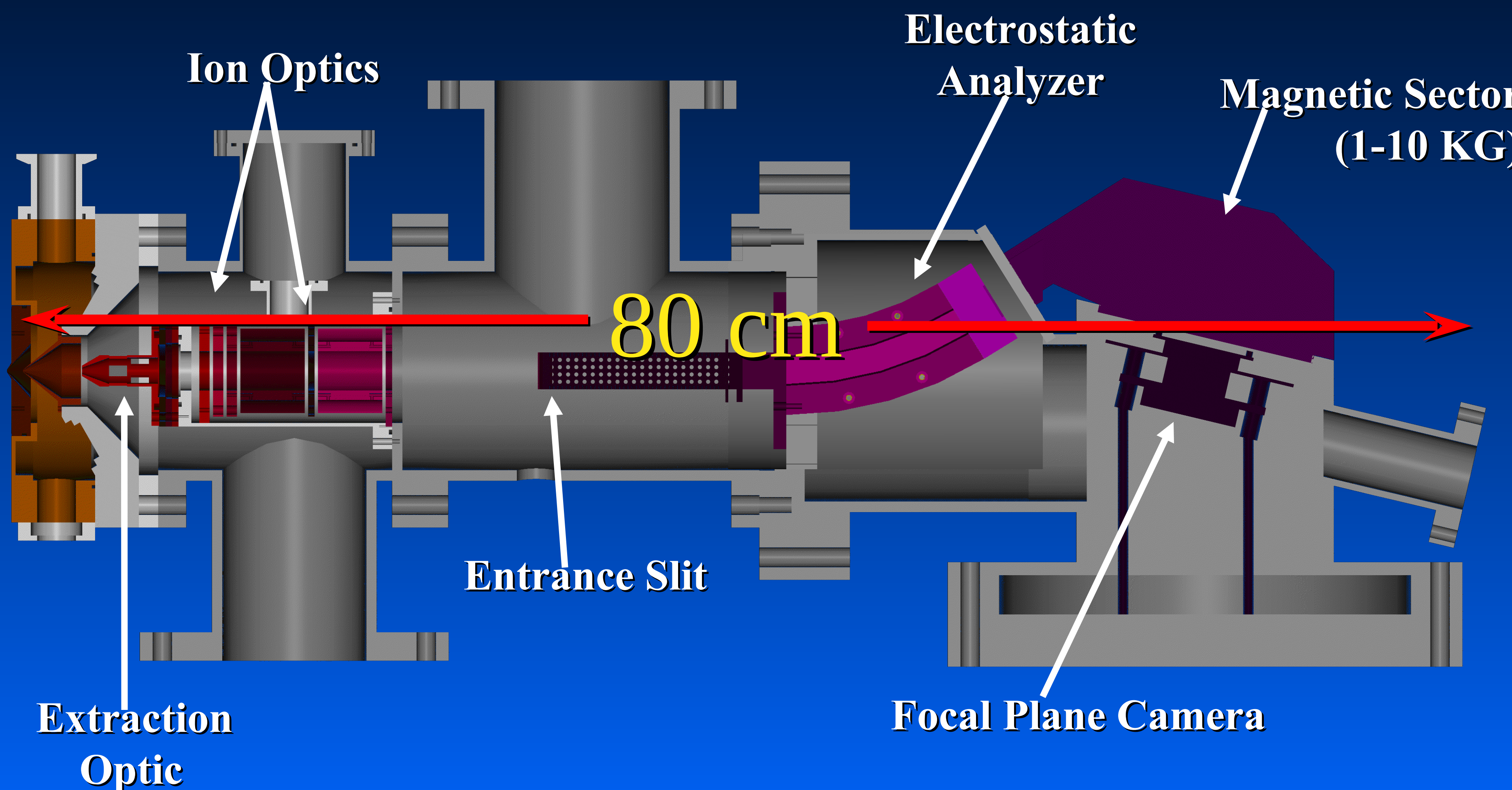


SSMS photoplate courtesy of D.W. Koppenaal



Bias Potential
5 μm Wide
Shield Electrode
1 mm
30 μm
Ceramic Electrode
Holder or SiO2 Insulator
Active Pixel
(micro Faraday cup)
Silicon Metal Oxide
Semicondustor
Multiplexer

Mattauch-Herzog Mass Spectrograph

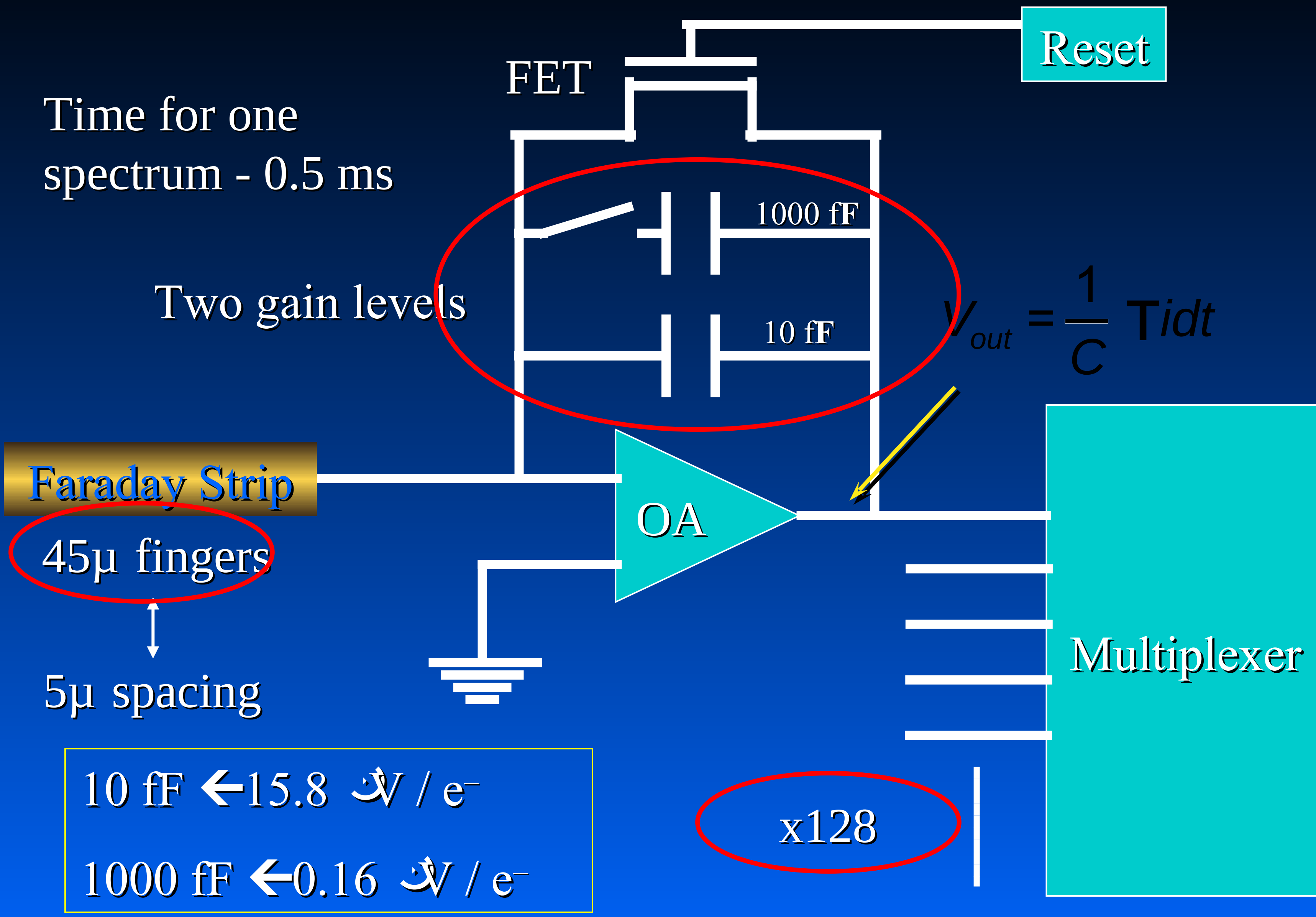


QuickTime™ and a
Cinepak decompressor
are needed to see this picture.

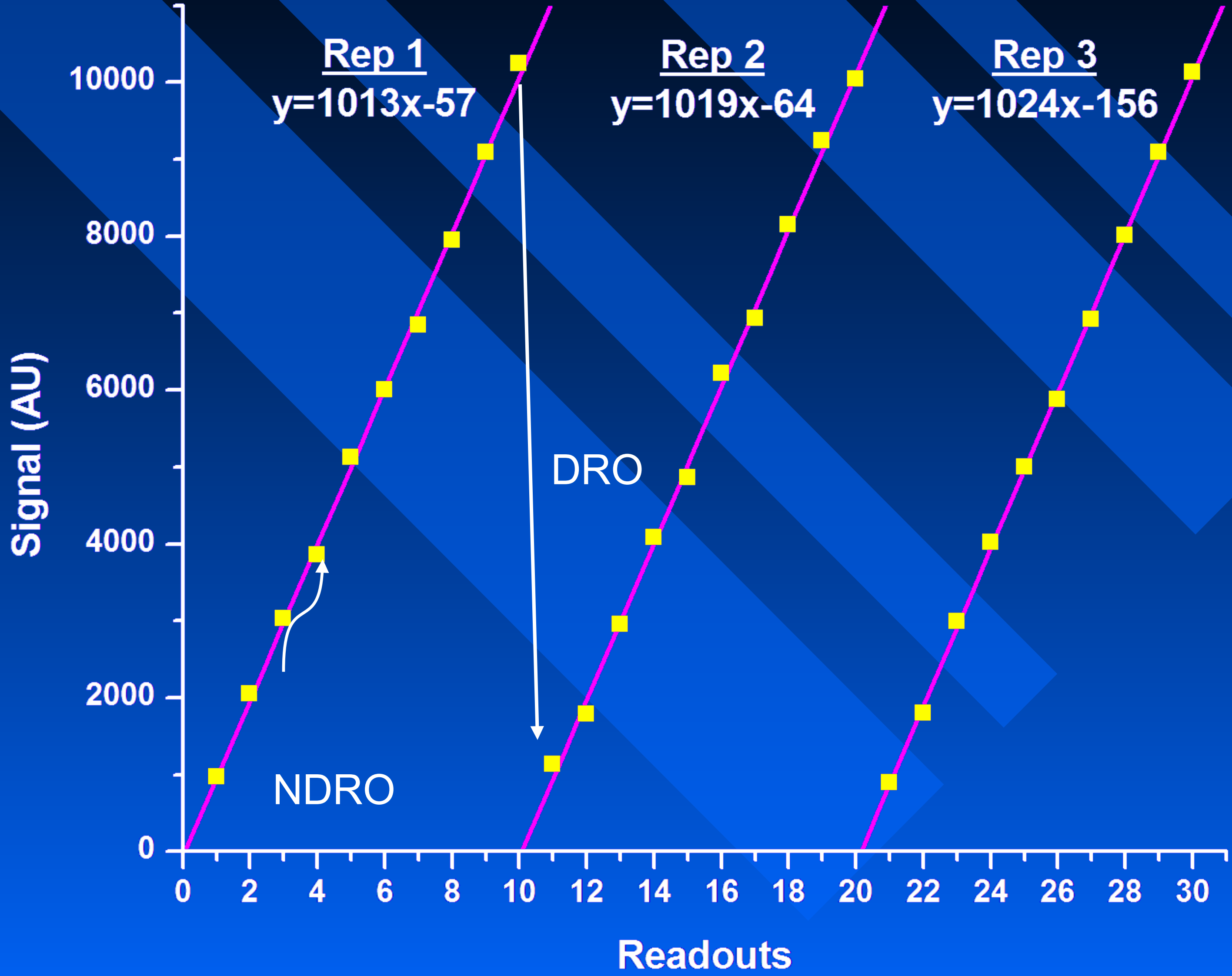
New Multichannel Detector

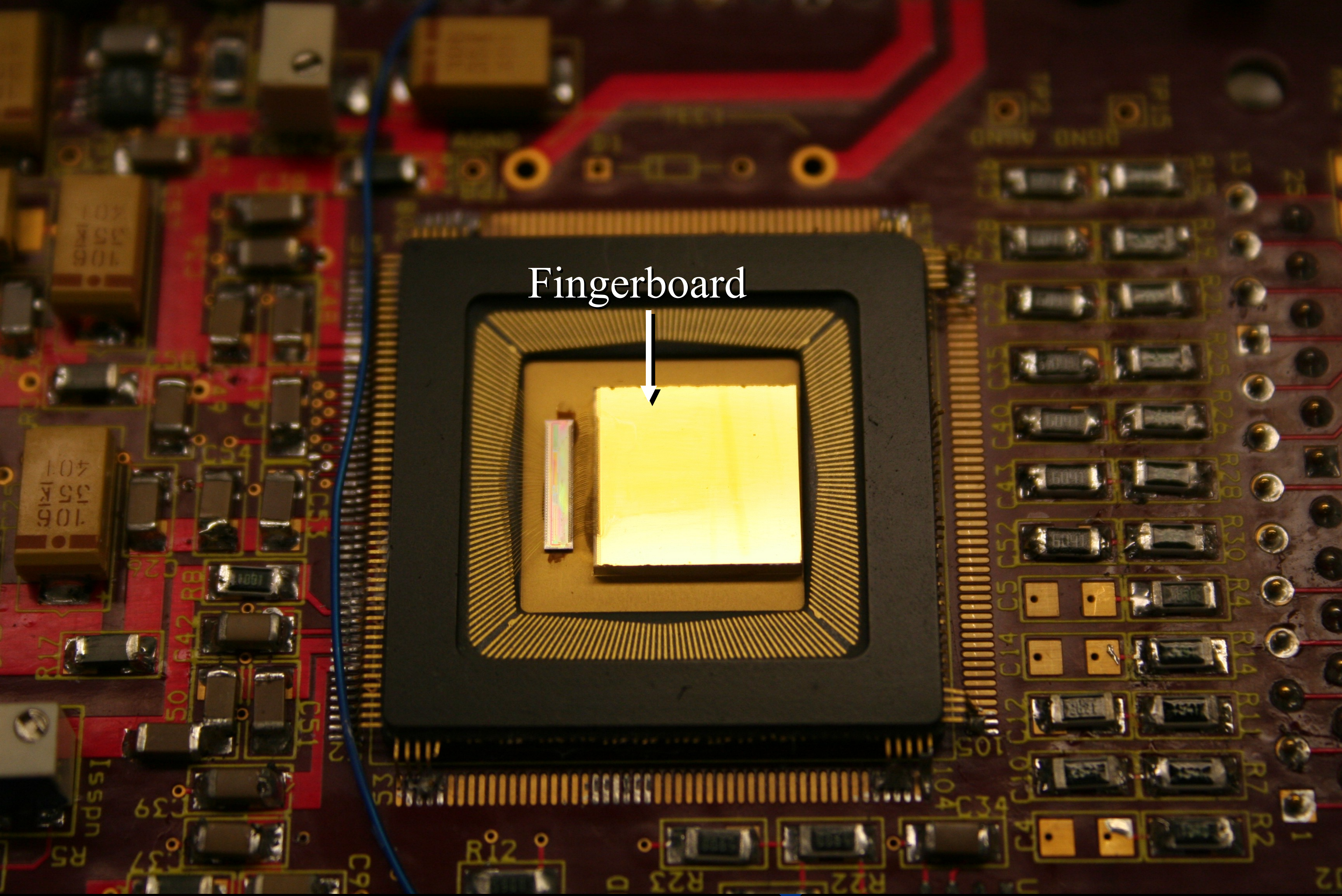
- Faraday-strip detection
  - One count per ion (no amplification)
  - No thermionic emission
  - No dynode statistics
  - No dependence on ion mass
- Continuous integration and random access of m/z
- Nondestructive or destructive readout option
  - Extended dynamic range; repetitive read

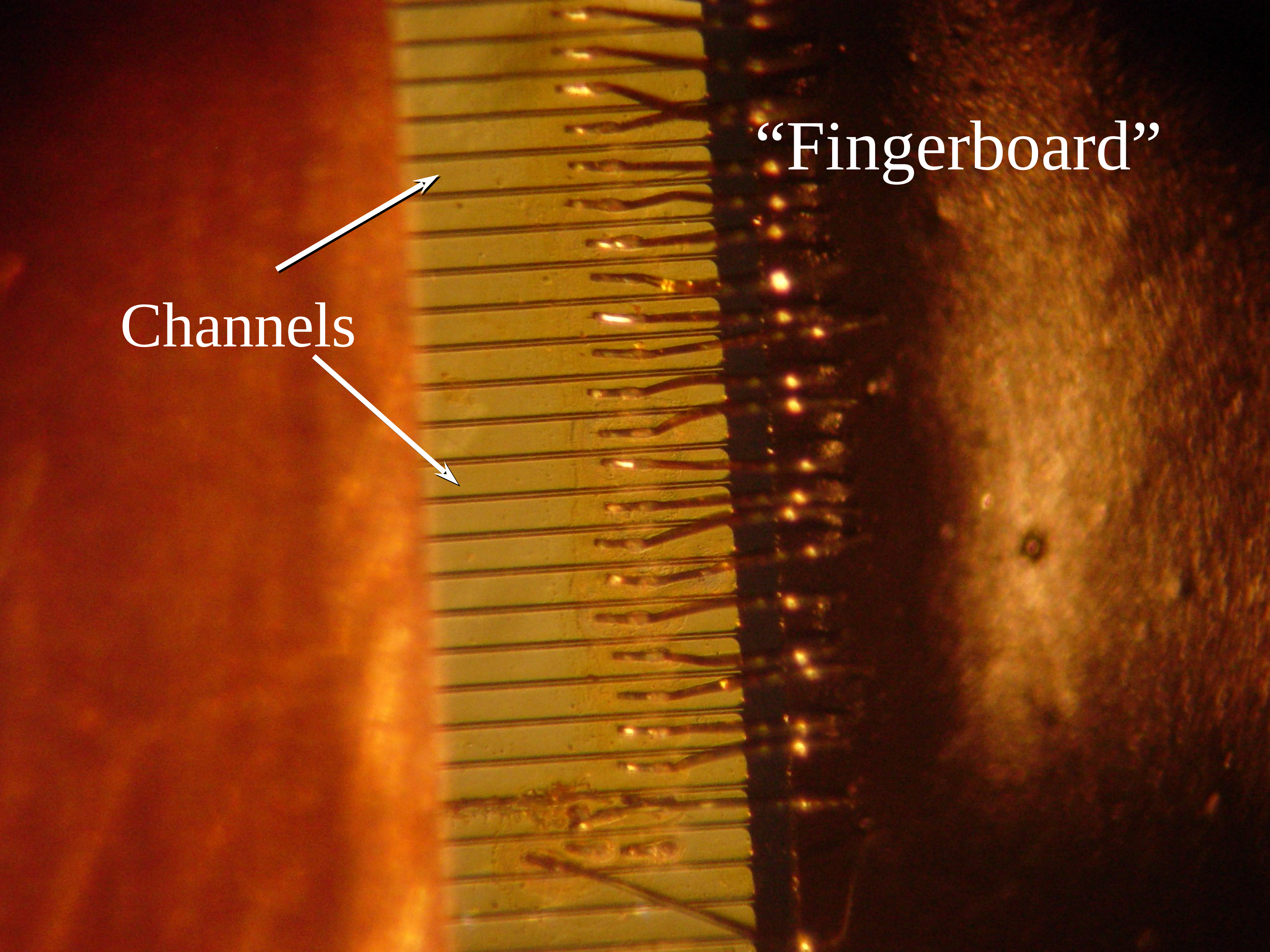
FPC-128 Multichannel Detector



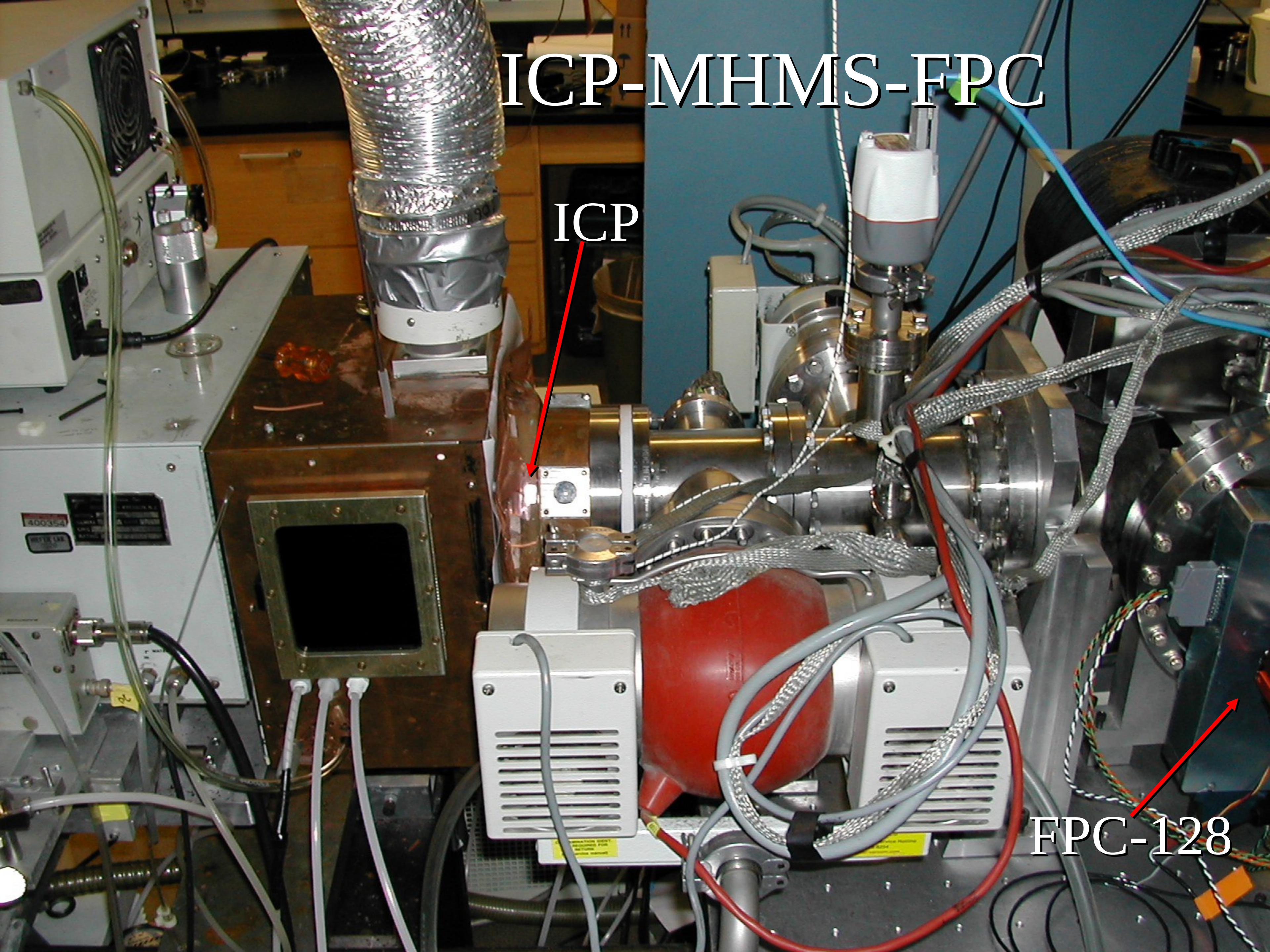
Data Acquisition



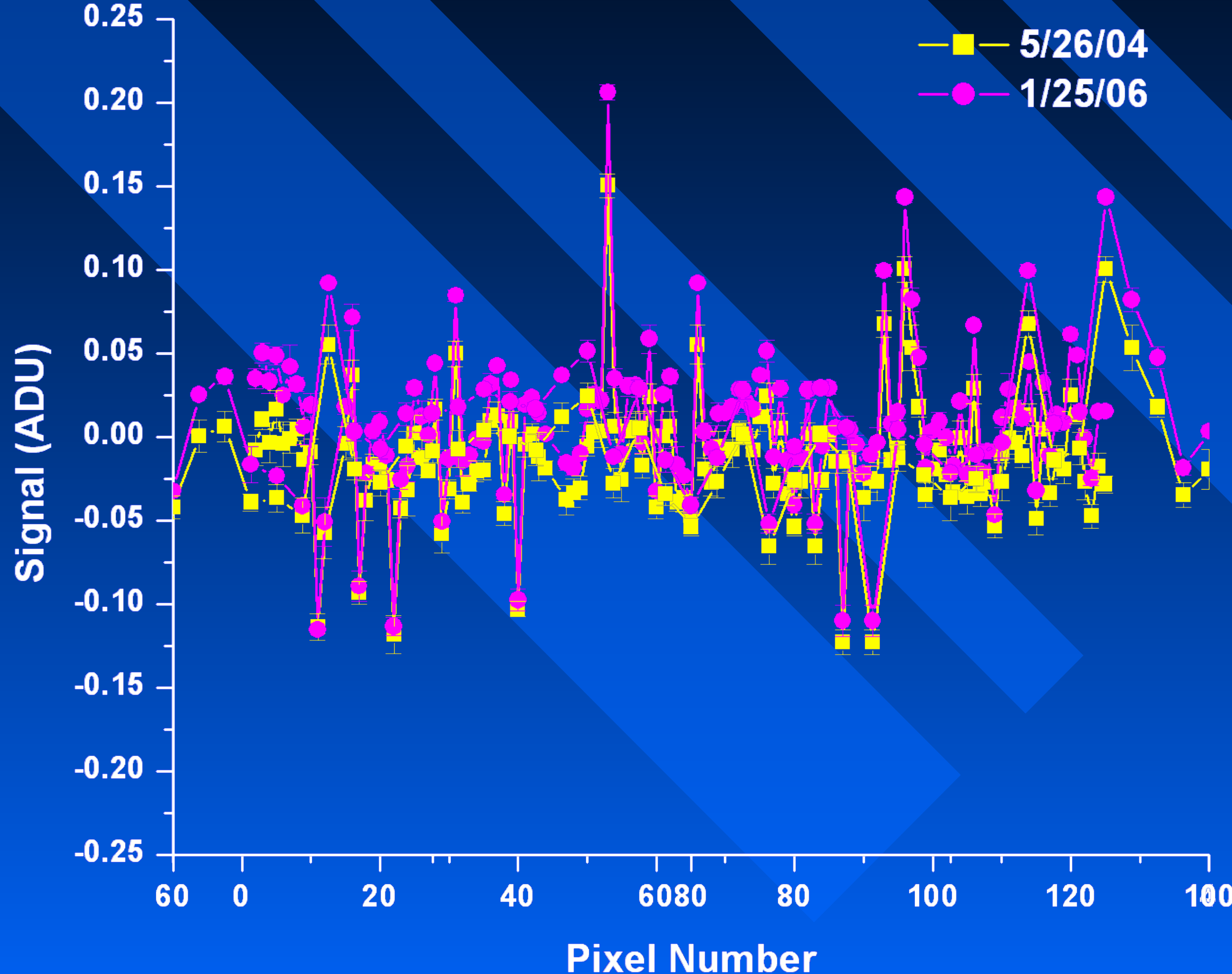

Fingerboard


"Fingerboard"
Channels

FPC-128 Installed in MHMS


ICP-MHMS-FPC
ICP
FPC-128

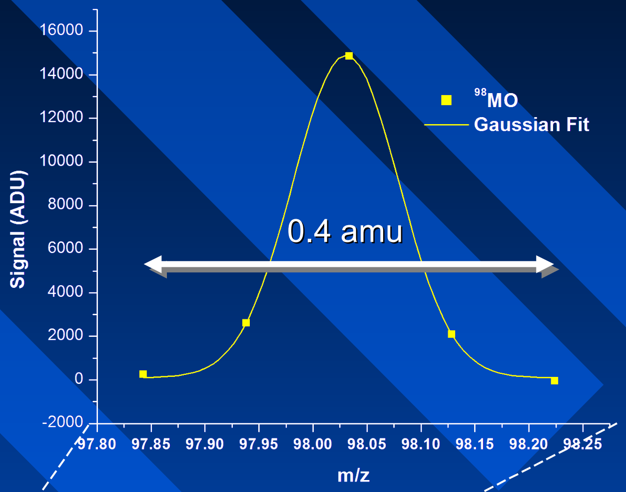
Fixed Pattern Noise

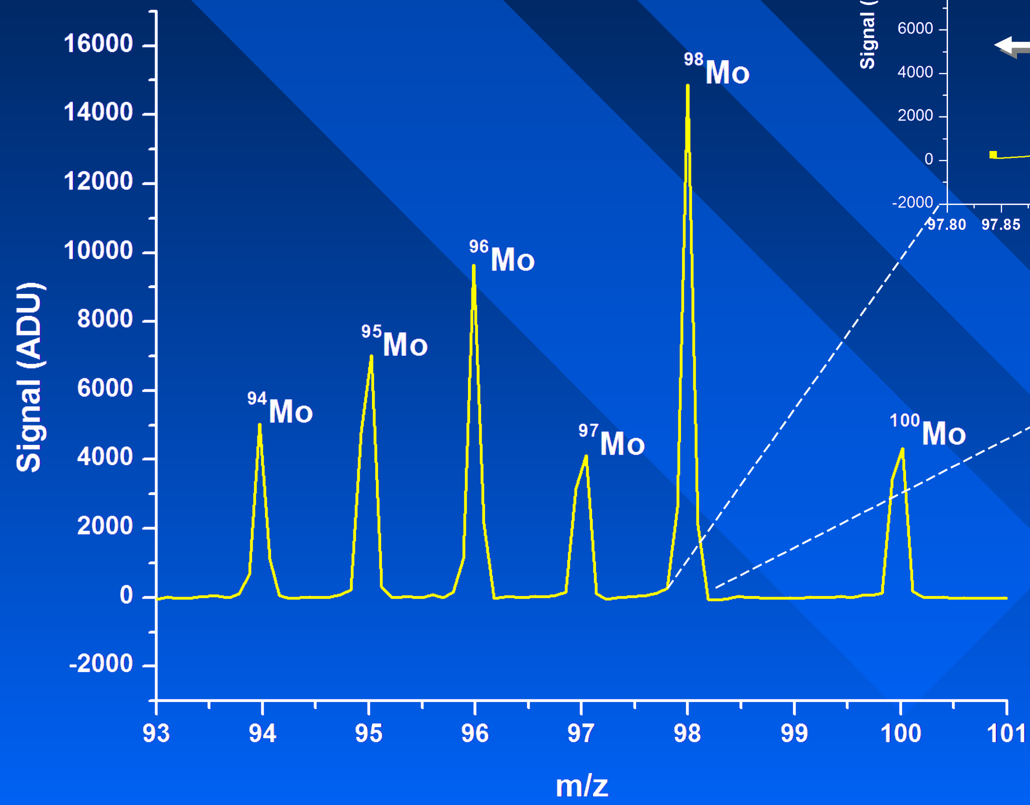


Improved Resolution

Operating Conditions

Sample Intro. – Laser Ablation
Sample – BNRM 44 (0.51% Mo)
Integration Time – 1 s
MS Entrance Slit Width – 100 μm

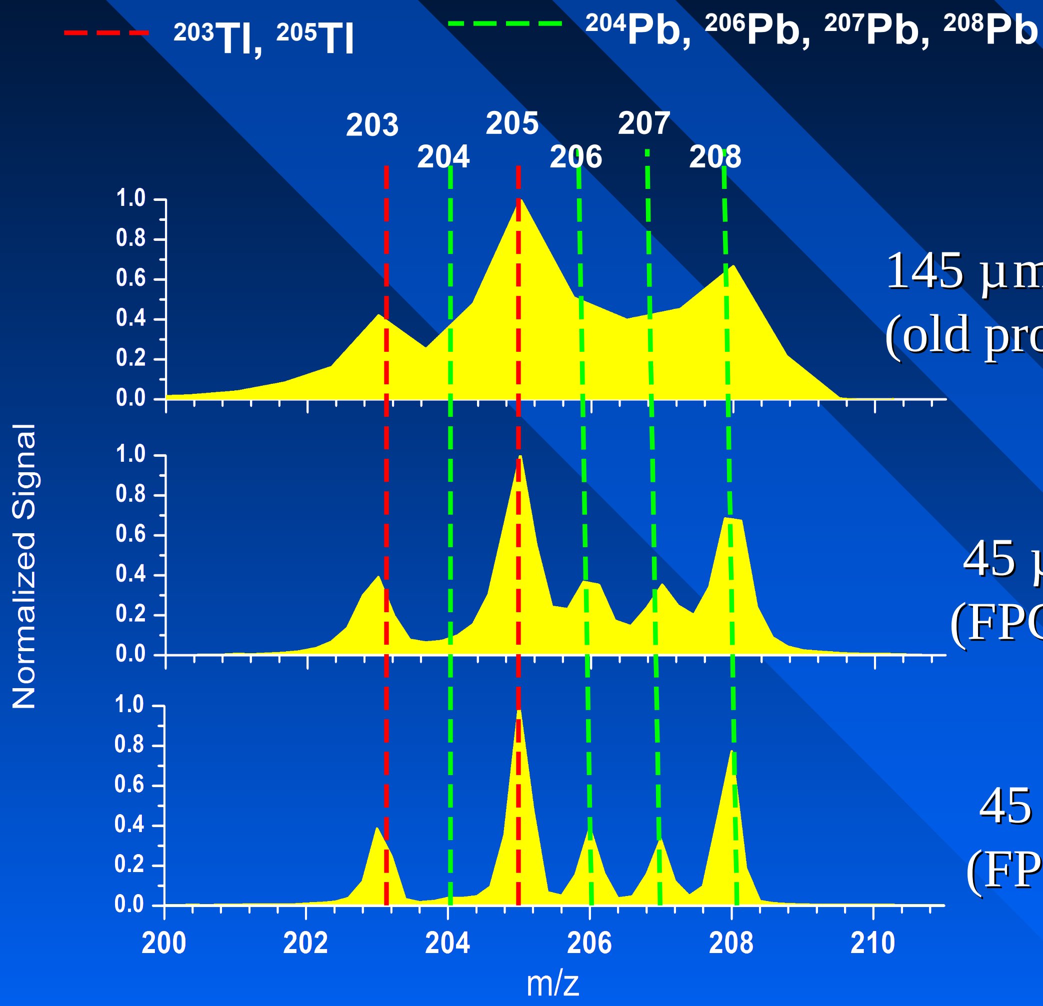




Resolution

Peak Center – 98.03
Peak Width – 0.12 FWHM
R = 817

Simultaneous Isotope monitoring
Mass Resolution



145 µm wide pixels, 100 µm slit
(old prototype detector with 32 pixels)

45 µm wide pixels, 100 µm slit
(FPC 128)

45 µm wide pixels, 50 µm slit
(FPC 128)

Limits of Detection (pptr)

Element	FPC	SEM	Element	FPC	SEM
Li	0.97	0.21	Y	3.0	0.12
Be	2.4	1.5	Mo	1.1	0.073
Mg	0.24	0.20	Ag	1.7	0.055
Al	0.44	0.25	Cd	0.23	0.026
V	7.1	0.44	In	0.54	0.10
Cr	3.6	0.20	Sn	0.49	0.23
Mn	0.66	0.23	Sb	7.2	0.18
Fe	0.084	0.25	Ba	0.74	0.17
Co	0.53	0.43	La	2.4	0.42
Ni	1.1	0.49	Ce	1.8	0.14
Cu	0.17	0.33	Ho	0.60	1.2
Zn	0.35	0.44	W	0.74	0.63
Ga	0.71	0.16	Ir	0.51	0.89
As	8.6	2.6	Tl	1.1	0.11
Se	1.3	3.0	Bi	0.91	0.22
Sr	1.3	0.11	U	1.4	15

FPC ➡31-channel Focal-plane camera; SEM ➡slit + single-channel electron multiplier

Elemental Analysis with the FPC Array Detector: Limits of Detection (ICP source)

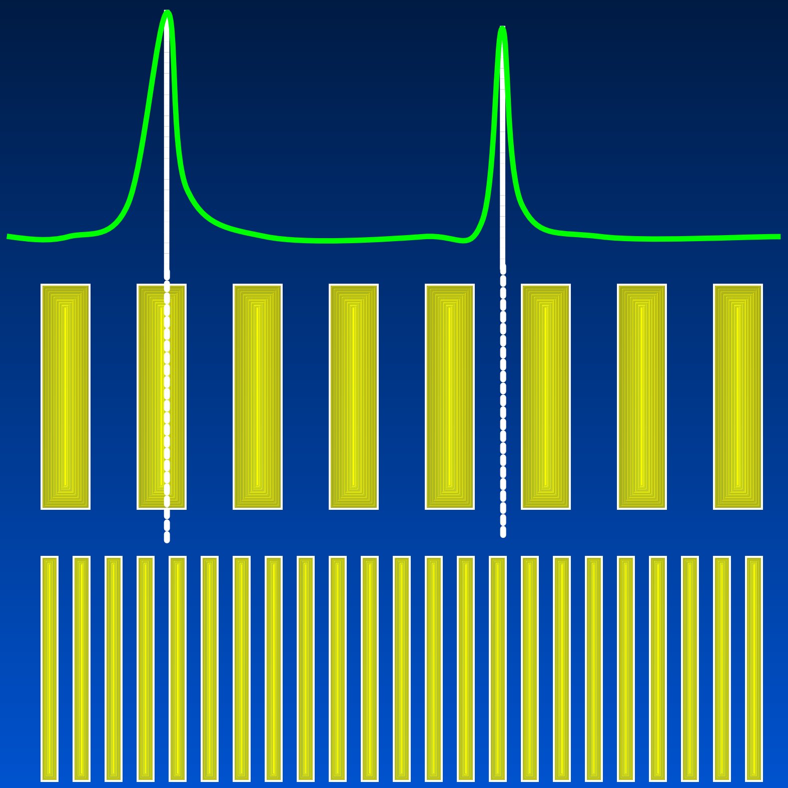
^{209}Bi
^{203}Tl
^{193}Ir
^{186}W
^{165}Ho
^{119}Sn
^{111}Cd
^{100}Mo
^{88}Sr
^{55}Mn
^{52}Cr
^{51}V
^{48}Ti

Limits of detection in the sub-part per trillion level for most elements

Values determined using continuous sample introduction via an ultrasonic nebulizer– 10 s integration time

Isotope Ratio Accuracy

Isotope Ratio Accuracy (% Error)*		
Isotope Ratio	FPC-128	FPC-31
$^{58}Ni/^{60}Ni$	4.3	2.1
$^{88}Sr/^{86}Sr$	14	33
$^{100}Mo/^{97}Mo$	7.3	6.6
$^{114}Cd/^{112}Cd$	1.8	2.1
$^{120}Sn/^{118}Sn$	2.9	0.43
$^{121}Sb/^{123}Sb$	2.6	25
$^{184}W/^{186}W$	10	3.5
$^{193}Ir/^{191}Ir$	0.085	5.0



*No correction for mass bias

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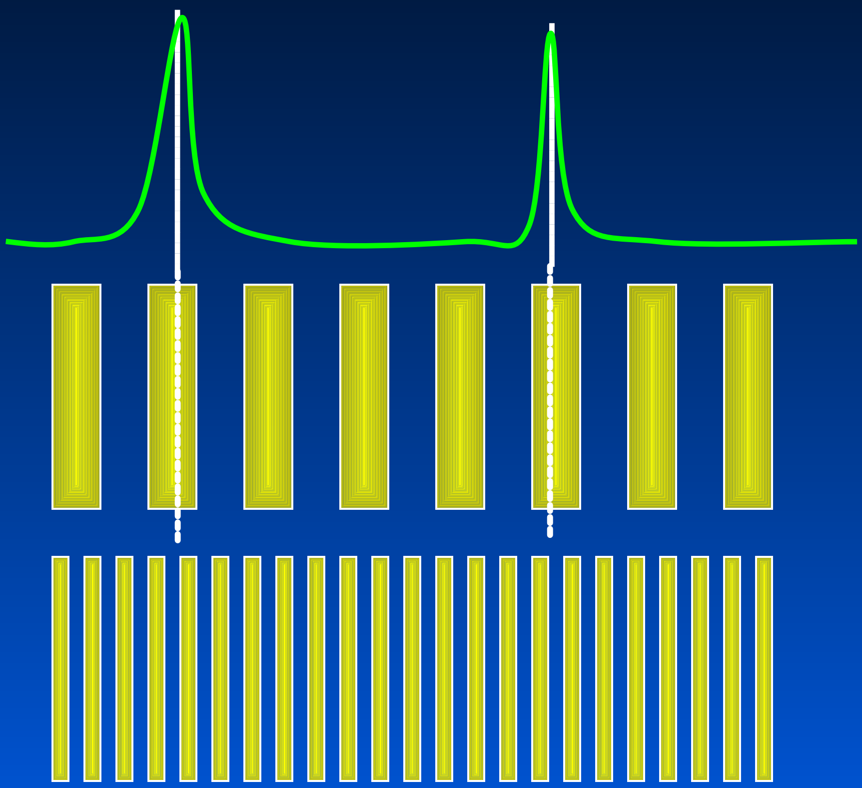

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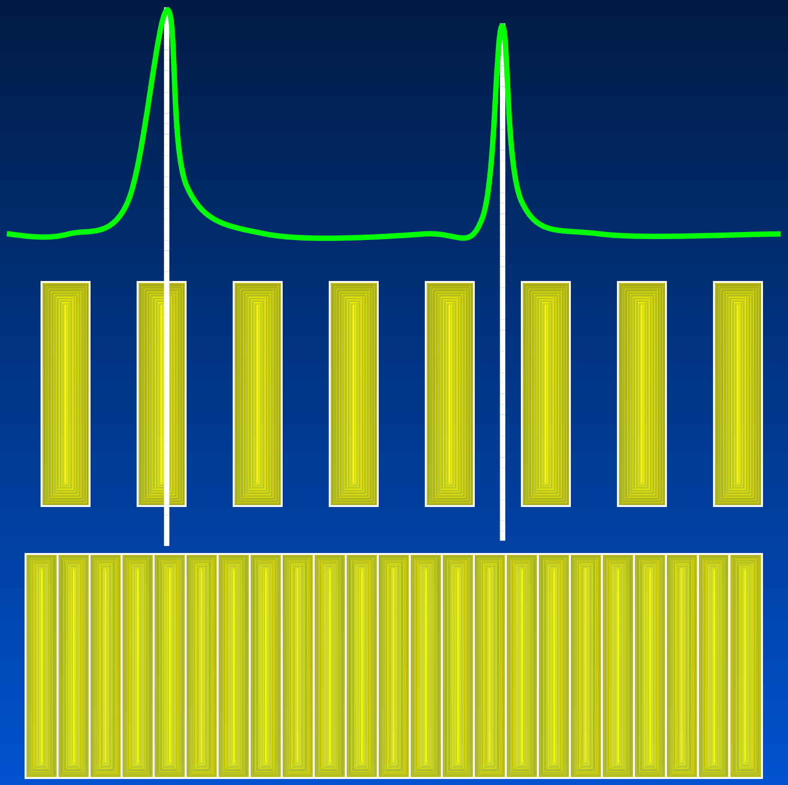
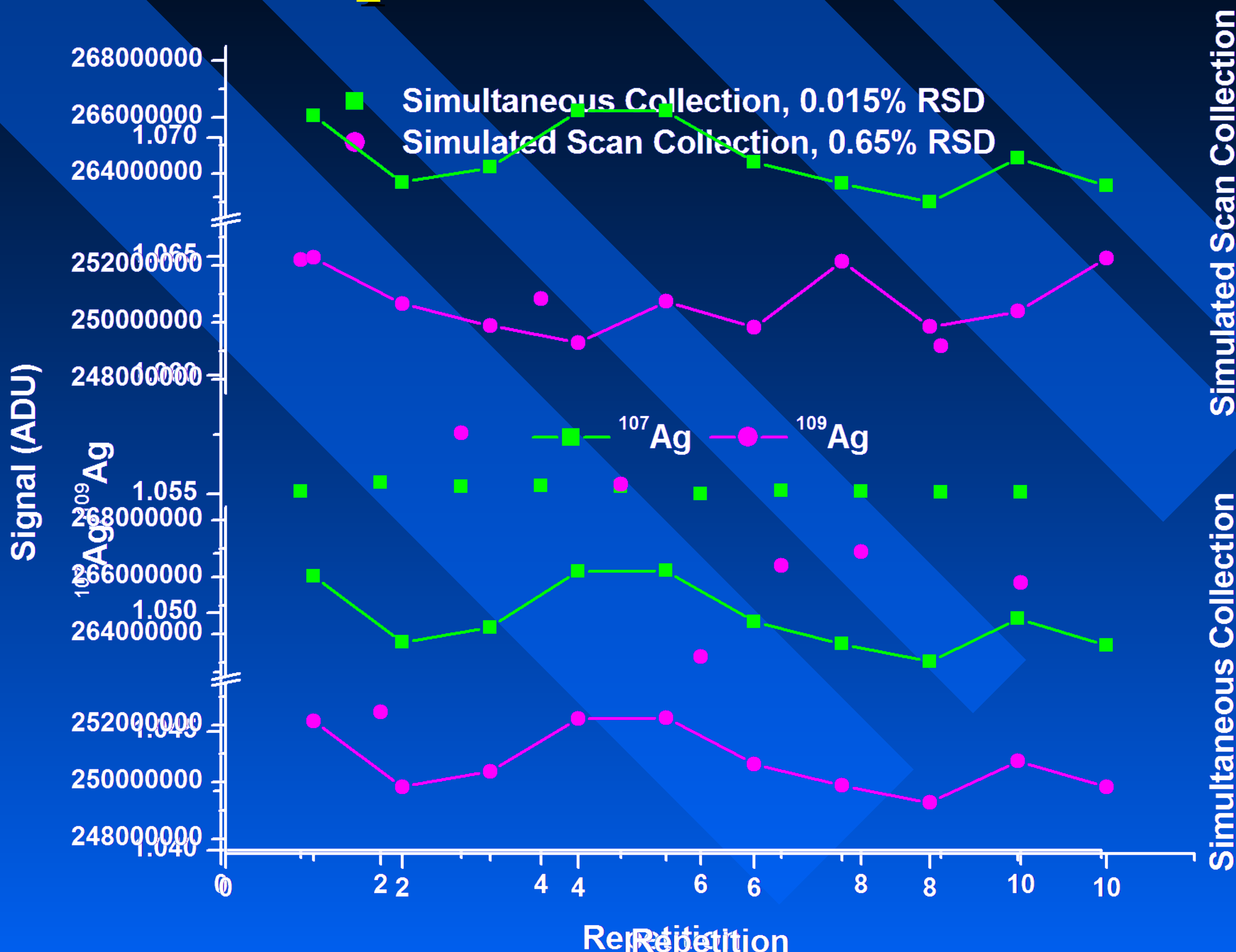


*No correction for mass bias

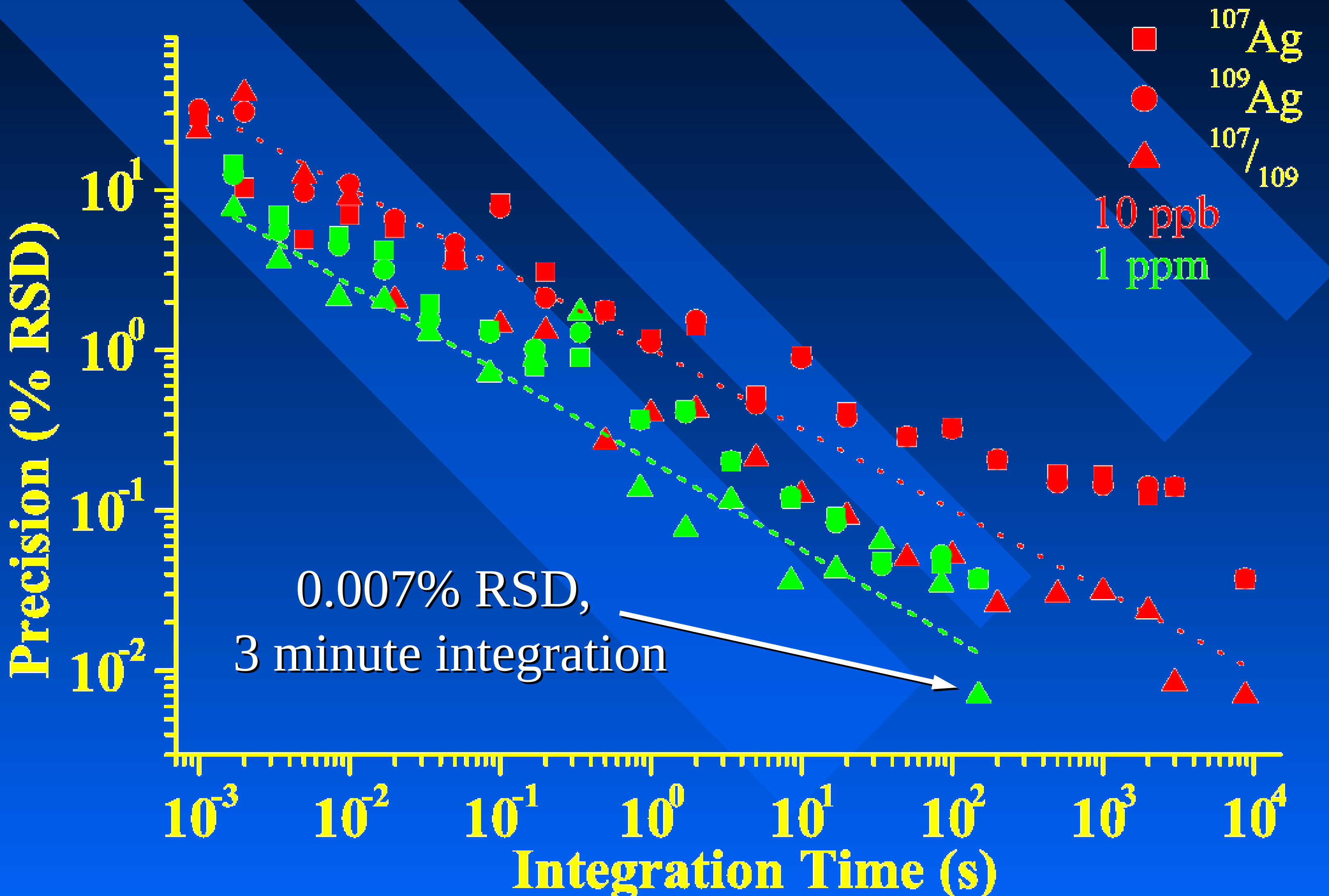
Isotope Ratio Accuracy

Isotope Ratio	Error	
	Uncorrected	Bias Corrected
$^{88}Sr/^{86}Sr$	14%	8%
$^{100}Mo/^{97}Mo$	11%	3%
$^{114}Cd/^{112}Cd$	4%	0.8%
$^{120}Sn/^{118}Sn$	5%	0.4%
$^{121}Sb/^{123}Sb$	5%	0.7%
$^{184}W/^{186}W$	4%	1%
$^{193}Ir/^{191}Ir$	3%	0.03%

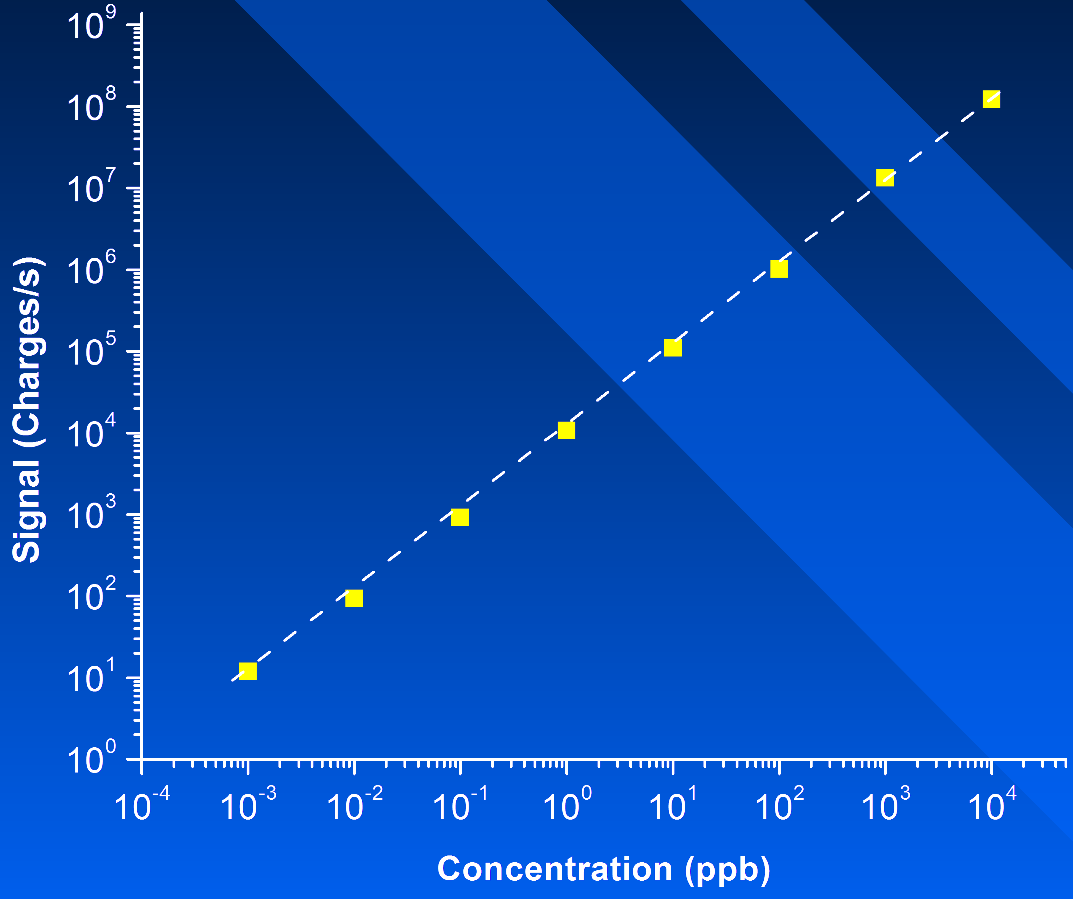
Isotope-Ratio Precision



Isotope Ratio Precision

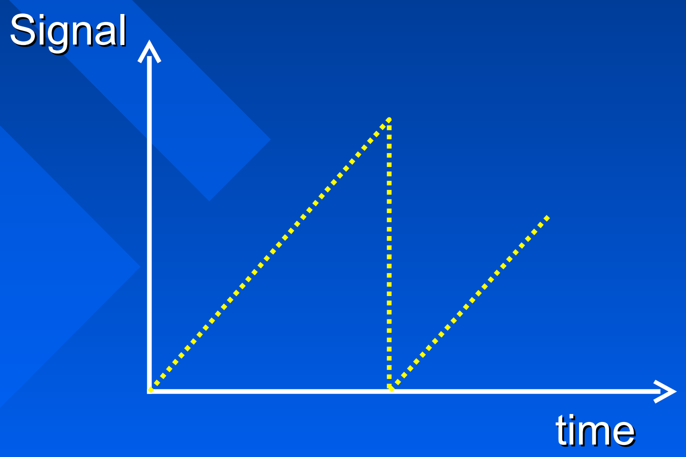


Elemental Analysis with the FPC Array Detector: Linear Dynamic Range



Linearity over 7 orders
1pptr to 50 ppm

Pixel full well capacity:
~10^5 charges (low gain)
~10^7 charges (high gain)



Where speed & simultaneous measurement really matter

- High-precision isotope ratios
- Optimal internal standardization
- Situations where the signal shape is critical
  - Flow injection
  - Electrothermal (carbon-furnace) vaporization
- Time-varying signals (e.g. LC, GC, CE)
- Modulation methods
- Fast transients (e.g. laser ablation)

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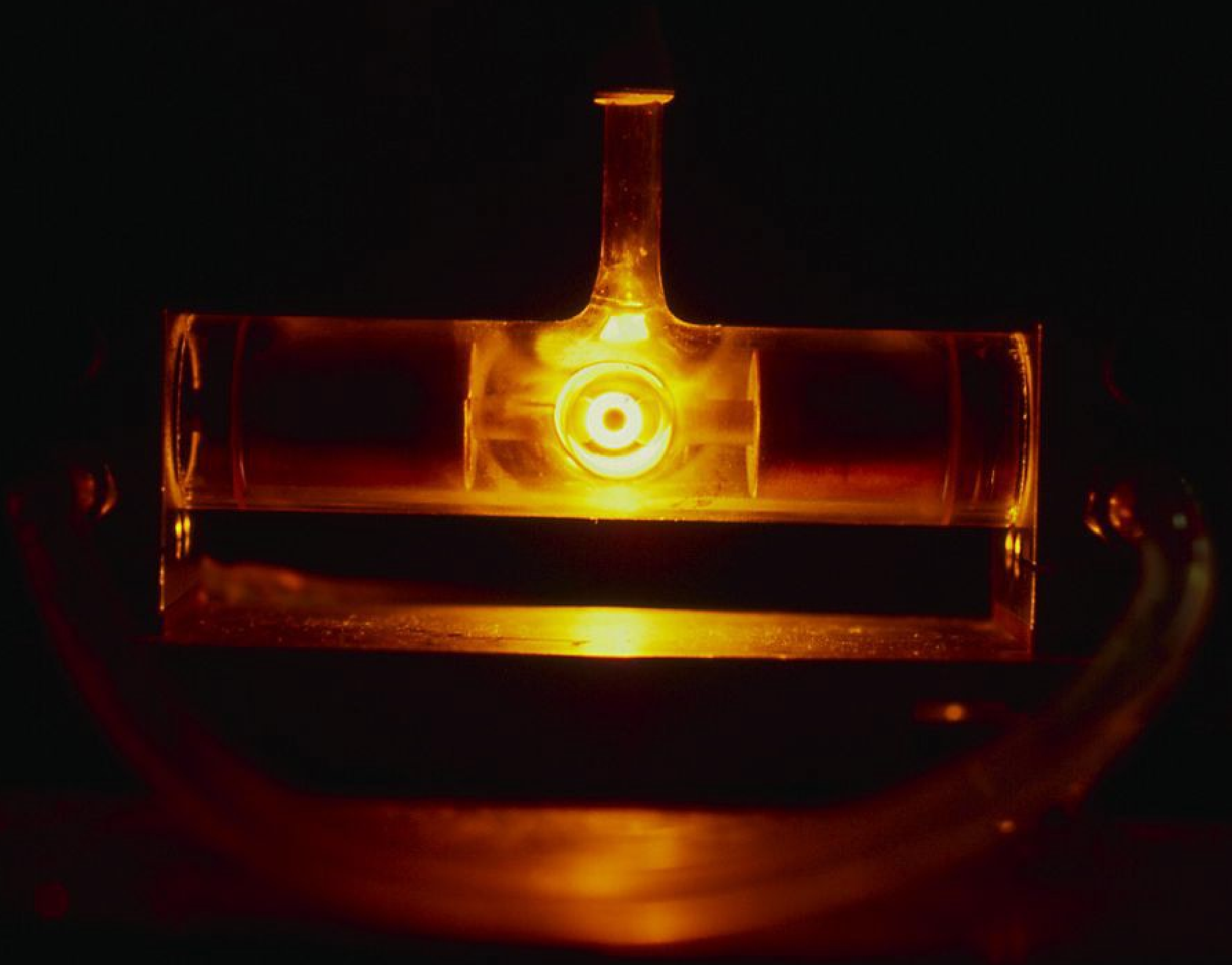
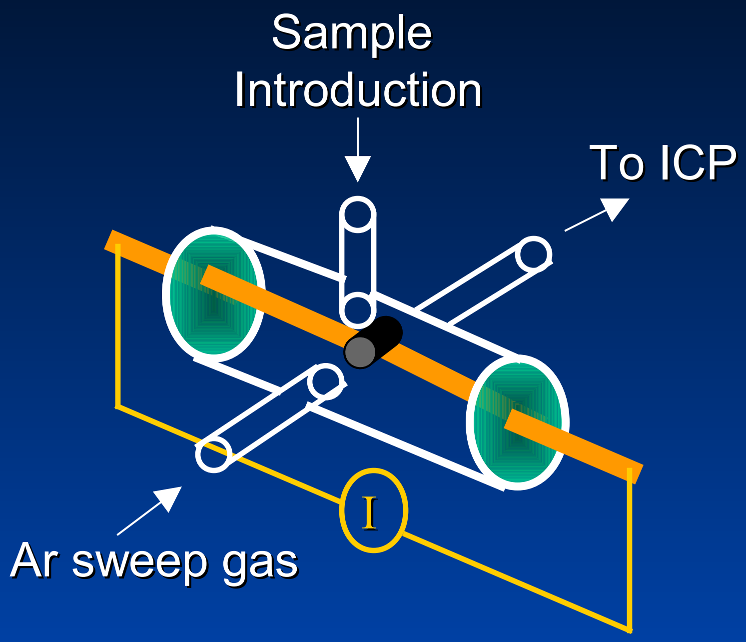
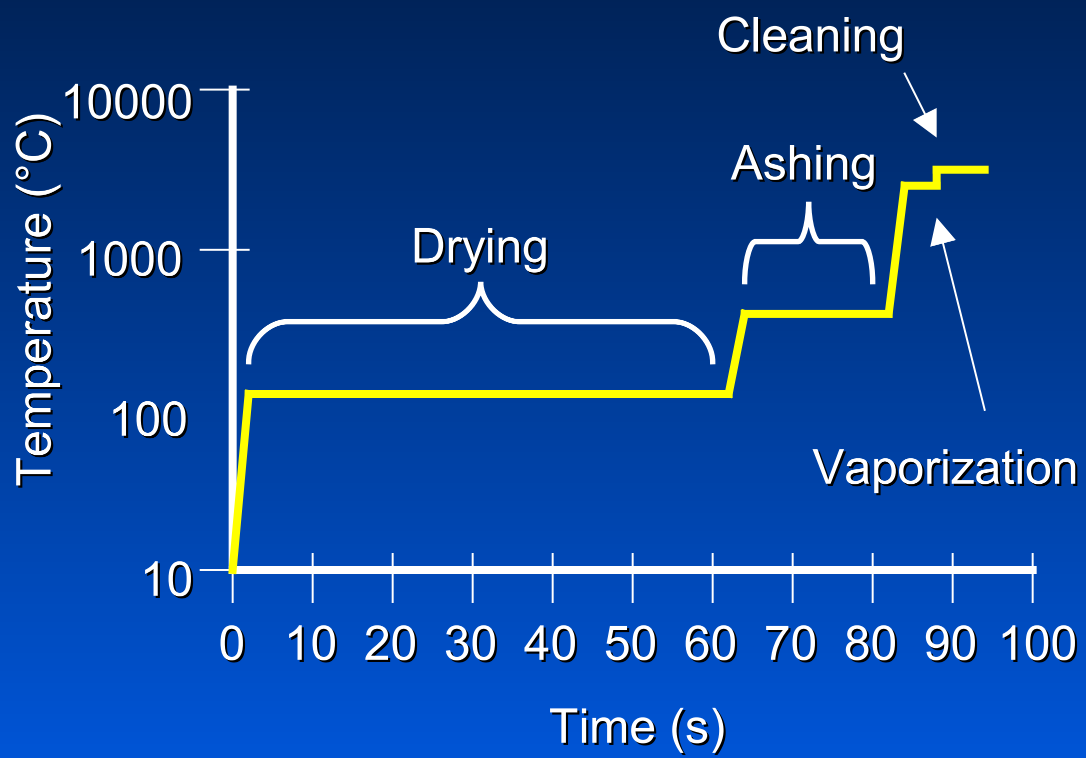
ETV-ICP-ADAMS

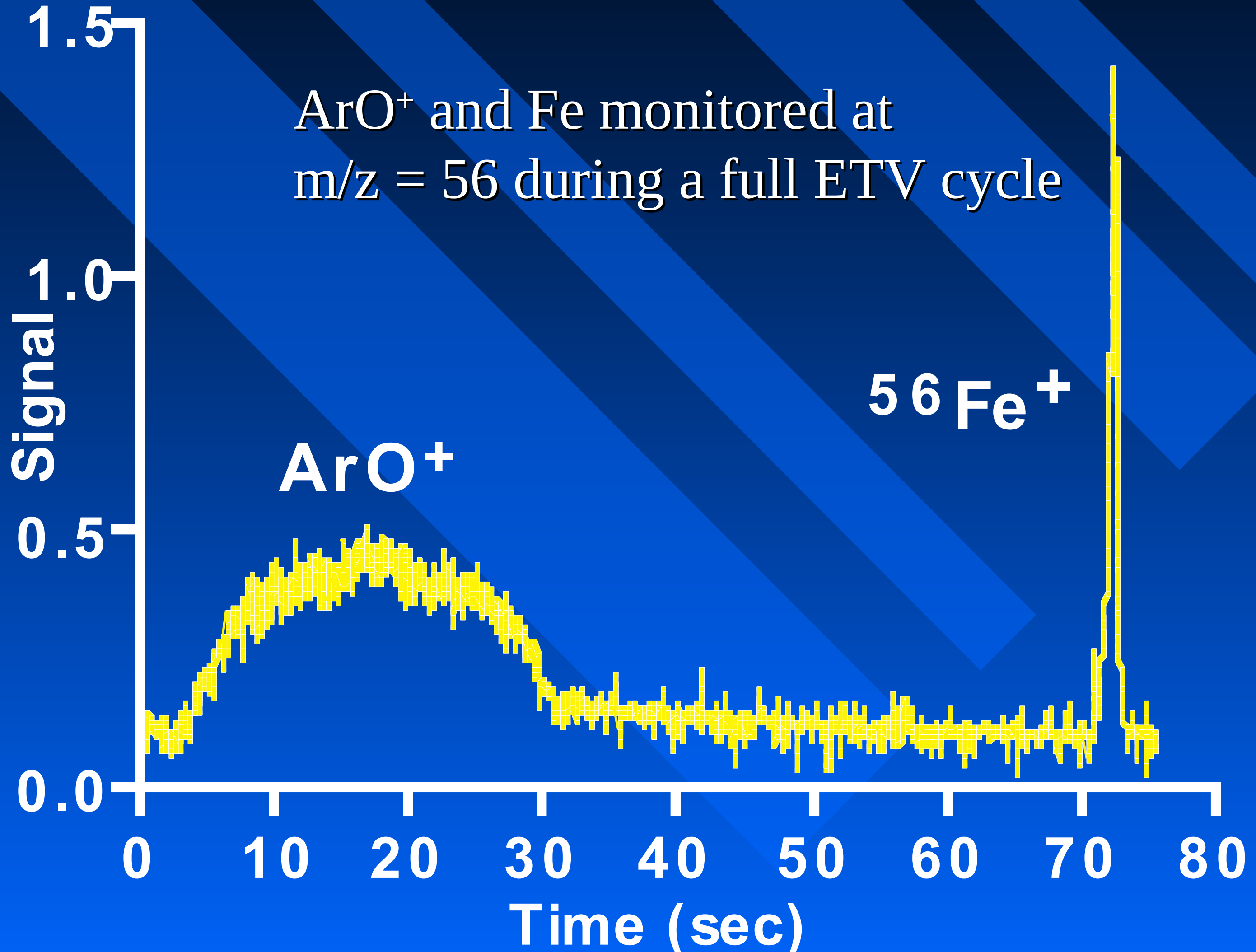


Electrothermal Vaporization





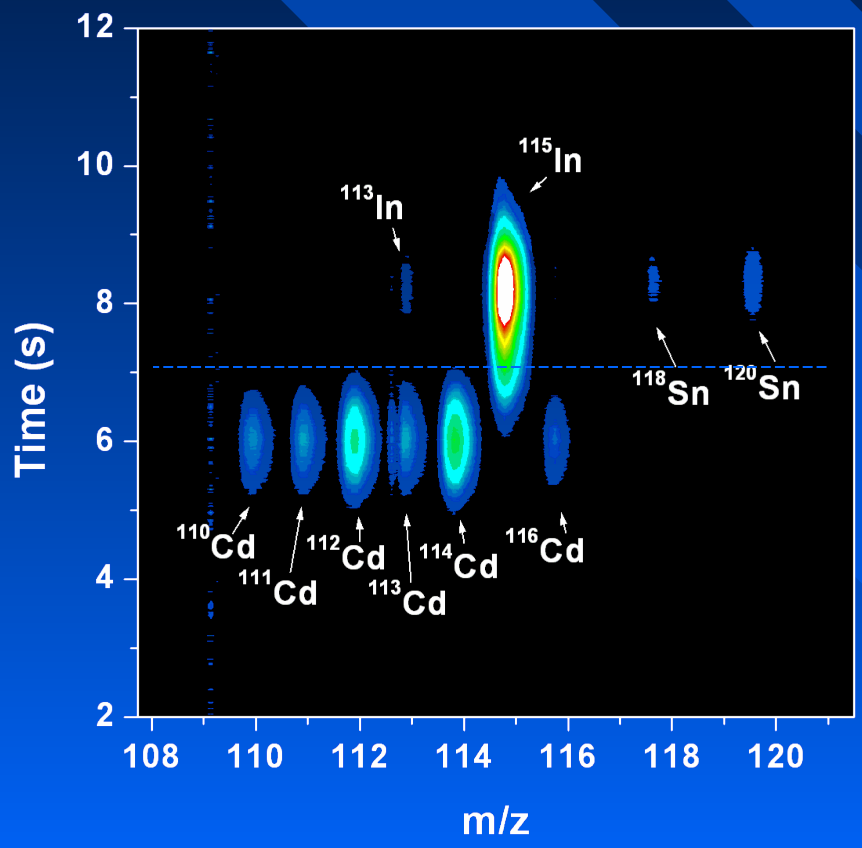
Temporal Separation of Isobaric Interferences

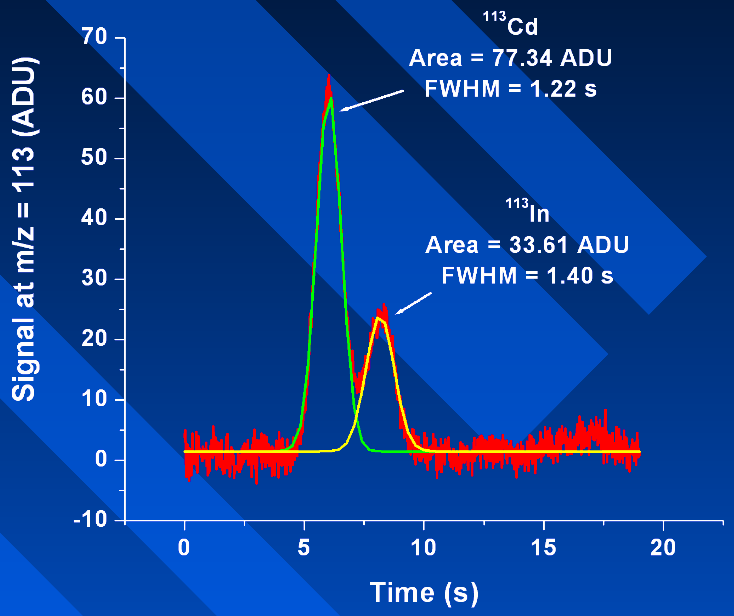


Elimination of Isobaric Overlaps Through Temperature Program

Necessary m/z Resolving Power: ~330,000

10 µL injection, 10 ppb Cd and In solution





<u>Temperature Program</u>

Dry: 100°C, 90s
Ash: 250°C, 10s
Atomize: 1700°C, 4s
Ramp: 250°C/s

ETV Limits of Detection (pptr)

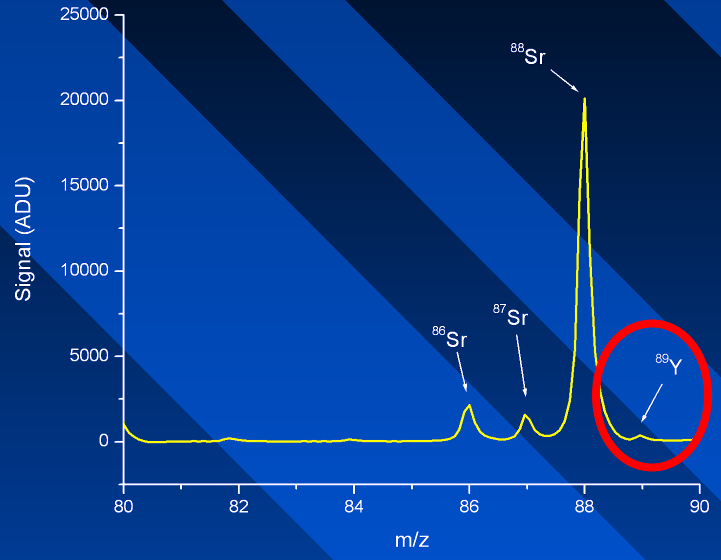
Isotope	FPC	SEM	Isotope	FPC	SEM
V-51	7	0.4	Sn-120	0.5	0.2
Cr-53	4	0.2	Sb-123	7	0.2
Mn-55	0.7	0.2	Ba-138	0.7	0.2
Co-59	0.5	0.4	Ho-165	0.6	1
Ni-60	1	0.5	W-186	0.7	0.6
Zn-66	0.4	0.4	Ir-193	0.5	0.9
Sr-88	1	0.1	Tl-203	1	0.1
Ag-107	2	0.06	Bi-209	0.9	0.2
Cd-114	0.2	0.03	U-238	1	20

10 s Integration Time

FPC ➡Focal-plane camera

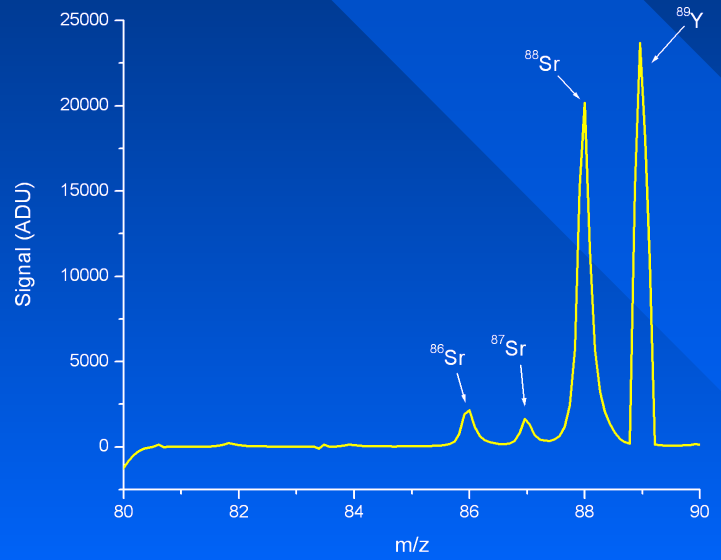
SEM ➡Single channel Secondary Electron Multiplier

ETV-ICP-ADAMS



1 ppm Sr and 10 ppb Y
2 s integration time

All pixels at low gain
(Pixels collecting ^{88}Sr signals saturate at high gain)

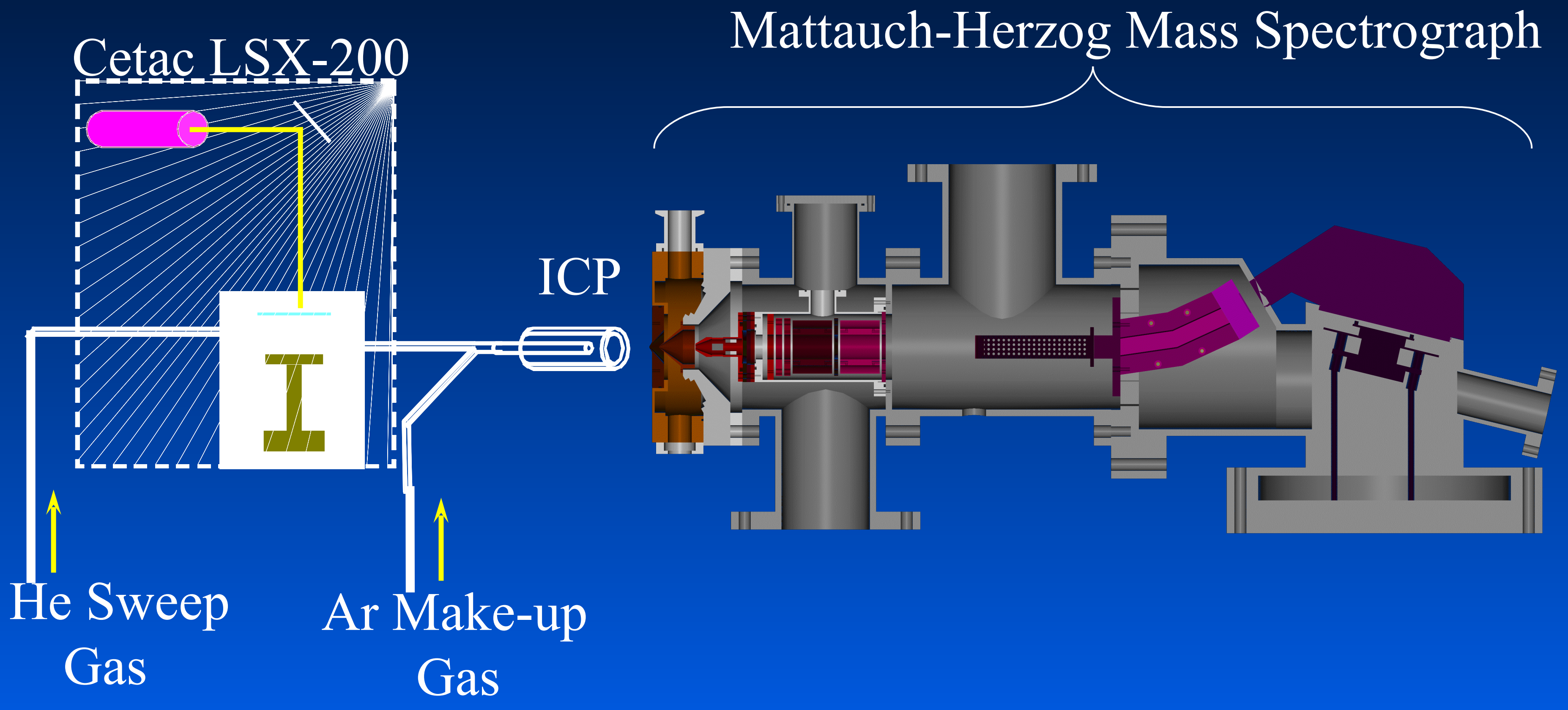


Signal for Y
collected at high gain

Where speed & simultaneity really matter

- High-precision isotope ratios
- Optimal internal standardization
- Situations where the signal shape is critical
  - Flow injection
  - Electrothermal vaporization
- Time-varying signals (e.g. LC, GC, CE)
- Modulation methods
- Fast transients (e.g. laser ablation)

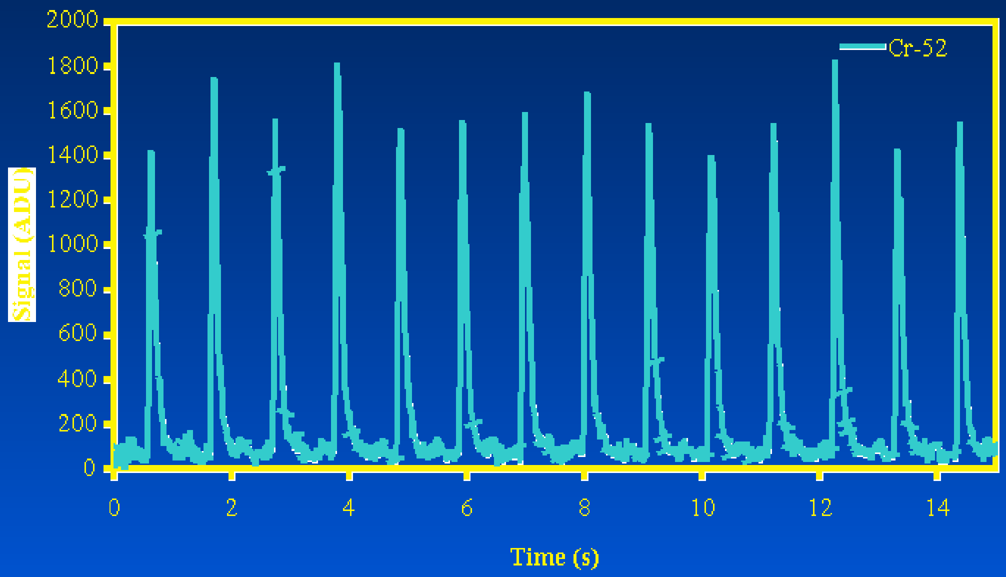
Laser Ablation ICP-ADAMS Setup



LA LODs – Steady state, single shot

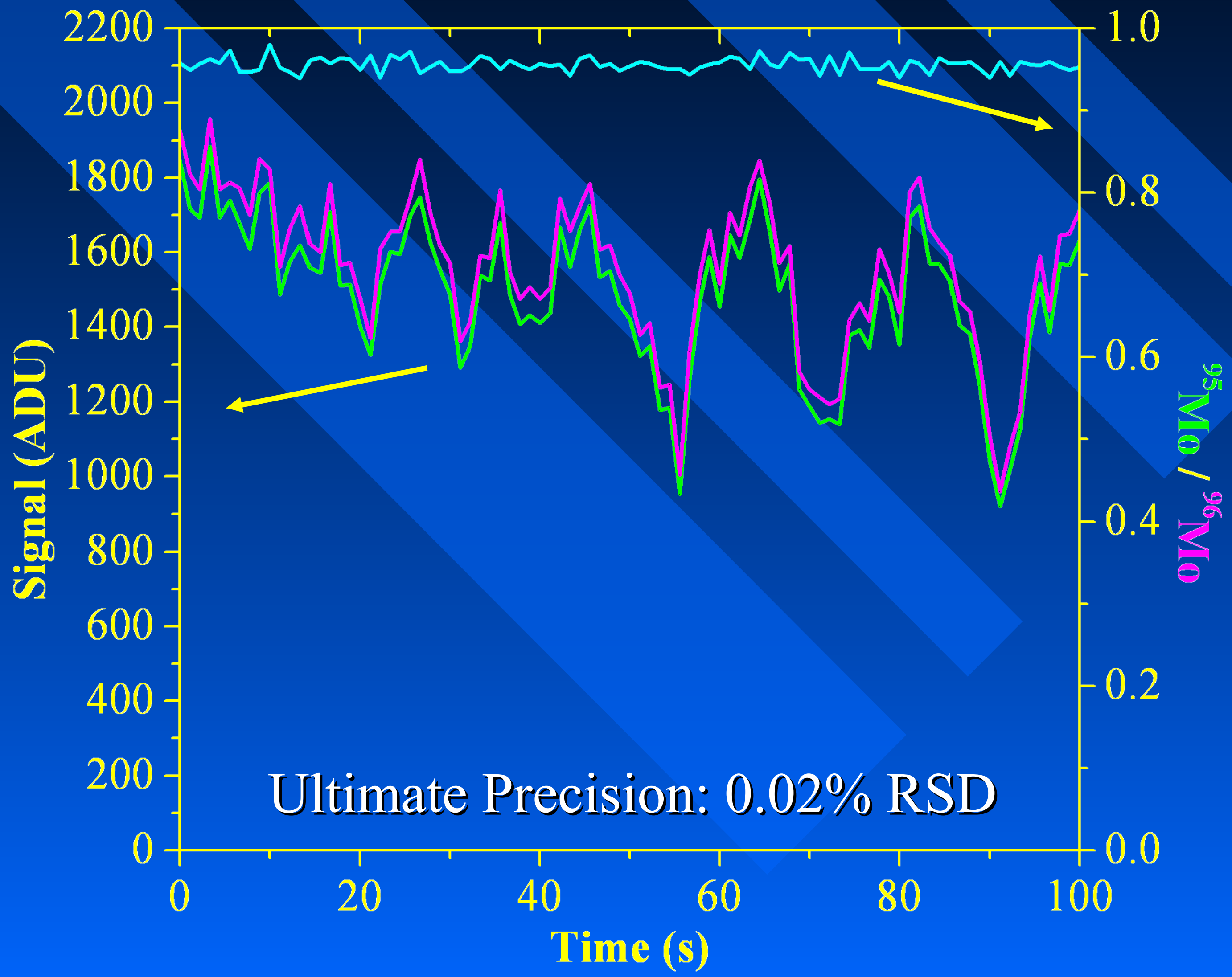
Element	Steady State (ng/g)	Single Shot (fg)	Element	Steady State (ng/g)	Single Shot (fg)
B	31	160	Sr	342	1770
Mn	51	261	Ag	15	76
Fe	36	186	Au	36	188
Co	41	210	Tl	10	50
Ni	41	216	Pb	9	46
Cu	31	163	Th	233	1200
Rb	112	577	U	53	272

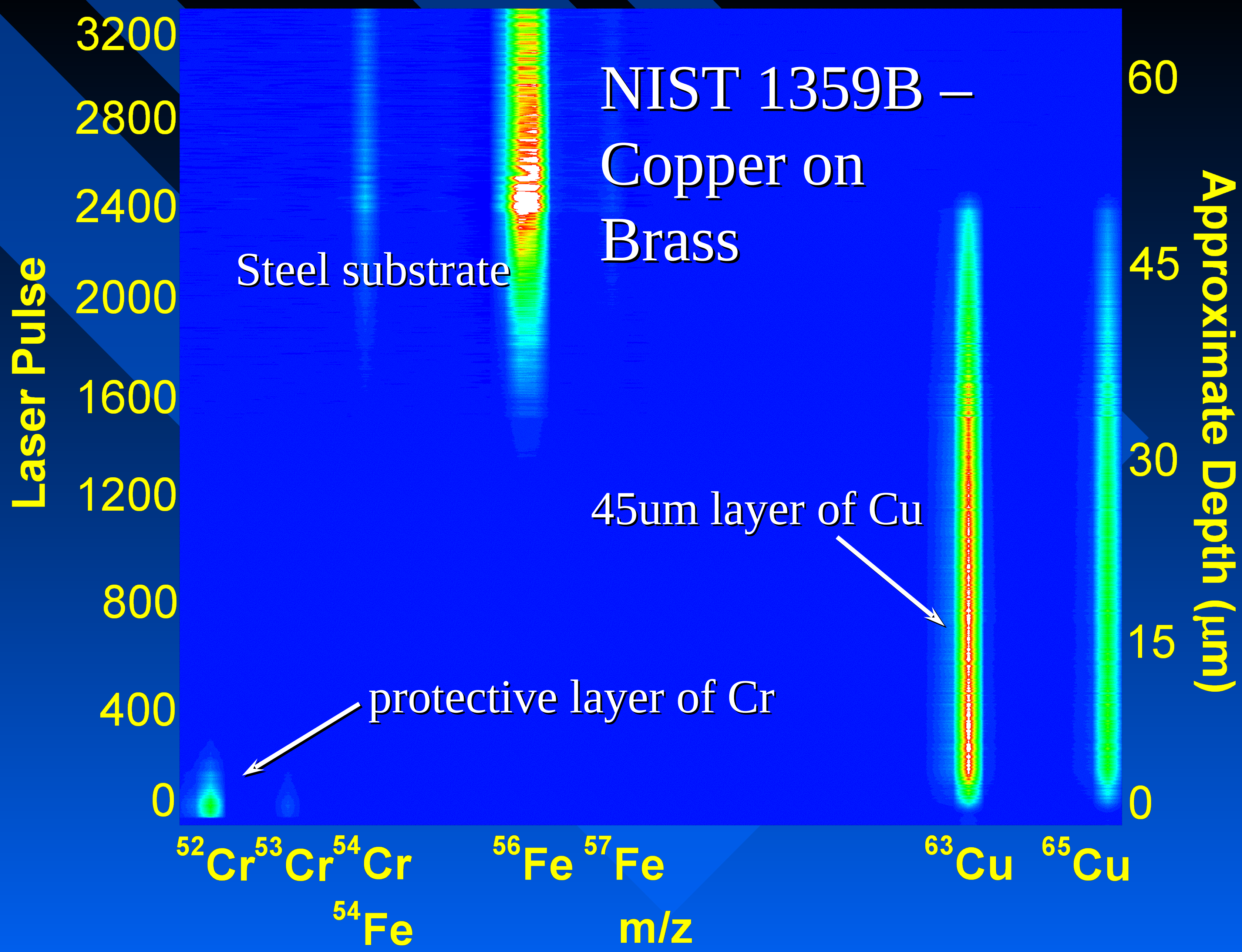
Laser Ablation ICP-ADAMS Shot-to-Shot Reproducibility



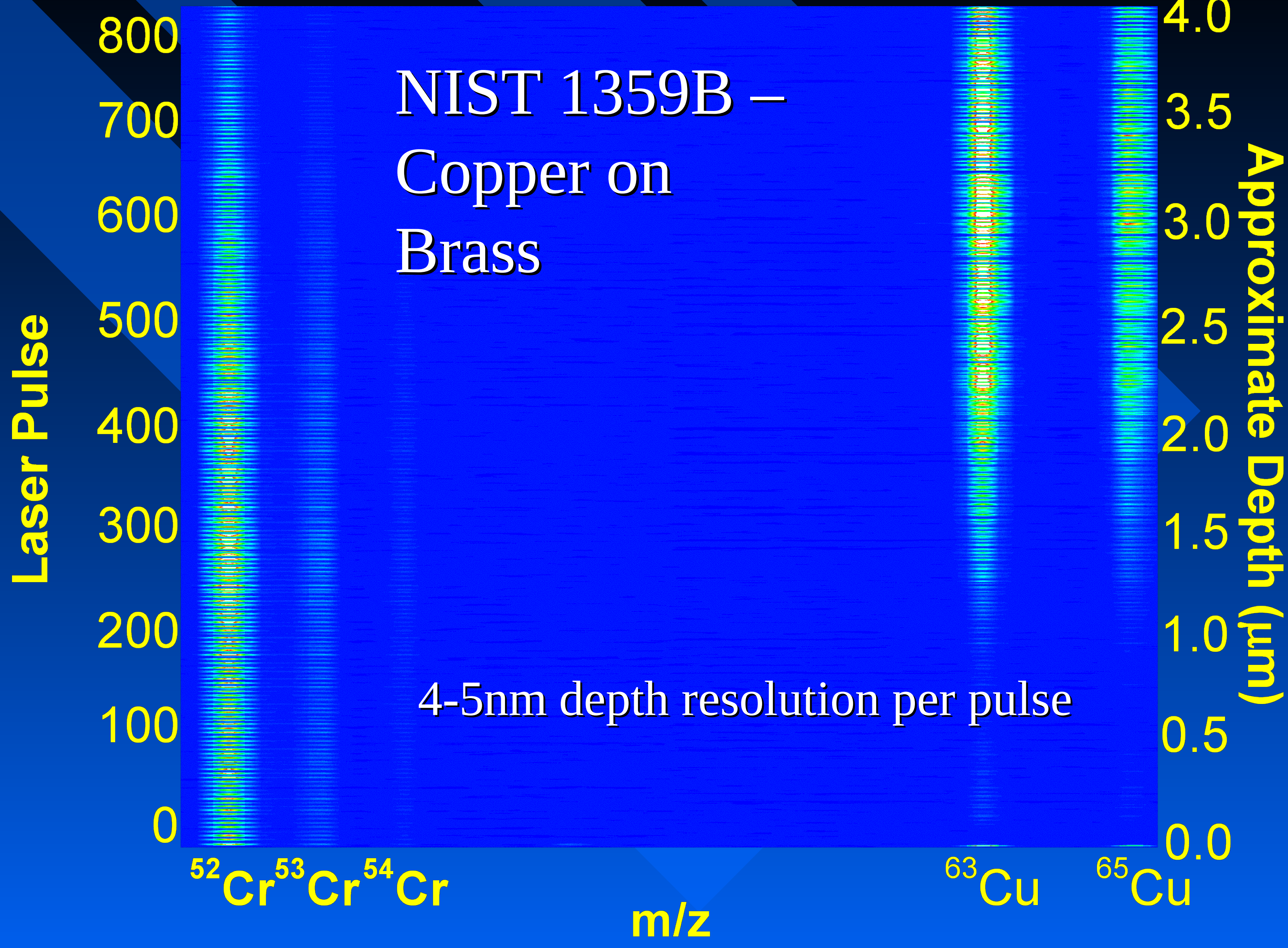
Isotope	%RSD	Isotope	%RSD
^{27}Al	3.3	^{65}Cu	9.5
^{28}Si	7.4	^{93}Nb	8.4
^{52}Cr	11.3	^{100}Mo	6.4
^{55}Mn	9.8	^{120}Sn	5.1
^{56}Fe	9.3	^{186}W	21.5
^{64}Ni	5.8	^{208}Pb	12.2

Laser Ablation Precision





NIST 1359B – Copper on Brass
Steel substrate
45um layer of Cu
protective layer of Cr
Laser Pulse
3200
2800
2400
2000
1600
1200
800
400
0
Approximate Depth (µm)
60
45
30
15
0
52Cr 53Cr 54Cr
54Fe
56Fe 57Fe
63Cu 65Cu
m/z



NIST 1359B – Copper on Brass
4-5nm depth resolution per pulse
Laser Pulse
800
700
600
500
400
300
200
100
0
Approximate Depth (μm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
52Cr 53Cr 54Cr
63Cu 65Cu
m/z

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- Modulation methods
- Fast transients (e.g. *in situ* laser ablation)

Chromatography with ICP-ADAMS

- GC, LC, CE being pursued

Lanthanides by LC-ICP-ADAMS