Increasing the Linear Dynamic Range of Sector Field ICP-MS

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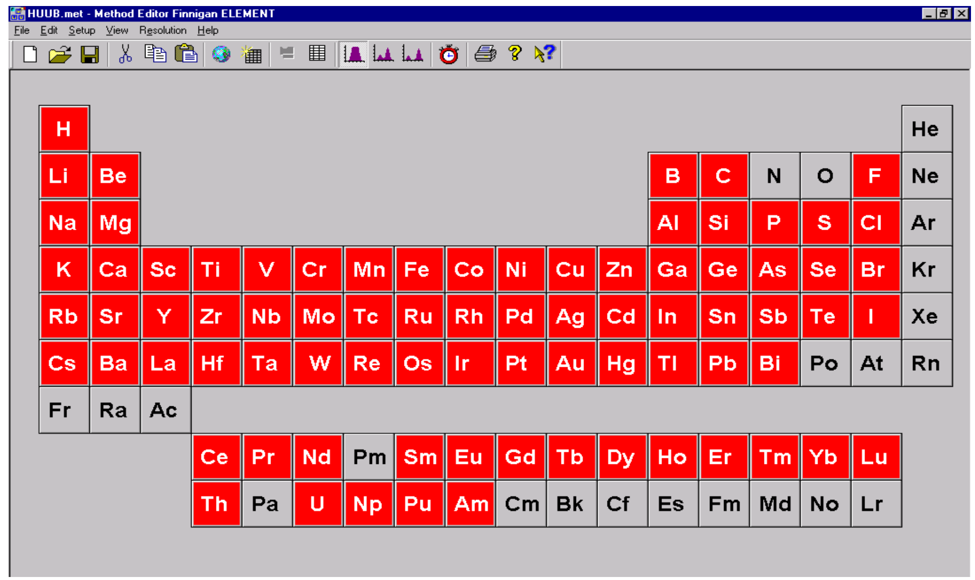
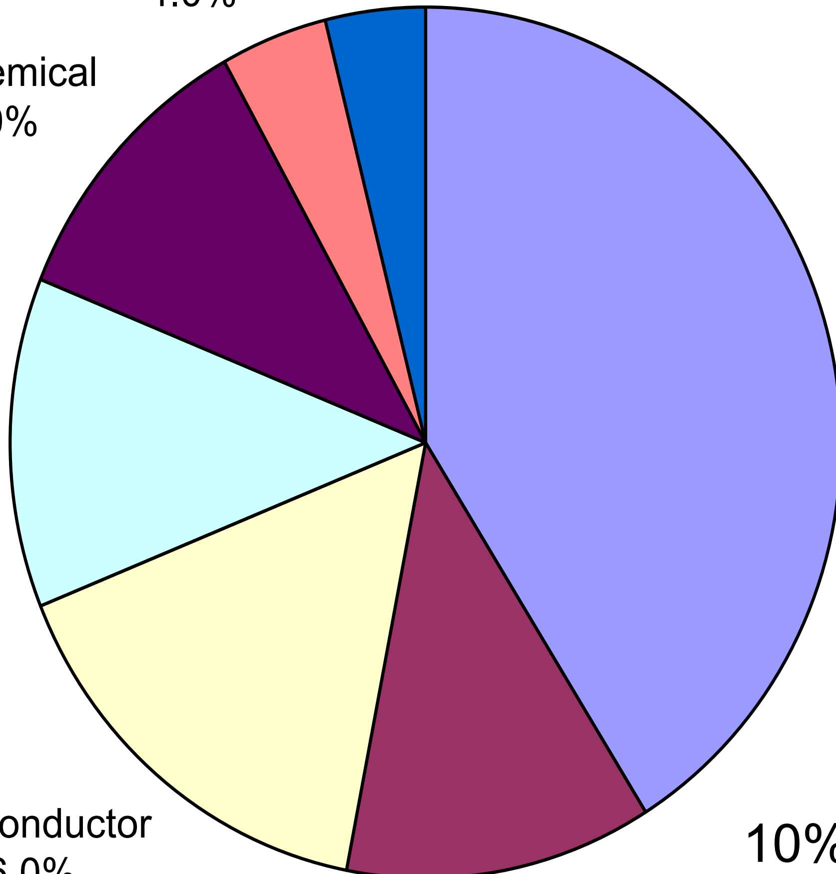
Benefits of ICP-MS

- Elemental determinations of almost the whole periodic table
  - *Multi-elemental analysis in a single analysis run*
  - *Lower detection limits compared to Graphite Furnace Atomic Absorption (GFAA) or ICP-OES*
  - *High productivity with > 30 samples/hour*
- Limitations due to spectral interferences
  - *From the matrix or argon plasma itself*
  - *Limits the accuracy*



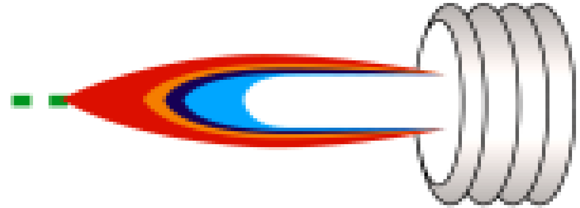
Who uses ICP-MS ?



10% Sector Field ICP-MS
90% Q-ICP-MS

Argon Plasma as Ion Source

- Both ICP-MS techniques (Quadrupole and Magnetic Sector) use the same ion source
- Samples are analyzed as solutions or solids
- The Sample is introduced into an argon plasma as a fine aerosol, via a nebulizer and spray chamber or by laser ablation of solid samples
- Within the plasma the solvent is evaporated and the sample species are decomposed into their constituent atoms and ionised
- Ionisation process is extremely efficient in the plasma, and contributes to the high sensitivity of ICP-MS



- 27 MHz Argon Plasma
- 6000 K

The drawback of the Argon plasma as an ion source is the formation of spectral interferences

What are spectral interferences ?

- Molecular species which occur at the same nominal mass as the analyte, they are
  - *Formed in the plasma and/or interface*
  - *Matrix dependent*
  - *Plasma condition dependent*
- They originate from the Argon plasma and the sample matrix

Isotope	Interference
^{31}P	$^{15}N^{16}O$ $^{14}N^{16}OH$
^{44}Ca	$^{28}Si^{16}O$ $^{12}C^{16}O_2$ $^{14}N_2{}^{16}O$
^{56}Fe	$^{40}Ar^{16}O$ $^{40}Ca^{16}O$ $^{28}Si_2$
^{60}Ni	$^{44}Ca^{16}O$ $^{23}Na^{37}Cl$ $^{28}Si^{32}S$

Examples for spectral overlaps

The Biggest Problem in ICP-MS: Spectral Interferences

Instrumental Solutions

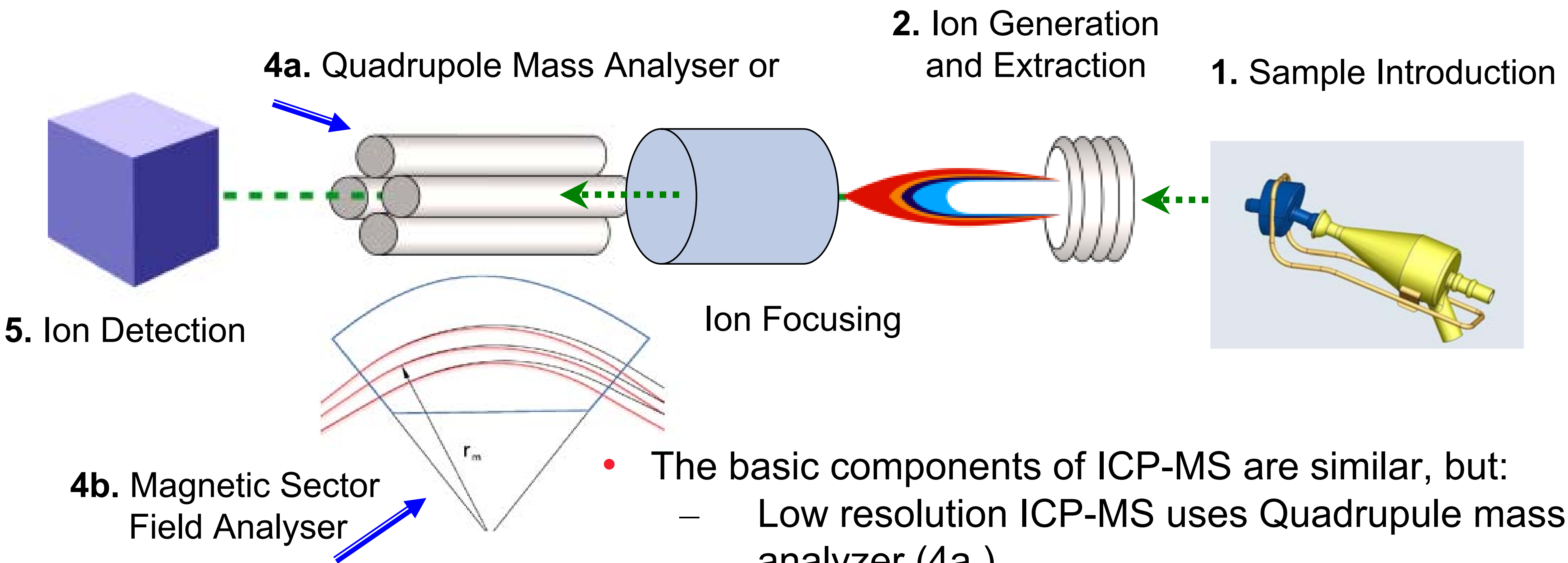
- *High Resolution (SF ICP-MS)*
- *Cold Plasma*
- *Collision Cell/Dynamic Reaction Cell (Q ICP-MS)*
- *Mathematical Calculation*

Sample Preparation (Time-consuming, error-prone)

- *Pre-concentration/matrix evaporation (off-line)*
- *Membrane desolvation (on-line)*
- *ETV*

Building Blocks of an ICP-MS

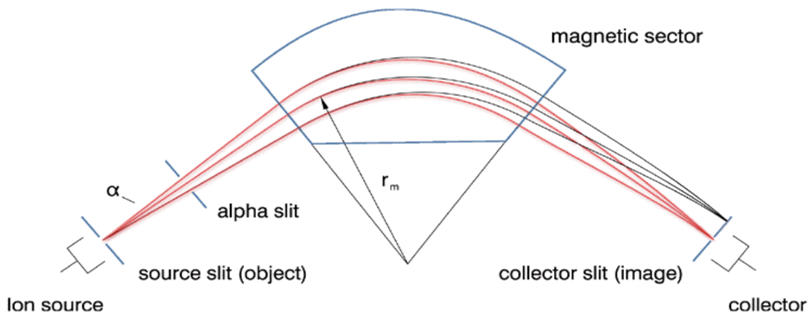
Inductively Coupled Plasma Mass Spectrometer



- The basic components of ICP-MS are similar, but:
  - Low resolution ICP-MS uses Quadrupule mass analyzer (4a.)
  - High resolution ICP-MS uses Magnetic Sector Field Analyzer (4b.)

Thermo Electron Factory in Bremen, Germany

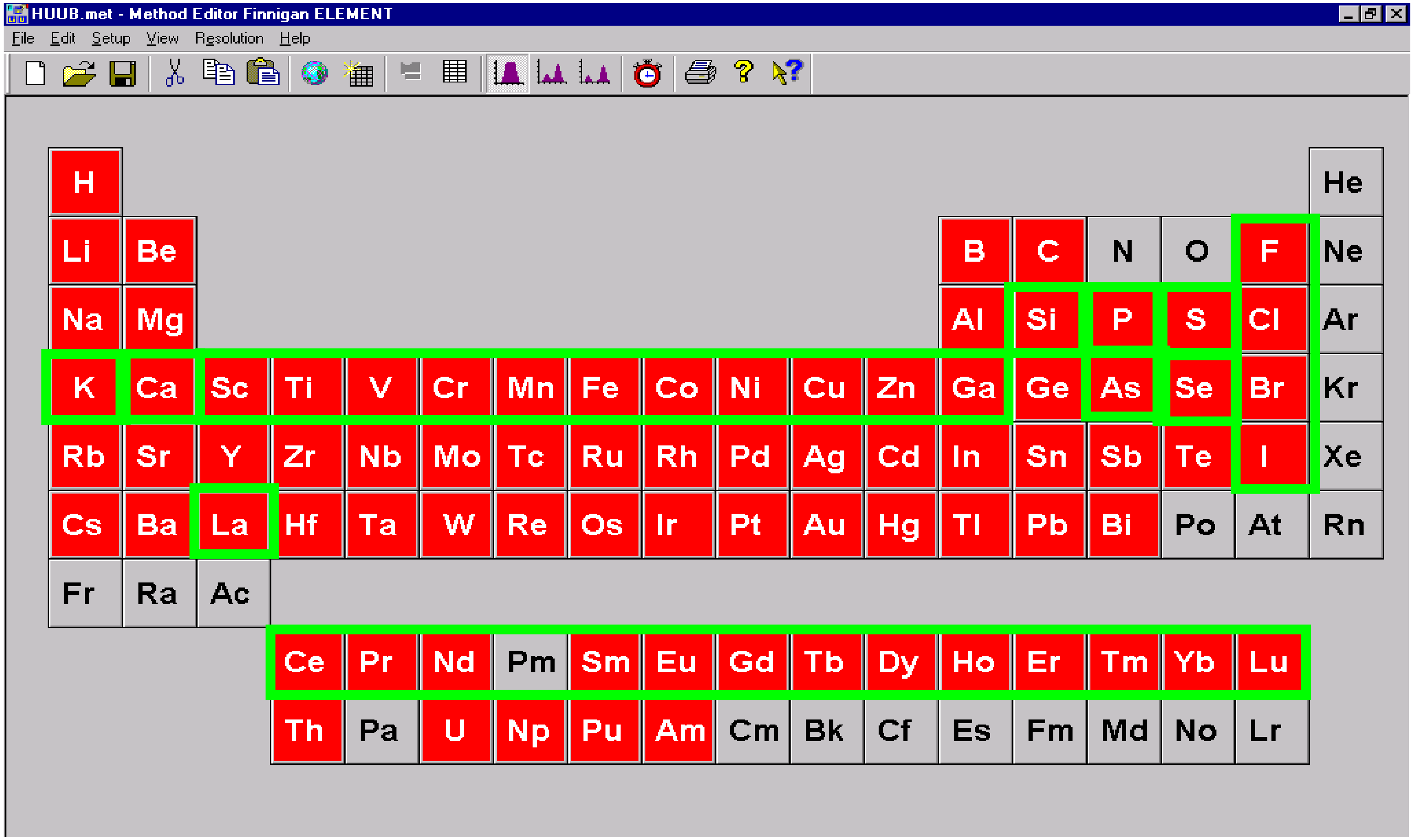
- Since 1948 producing mass spectrometers
- Organic (MAT 95), IRMS (Triton, Delta, MAT 253/271/281)
  LTQ-FTMS
  and since 1994 ICP-MS
  as single (ELEMENT) and multicollector (Neptune)
- 175 colleagues working on
  magnetic sector field
  technology



New Factory

Worldwide 350 ELEMENT

Multi-elementanalysis



Key characteristics

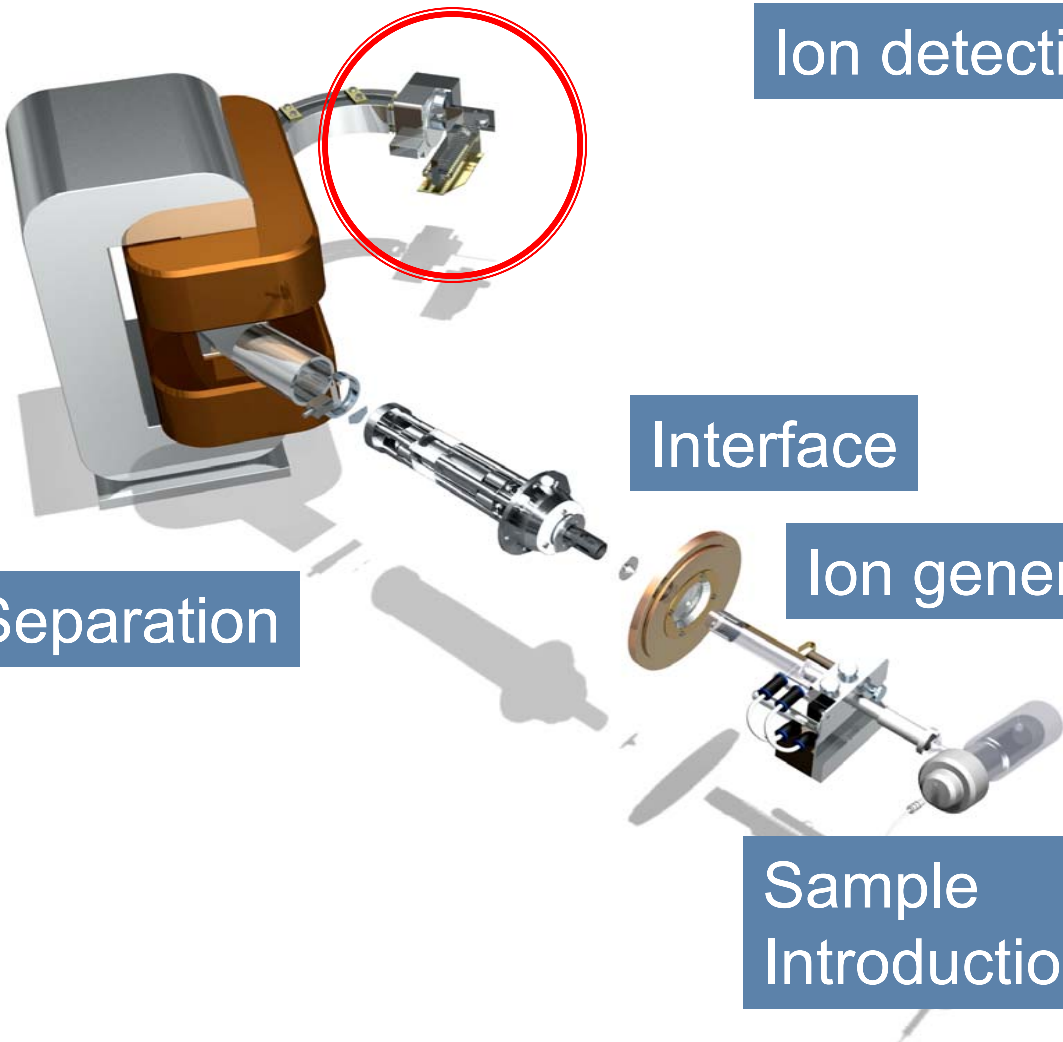
- Interference free analysis
- Matrix independent
  - *physical separation of interferences*
  - *multielement settings*
- High Signal to Noise Ratios
  - *< 0.2 cps for all 3 resolutions*
  - *across the mass range*
- Sensitivity:
  - *LR: 3,000,000 cps per from ~ ^{45}Sc upwards*
  - *MR: 3,00,000 cps per ppb from ~ ^{45}Sc upwards*
  - *HR: 50,000 cps per ppb from ~ ^{45}Sc upwards*

Under same set of conditions

SF ICP-MS for Demanding Applications

- Simultaneous ultra-trace to matrix analysis
- Ultra-trace determinations in complex matrices
- Analysis of radionuclides
- Isotope ratio analysis
- Analysis of fast transient signals
  - laser ablation, HPLC
- High throughput analysis

Principle components of a SF ICP-MS



Ion detection

Interface

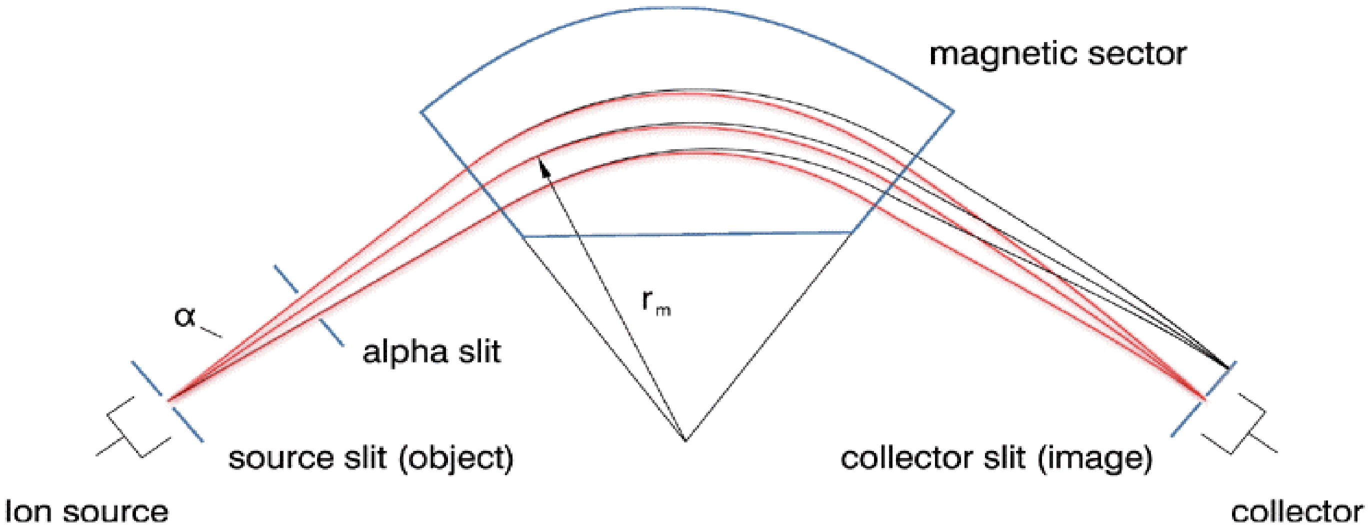
Ion generation

Mass Separation

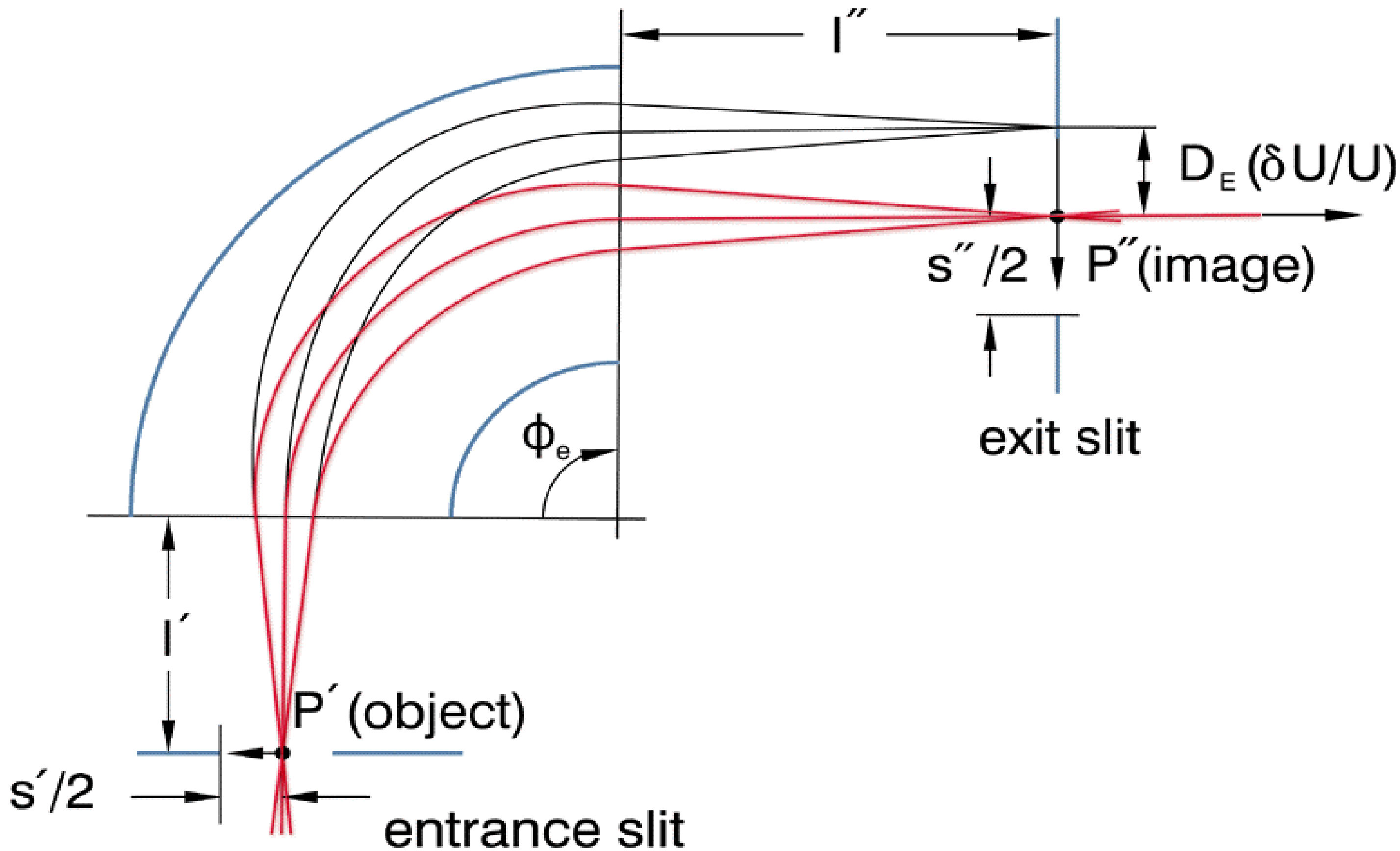
Sample Introduction

Laser
HPLC
GC
FFF
CE
....

Dispersion and Focusing – Magnetic Sector



Electrostatic Sector – Dispersion and Angular Focusing



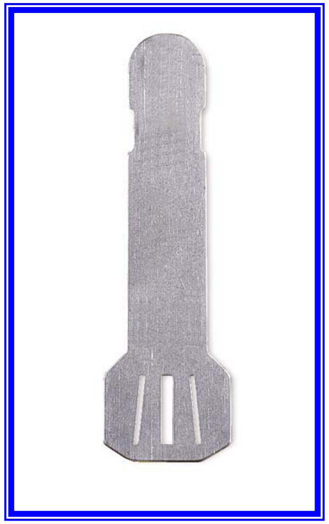
History

- Francis W. Aston
  - *Tandem Electric field – Magnet field*
  - *Resolution ~ 130 (1919)*
  - *Stable Isotopes*
- Arthur J. Dempster (1918)
  - *180° magnetic sector*
- Josef Mattauch / Richard Herzog (1934)
  - *Double focusing mass spectrometer*
- Alfred Nier / Edgar G. Johnson (1953)
  - *Double focusing mass spectrometer with corrected second order aberrations*

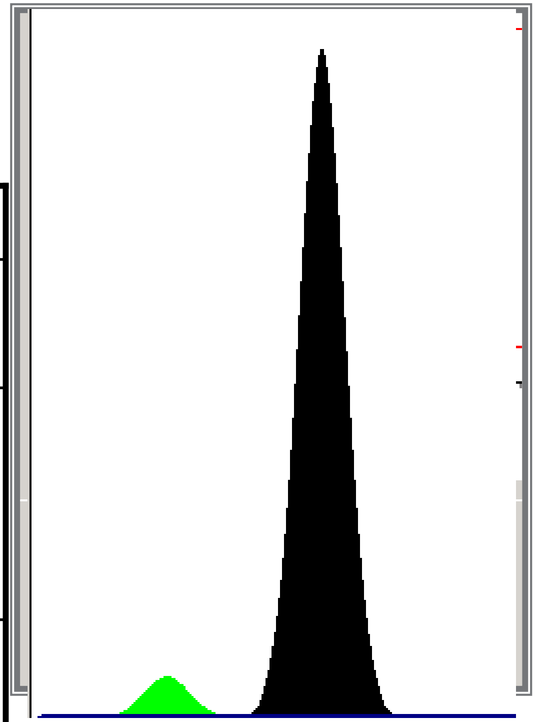
Physical, matrix independent separation of interferences

- Definite relation between analyte and interference

$R = m/\Delta M$

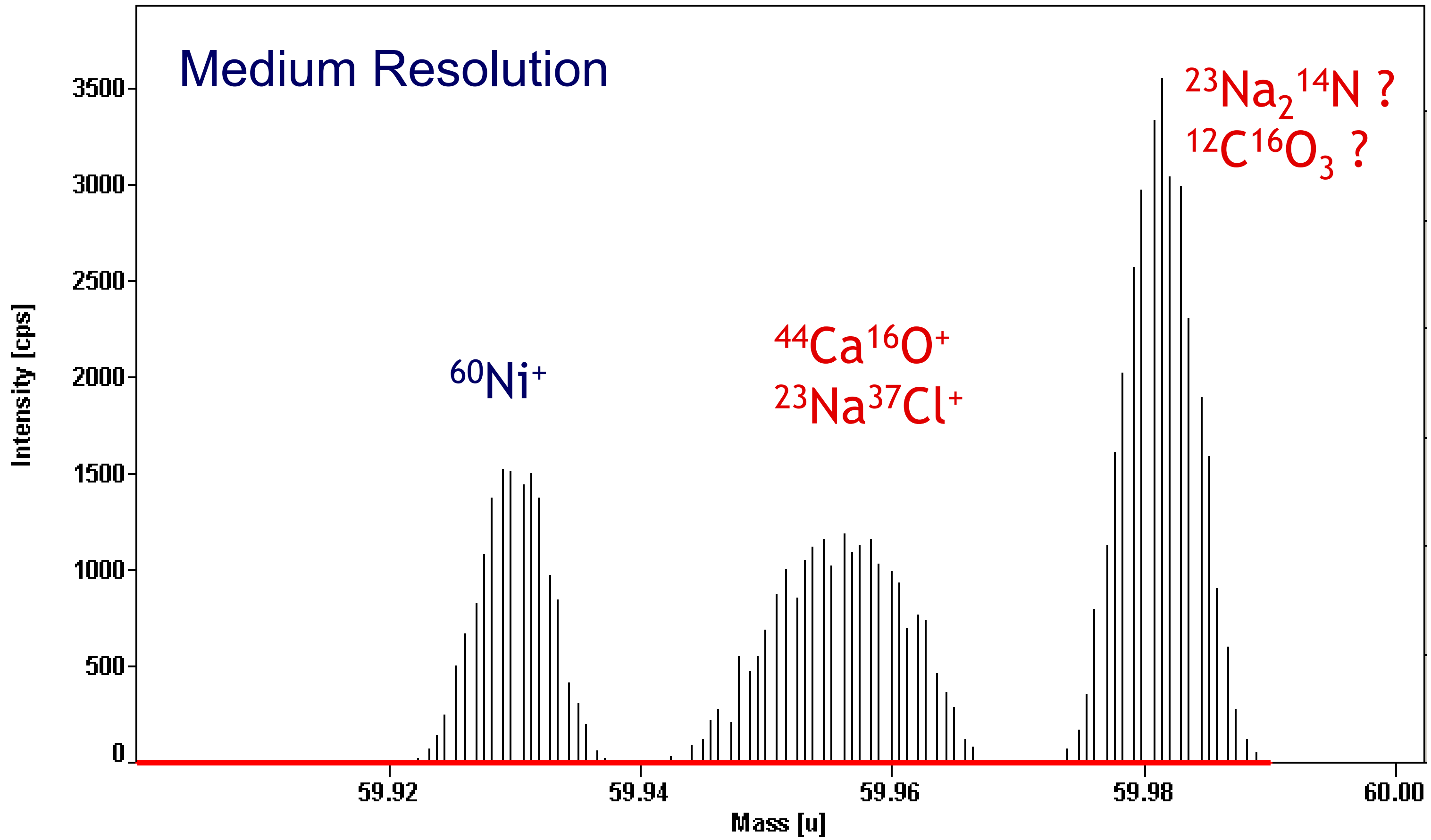


Isotope	Interference	Resolution
^{31}P	$^{15}N^{16}O$ $^{14}N^{16}OH$	1457 967
^{44}Ca	$^{28}Si^{16}O$ $^{12}C^{16}O_2$ $^{14}N_2{}^{16}O$	2687 1281 965
^{56}Fe	$^{40}Ar^{16}O$ $^{40}Ca^{16}O$ $^{28}Si_2$	2503 2480 2957
^{60}Ni	$^{44}Ca^{16}O$ $^{23}Na^{37}Cl$ $^{28}Si^{32}S$ $^{25}Mg^{35}Cl$	3058 2409 3292 3467

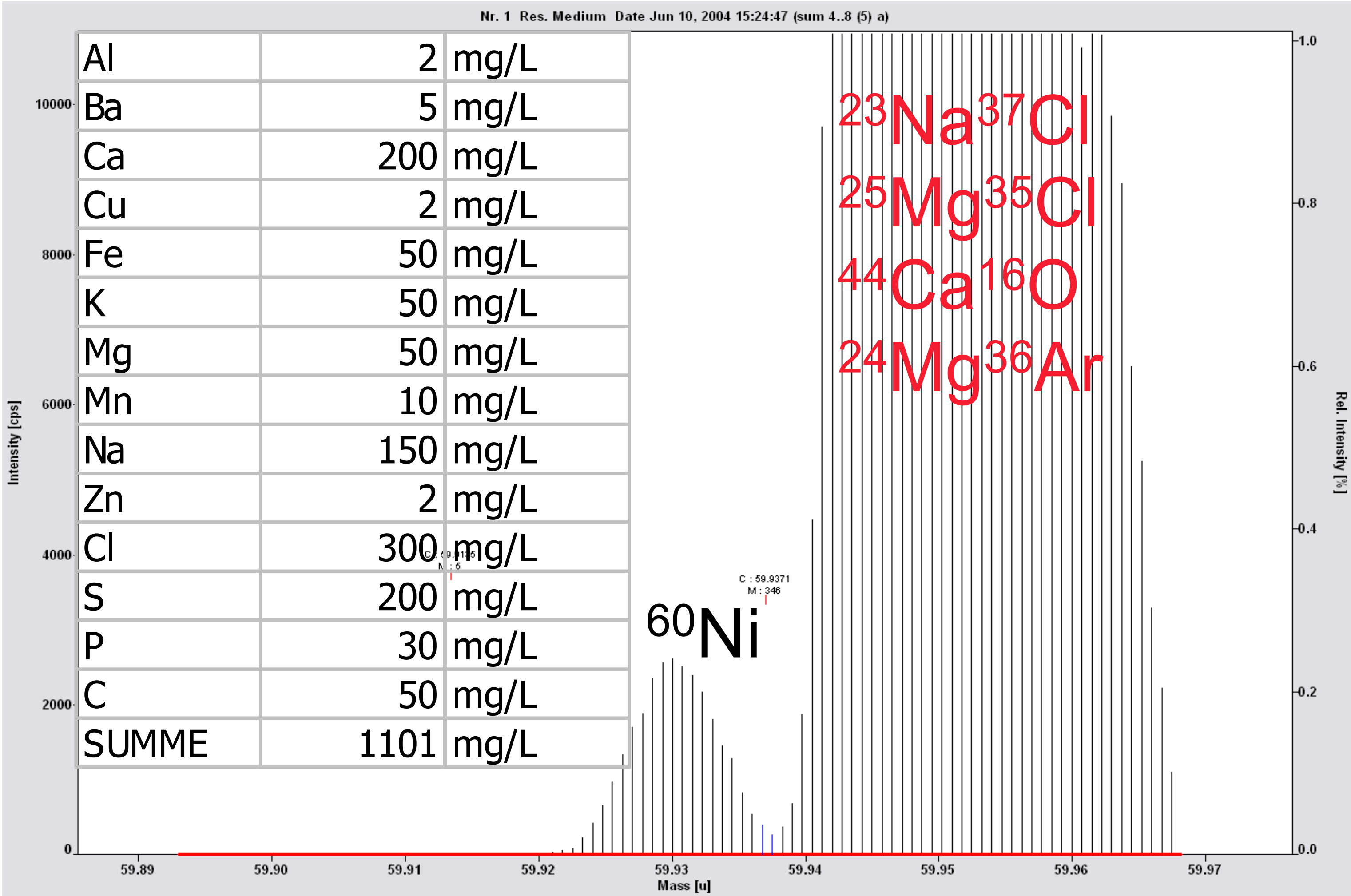


R = > 300
> 4000
> 10000

^{60}Ni in Urine



Key: matrix independent analysis



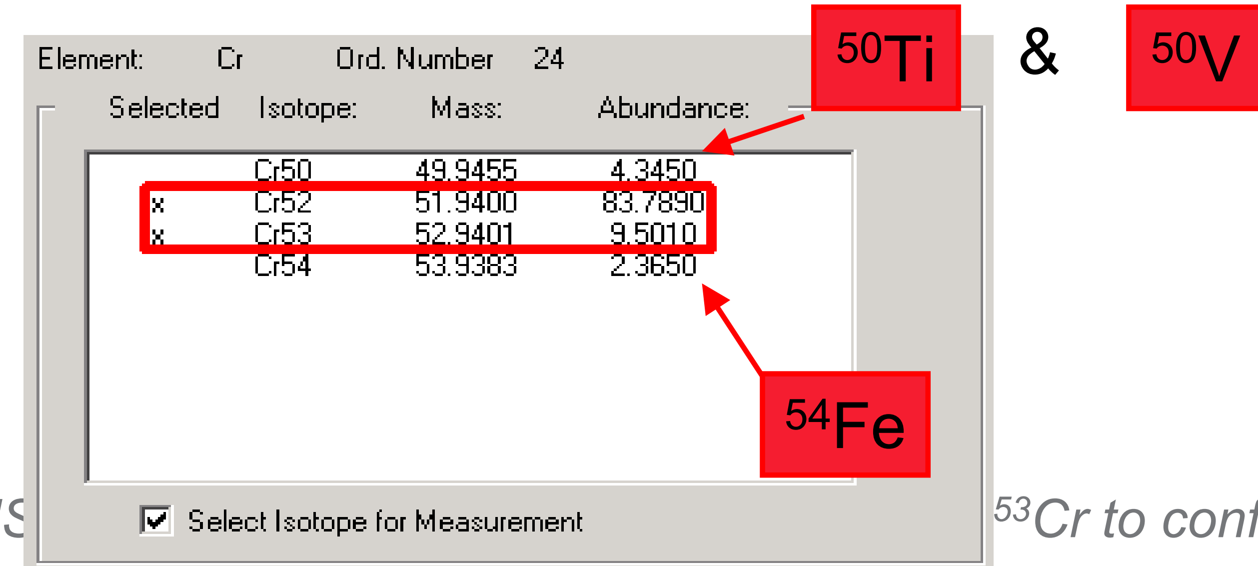
Al	2	mg/L
Ba	5	mg/L
Ca	200	mg/L
Cu	2	mg/L
Fe	50	mg/L
K	50	mg/L
Mg	50	mg/L
Mn	10	mg/L
Na	150	mg/L
Zn	2	mg/L
Cl	300	mg/L
S	200	mg/L
P	30	mg/L
C	50	mg/L
SUMME	1101	mg/L

Why Use High Resolution for ICP-MS ?

Example: analysis of chromium in blood

Chromium has four naturally occurring isotopes

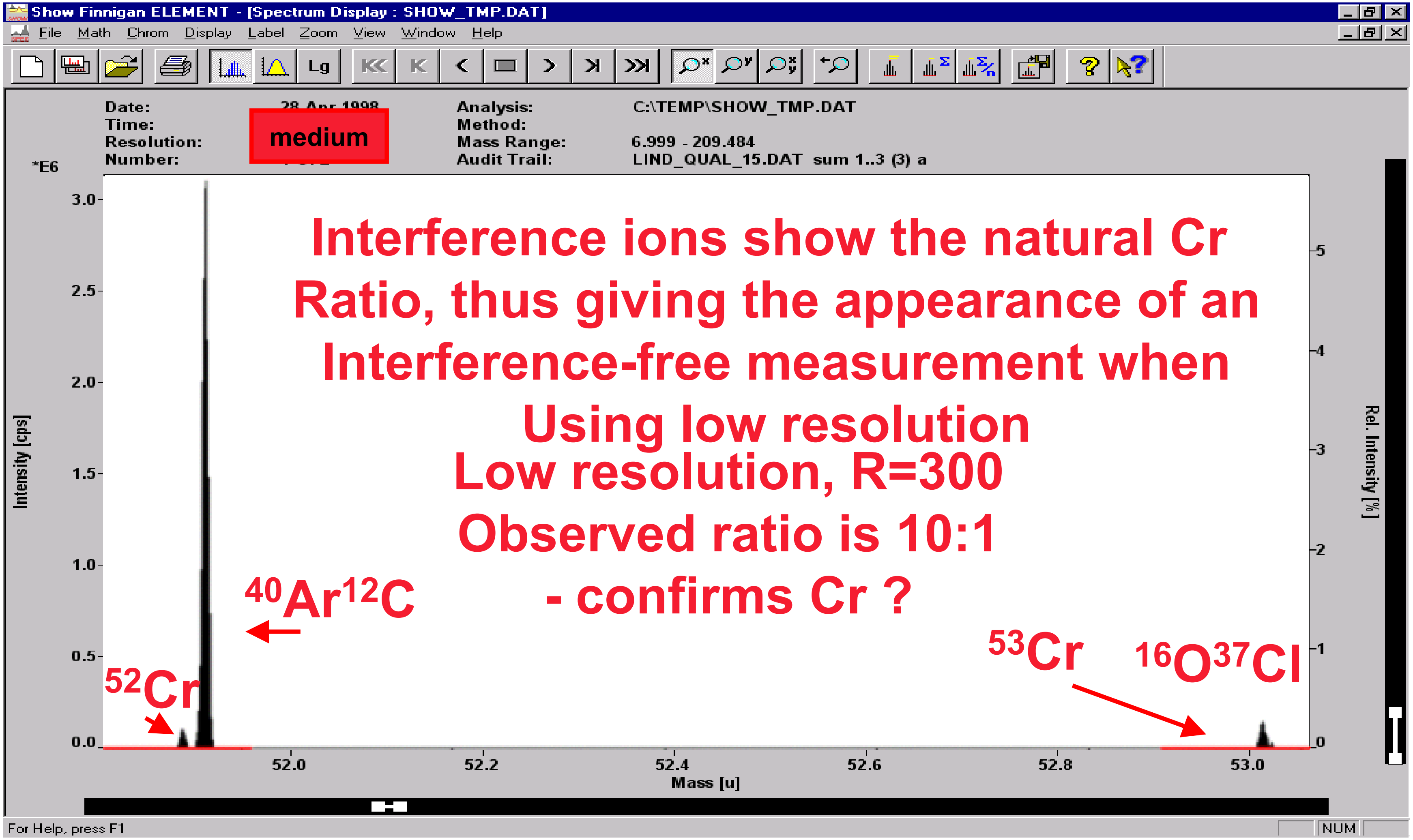
Only ^{52}Cr and ^{53}Cr are available:



Q-ICP-MS ... ^{53}Cr to confirm presence of Cr in sample

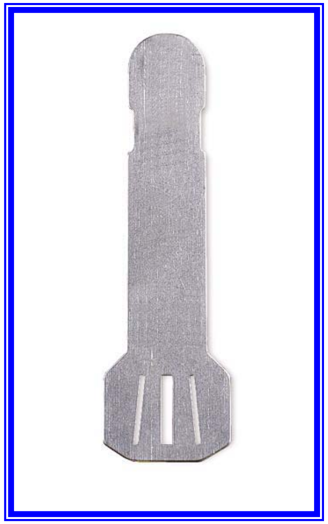
Chromium in Blood

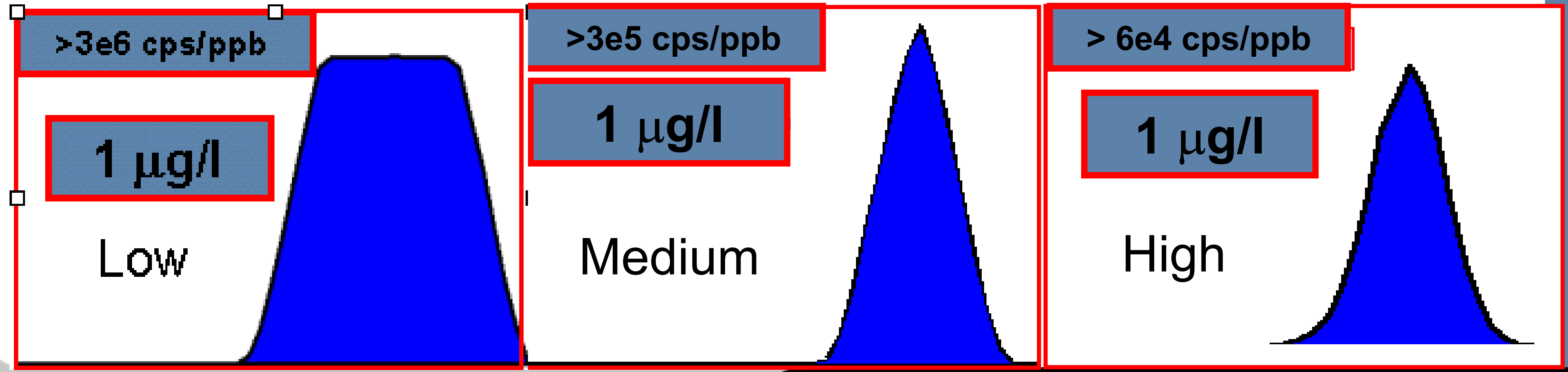
Serum/Urine/Seawater/Soil/Plants…..



Resolution vs. Sensitivity

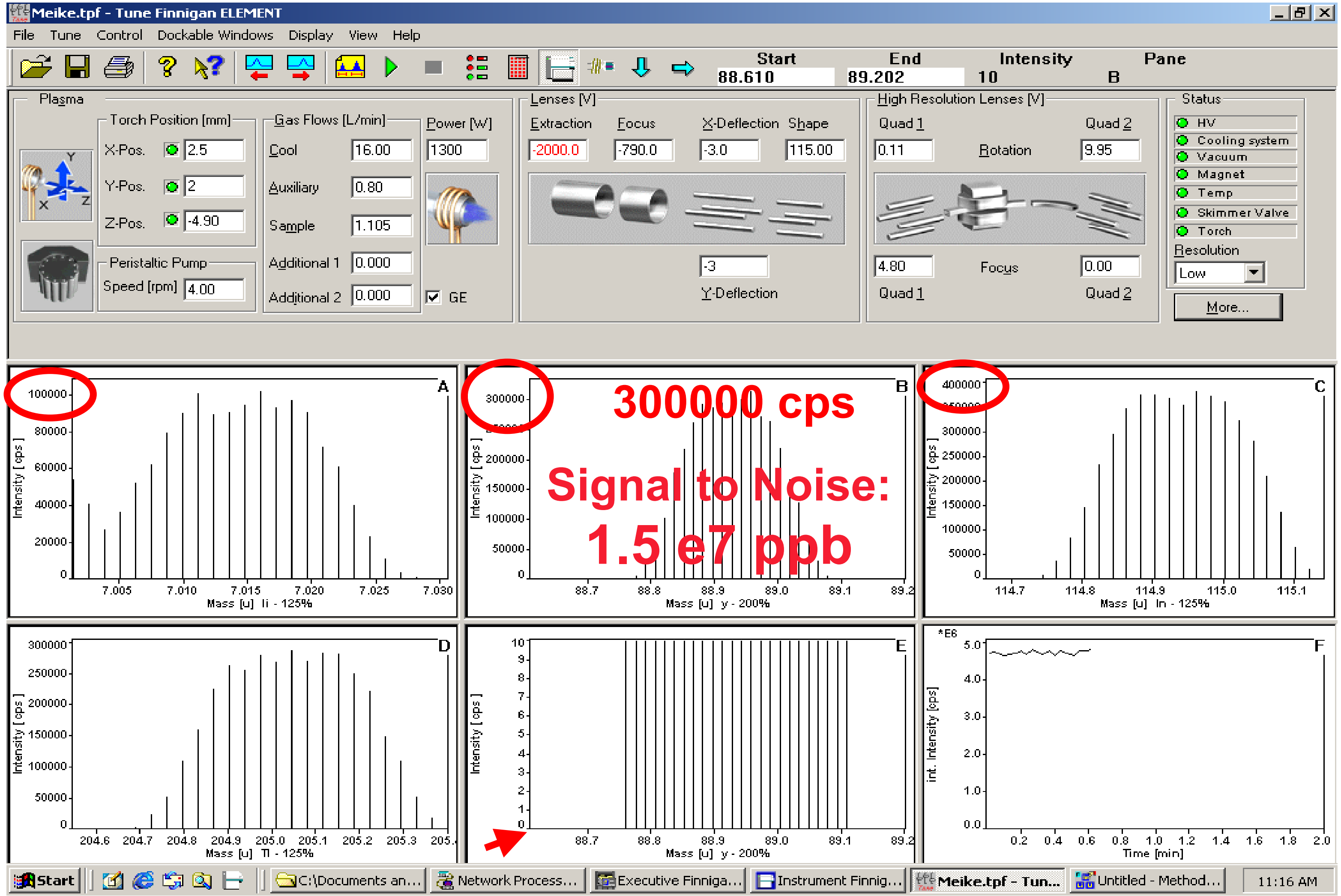
- The change in mass resolution is achieved by changing the width of the entrance and exit slits of the mass spectrometer:
    - The wider the slit the higher the sensitivity
    - Fixed ratio between resolutions ⇒ independent of mass and matrix





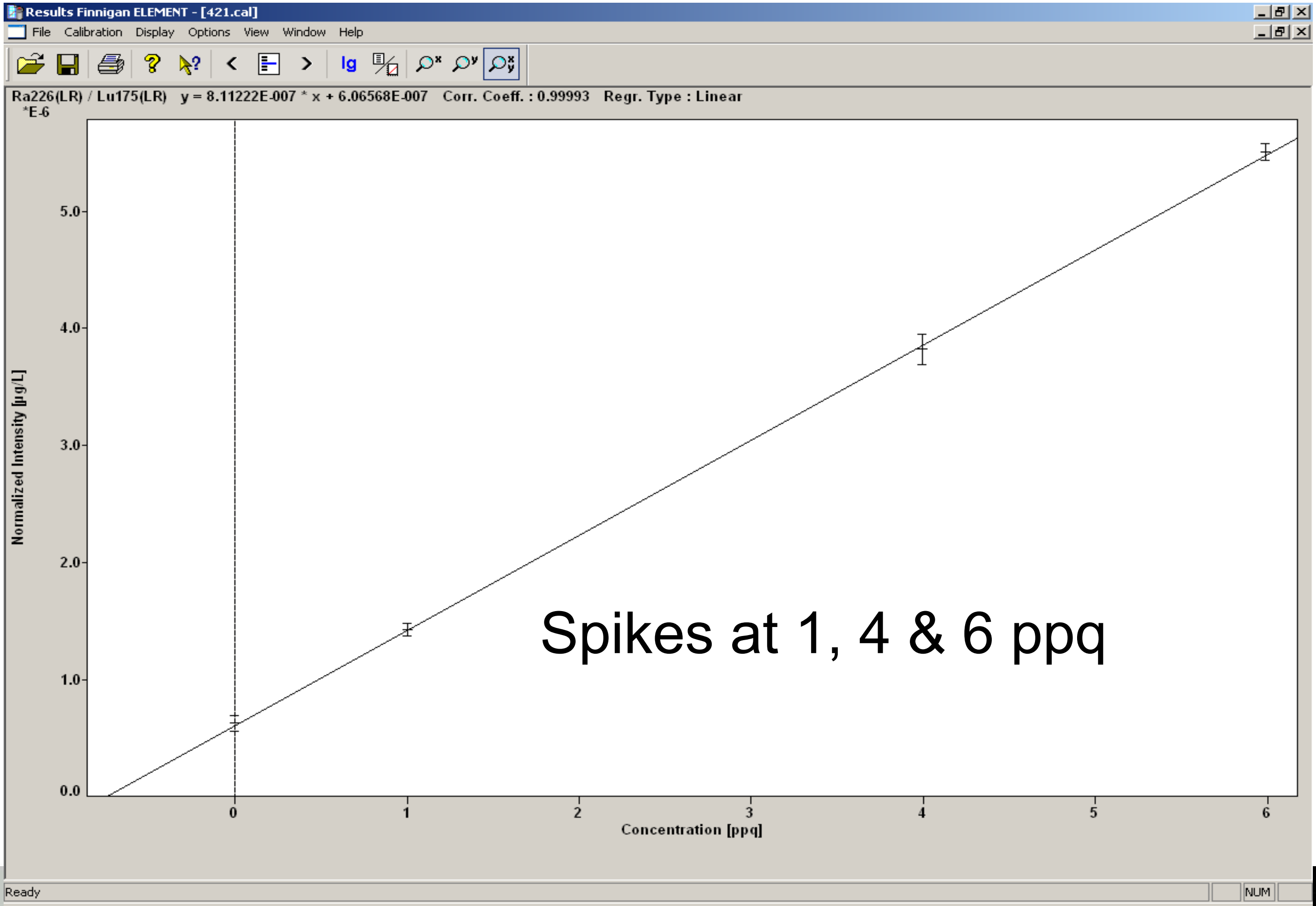
Signal to Noise Ratio Sector Field ICP-MS

100 ng/L Li, Y, In, Tl (<0.2 cps in all resolutions)

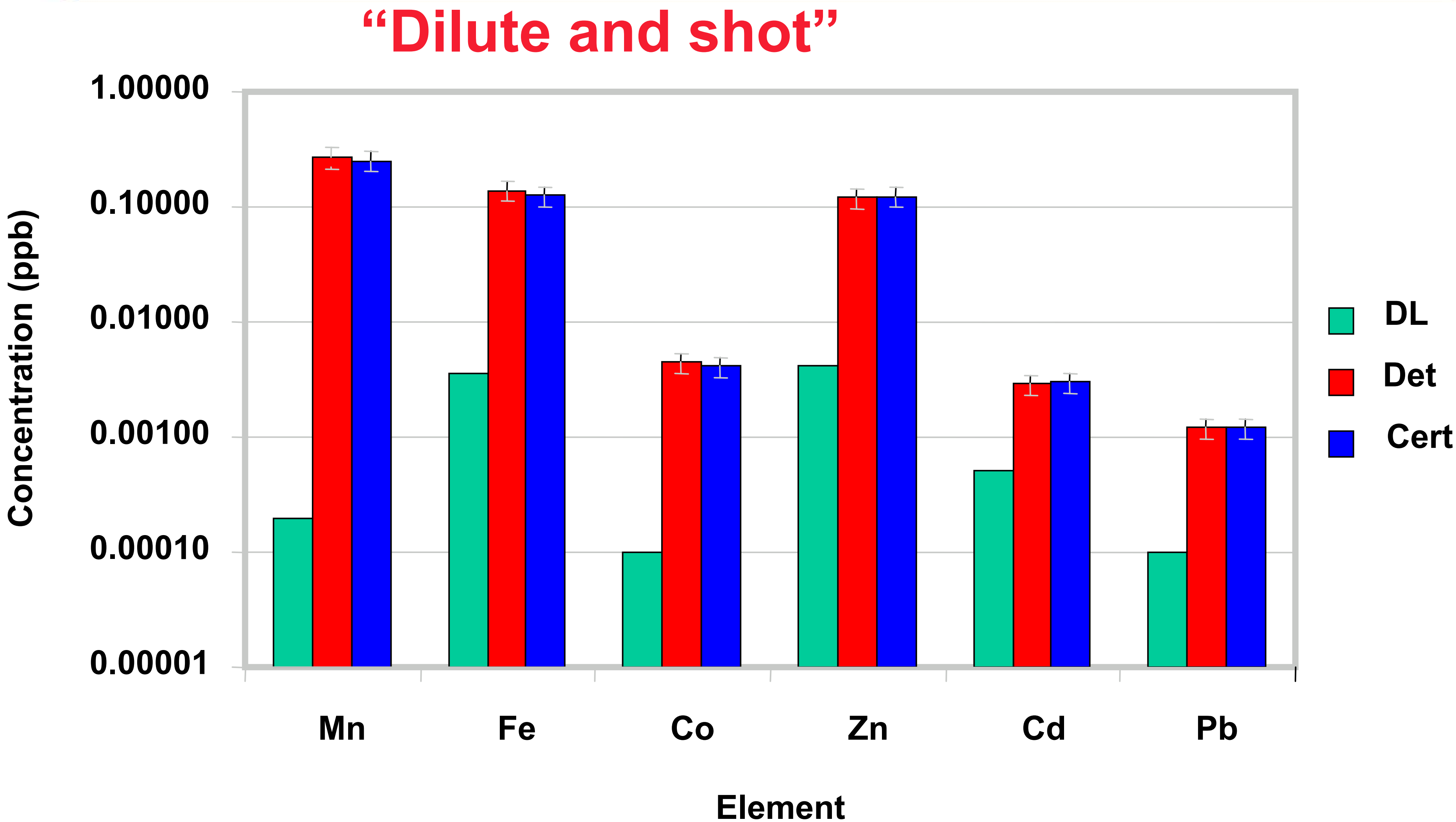


Calibration Curve

– **IAEA 421 (water), dilution 1+1, Ra-226, Standard Addition**

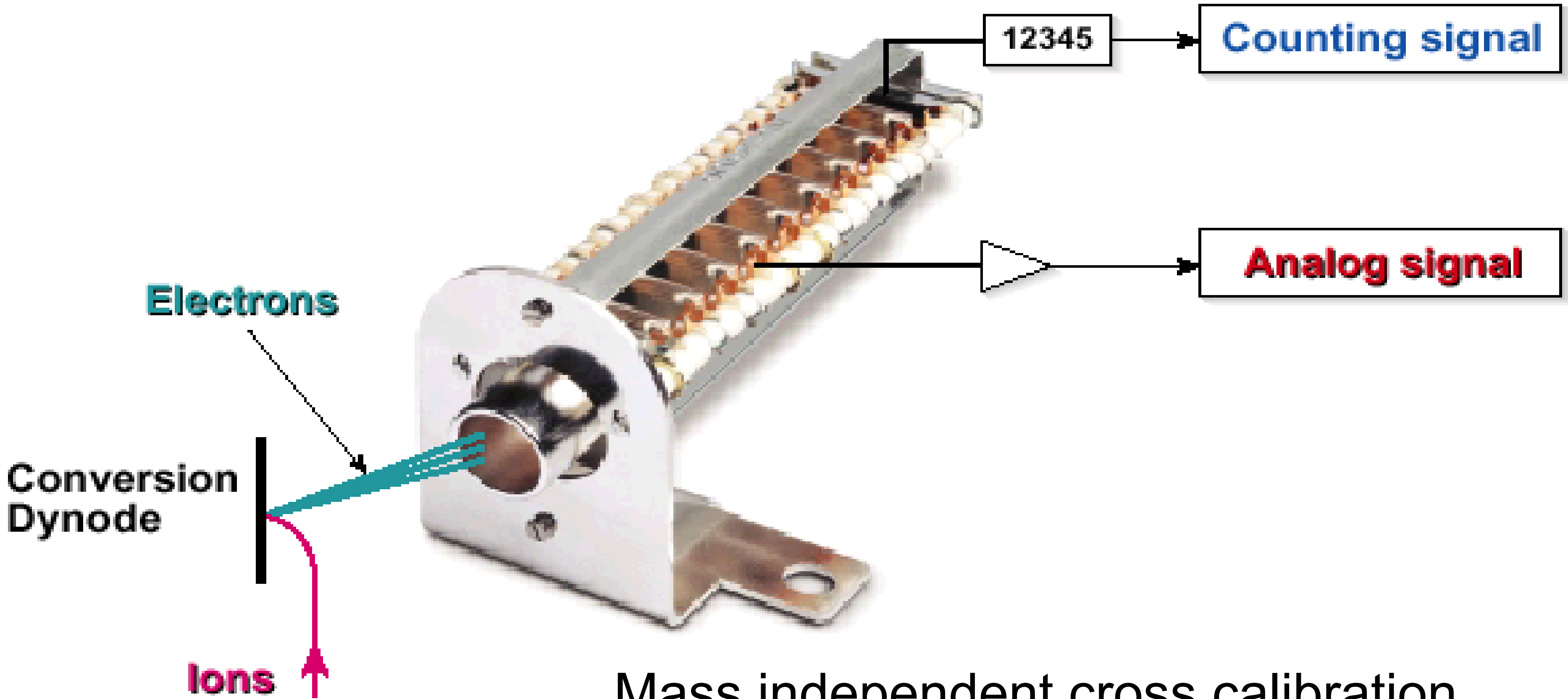


Accuracy and precision CASS3 (0.3% saltmatrix)



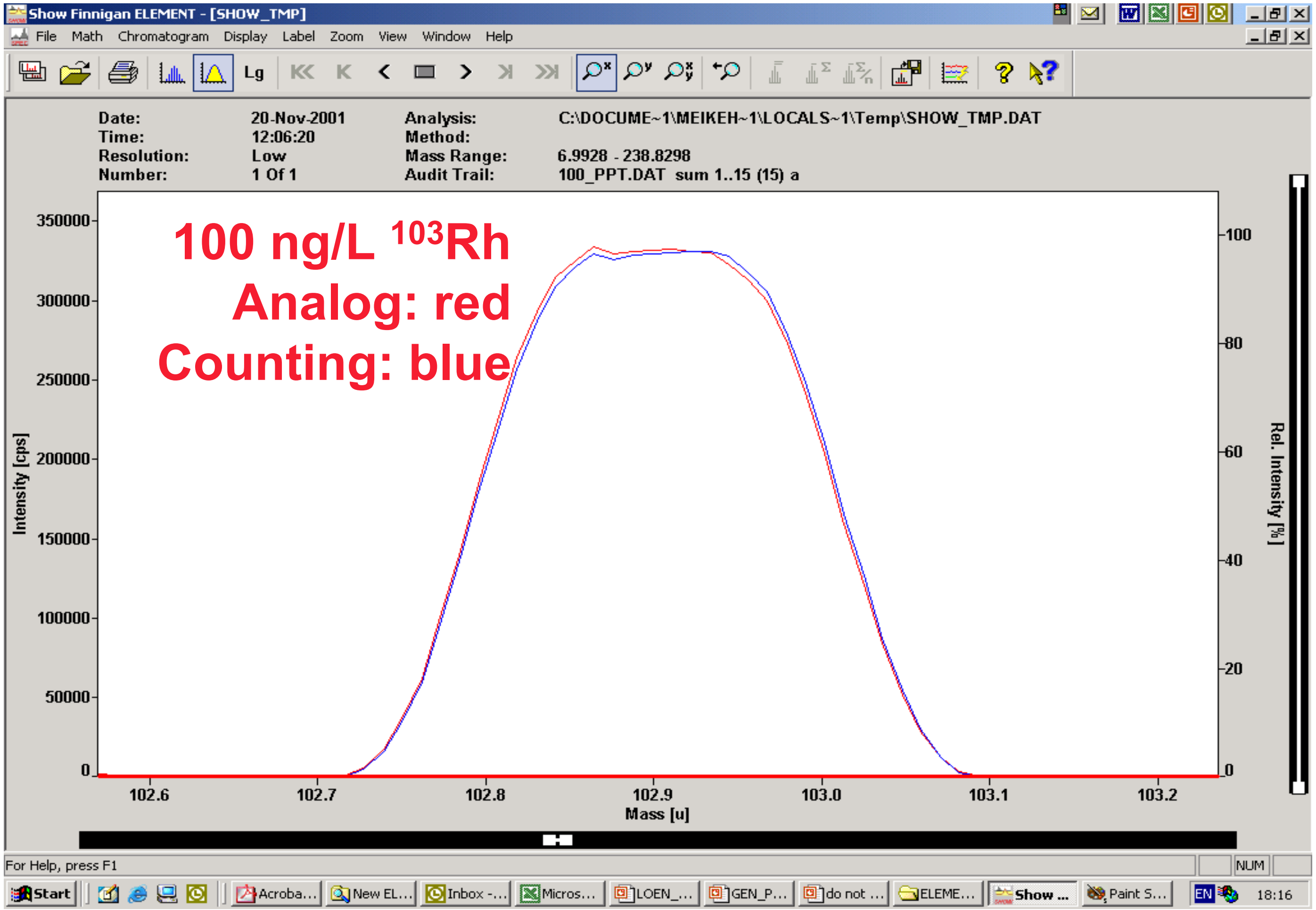
Paul Field, Rutgers University

Dual Mode Detection System



Mass independent cross calibration
= no cross calibration

Dual Mode Detection System



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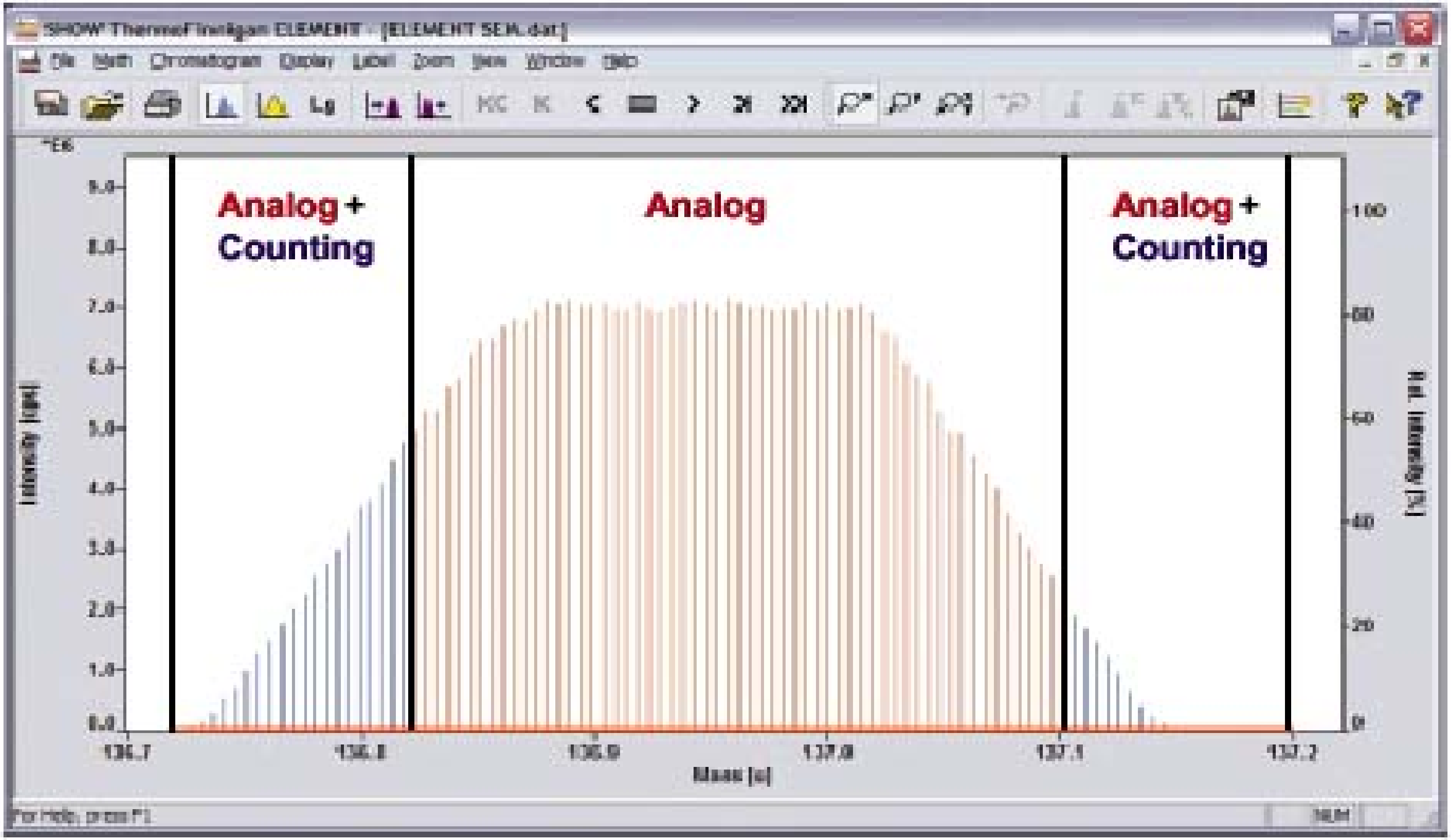
Finnigan ELEMENT 2 Dual Mode Detection System

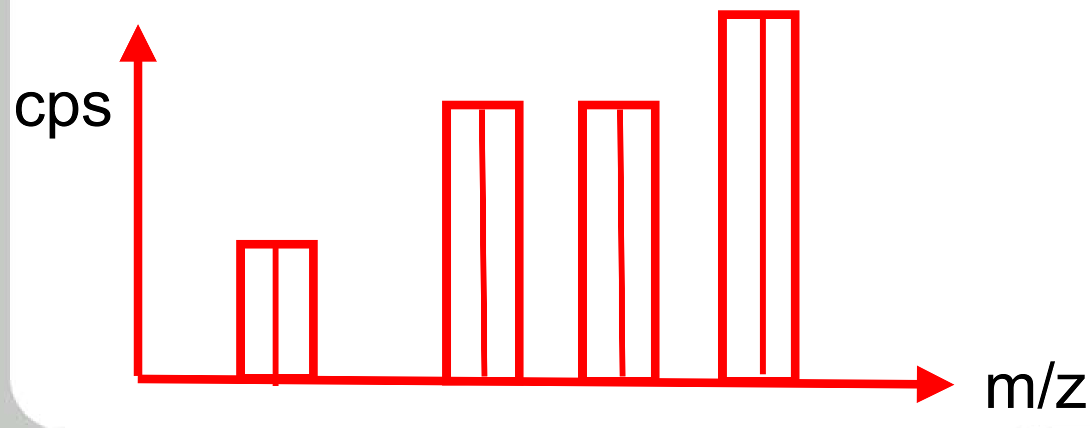


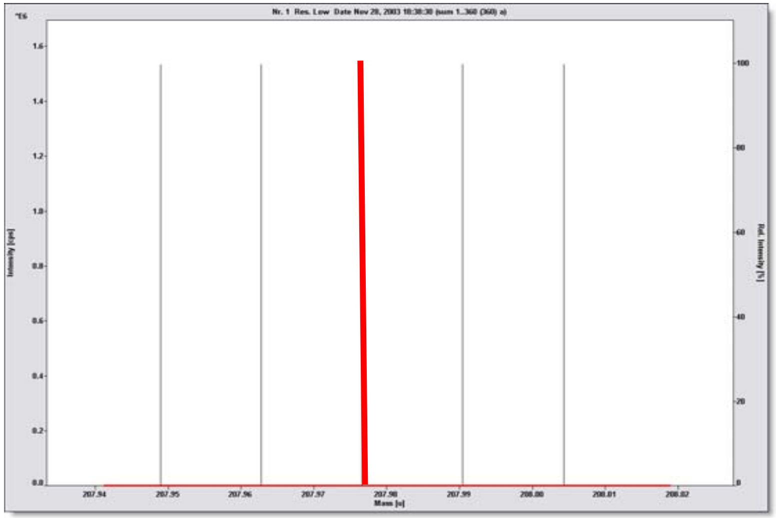
Peak Top Hopping in Both Mode

- Transient signals
  - Laser ablation
  - Chromatography coupling

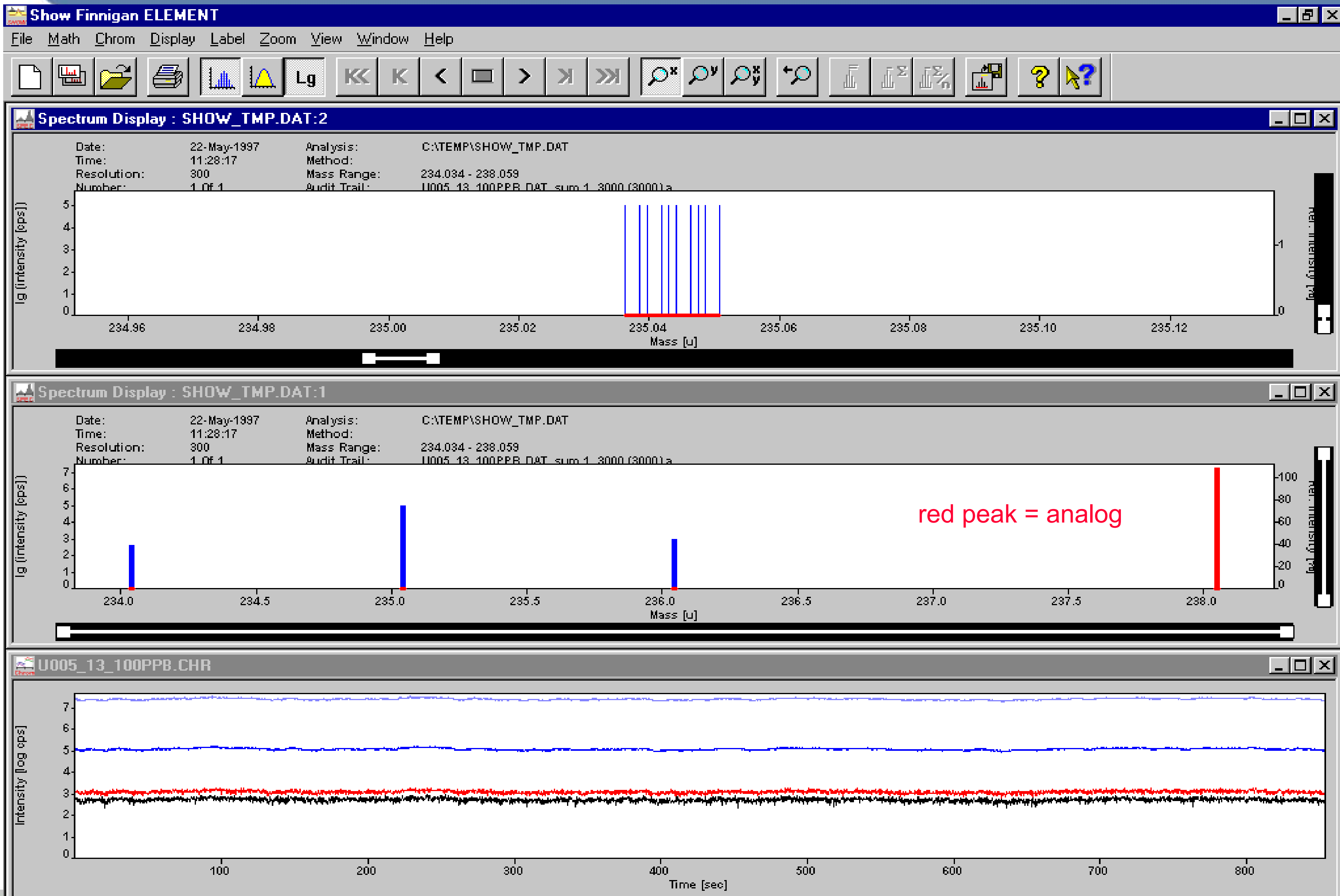
- Isotope ratio analysis

One channel per isotope





Determination of large isotope ratios



Peak Shape

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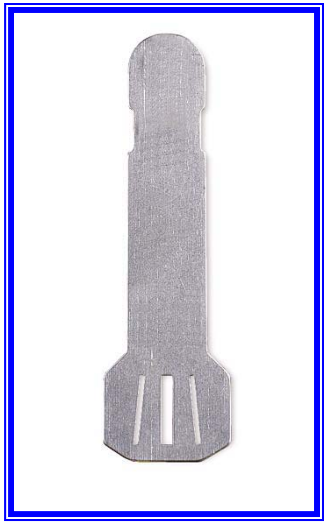
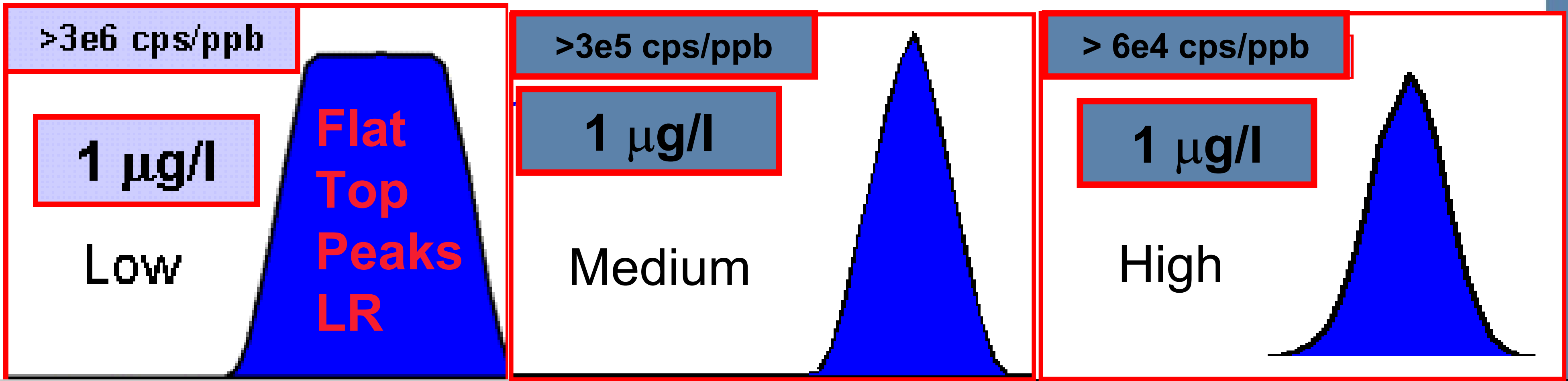
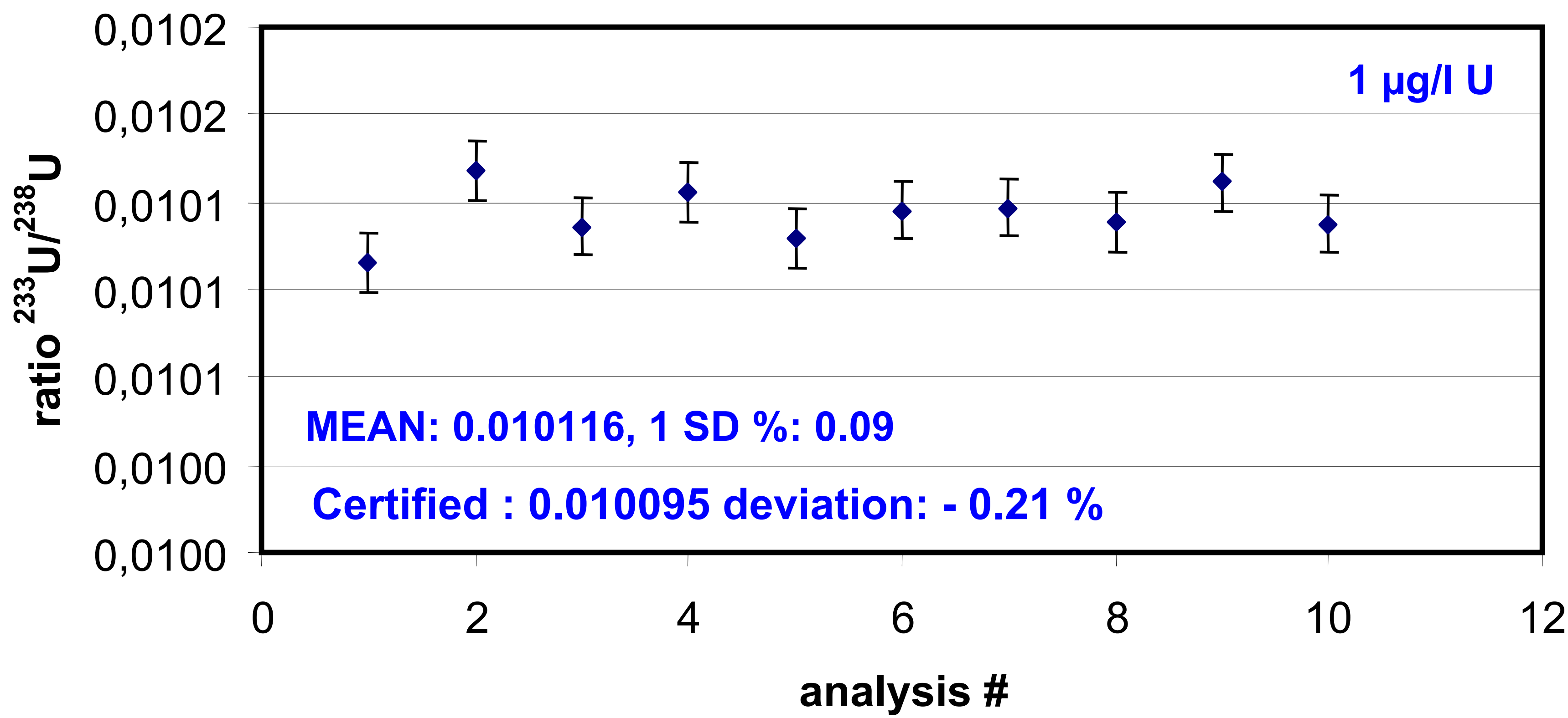




Isotope Ratio Analysis
$^{233}U/^{238}U$ Ratio IRMM 072/8

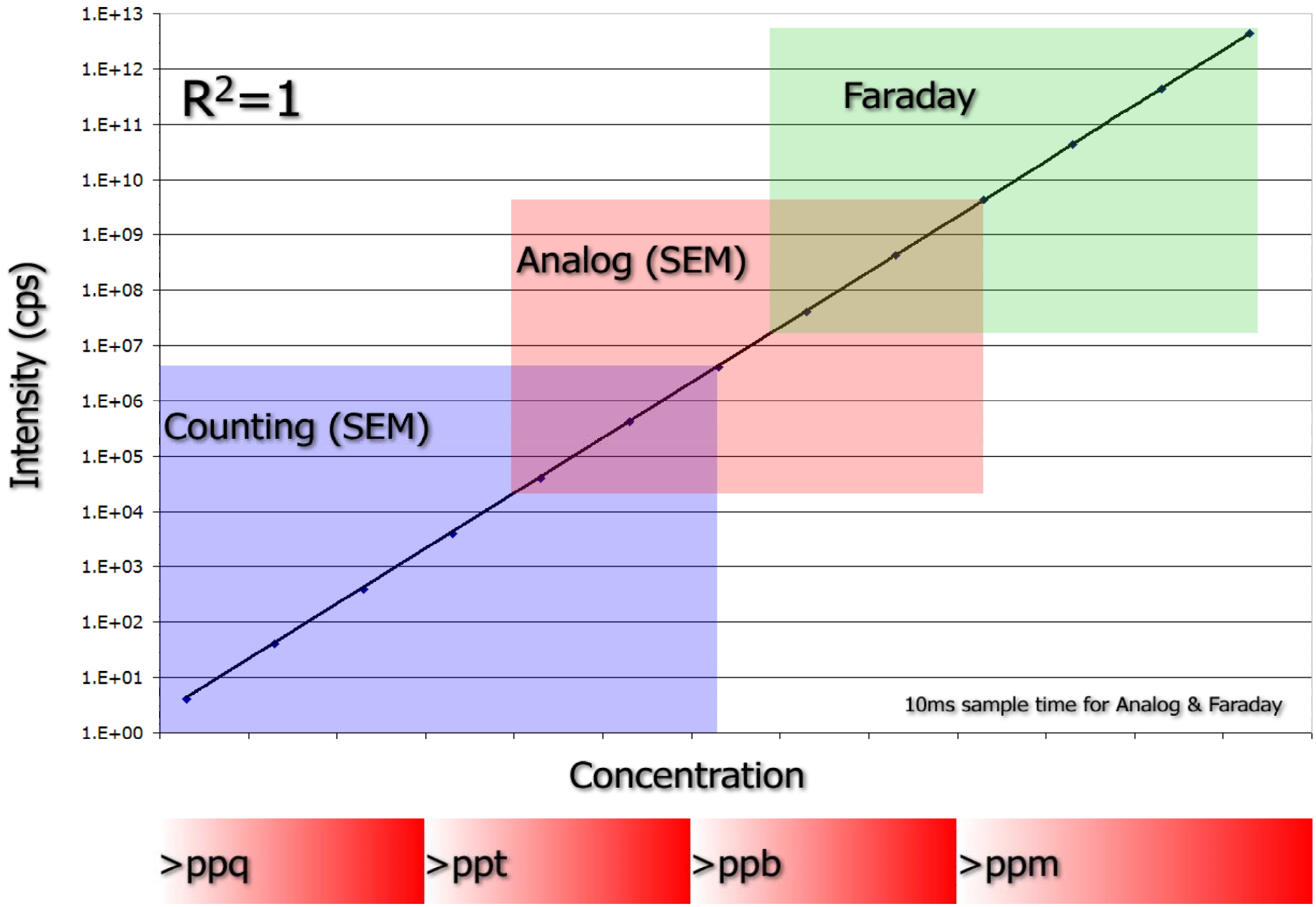


Finnigan ELEMENT2: NIST 981 Isotope Ratio Analyses

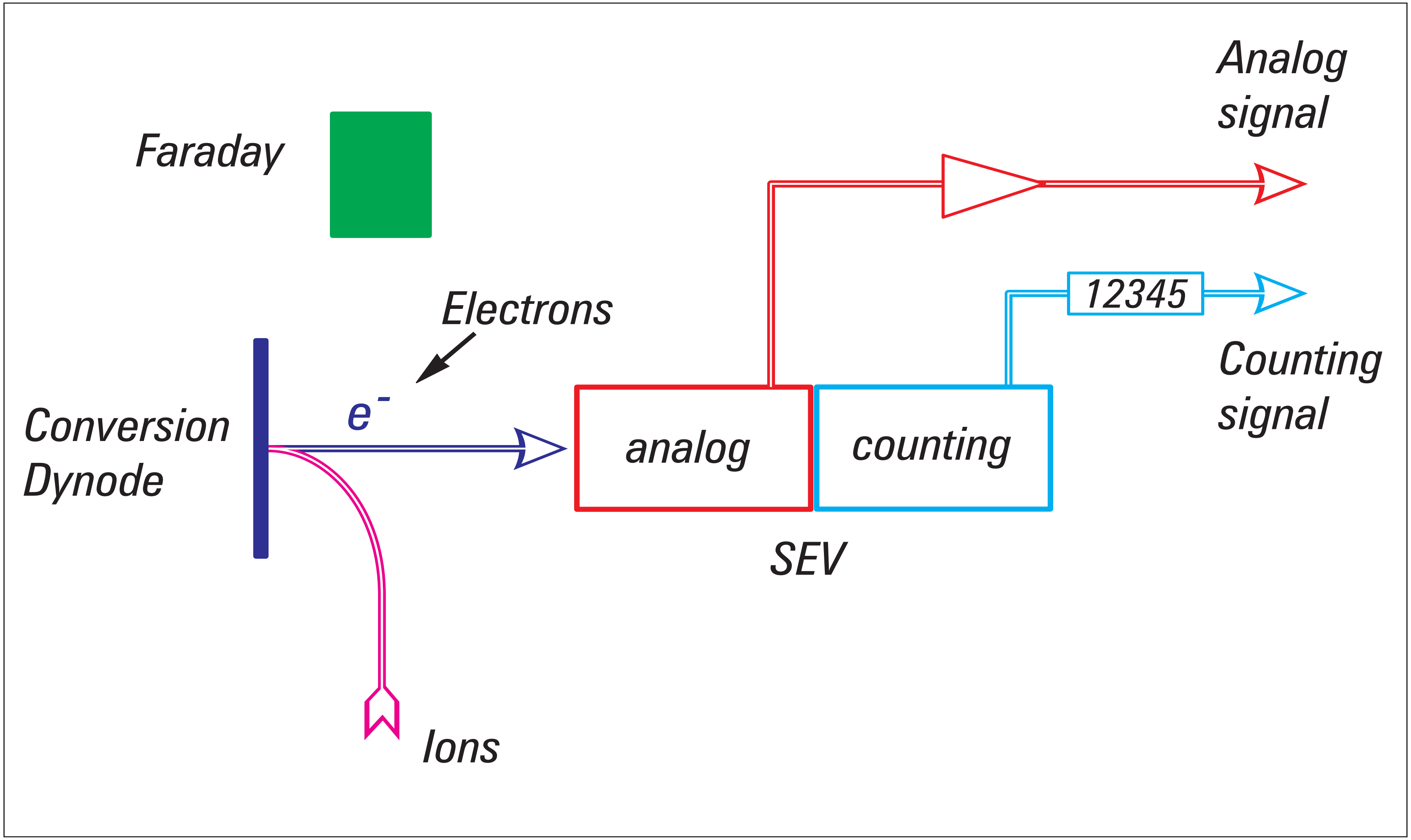
- NIST981 (Natural Pb)
  - *1ppb Pb (1.6*10e^6 cps)*
  - *3 Measurements (each consisting of 10*1min analyses)*
  - *All Pb ratios measured*
    - ^{204}Hg on ^{204}Pb corrected for on-line
    - No outlier rejection
    - No correction for mass bias

	Pb206/Pb204	Pb207/Pb204	Pb207/Pb206	Pb208/Pb206	Pb208/Pb204
Run 1	16.953611	15.541761	0.916724	2.163897	36.685854
Run 2	16.952012	15.539417	0.916673	2.164276	36.688759
Run 3	16.948784	15.539274	0.916837	2.163845	36.674535
Average	16.951469	15.540150	0.916745	2.164006	36.683049
%RSD	0.015	0.009	0.009	0.011	0.020
Reference NIST	16.937096	15.491345	0.914640	2.168100	36.721317
Accuracy %	-0.08	-0.32	-0.23	0.19	0.10

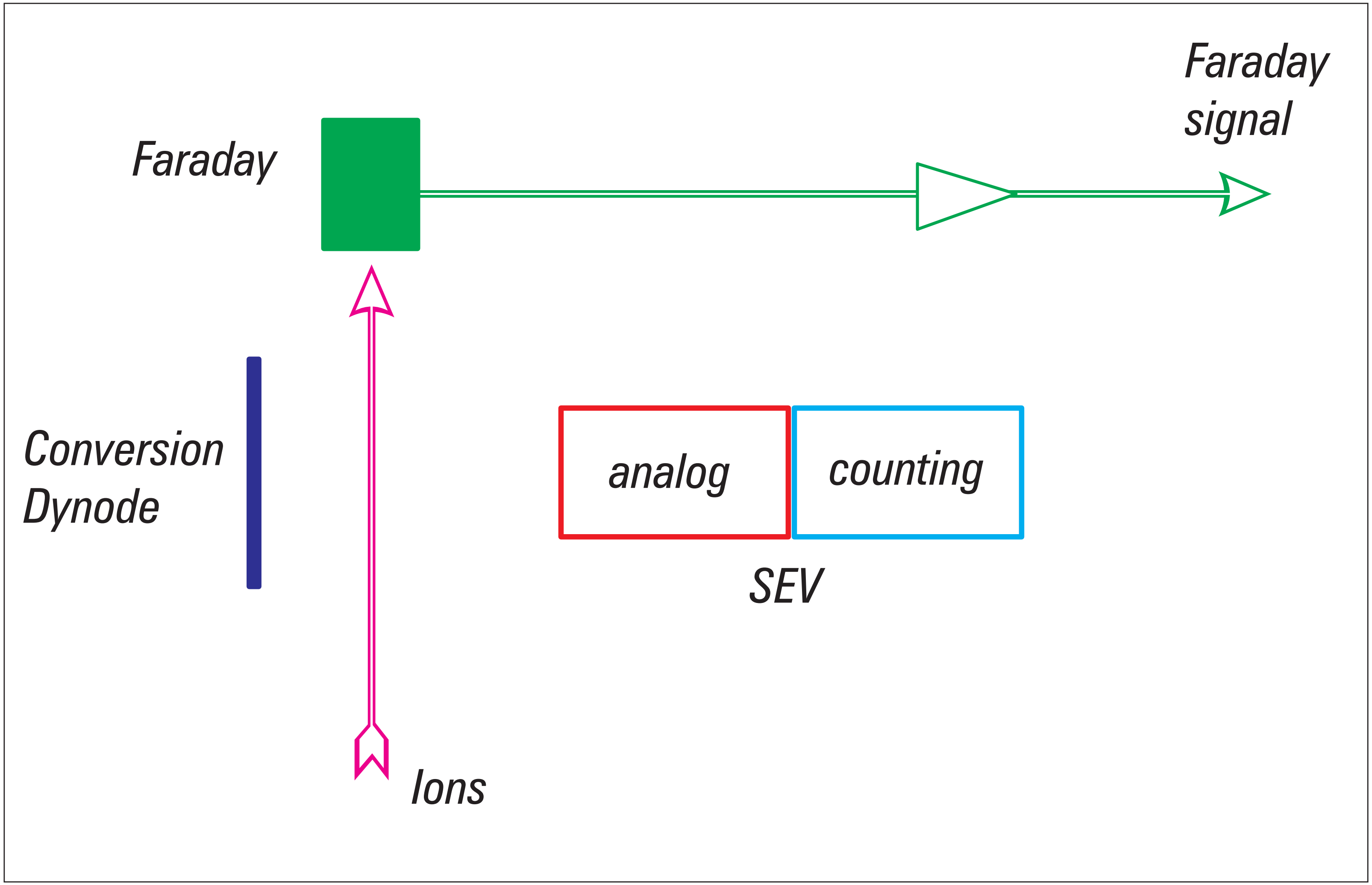
Extended Dynamic Range in the Finnigan ELEMENT XR



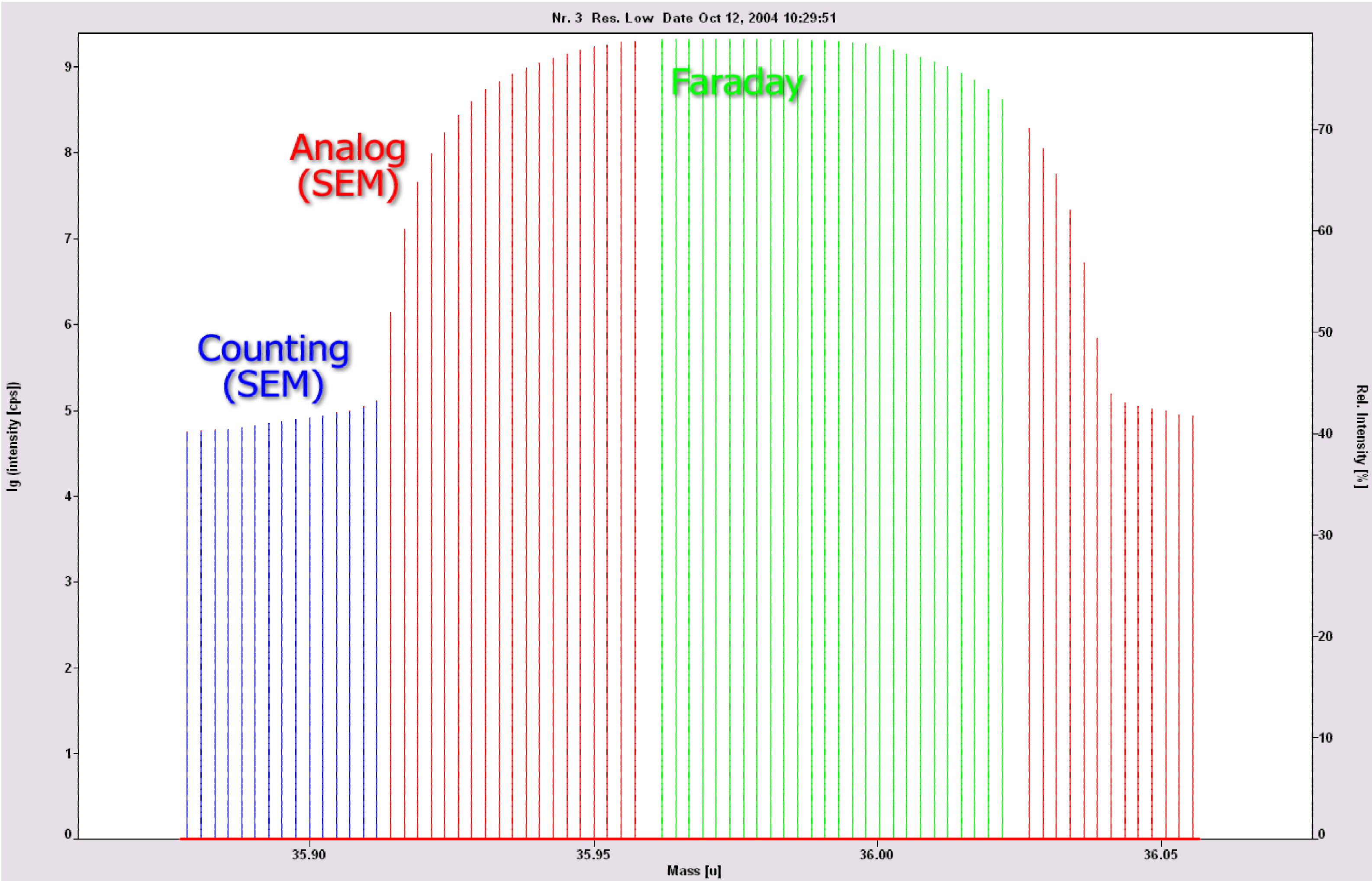
Finnigan ELEMENT XR Detection System



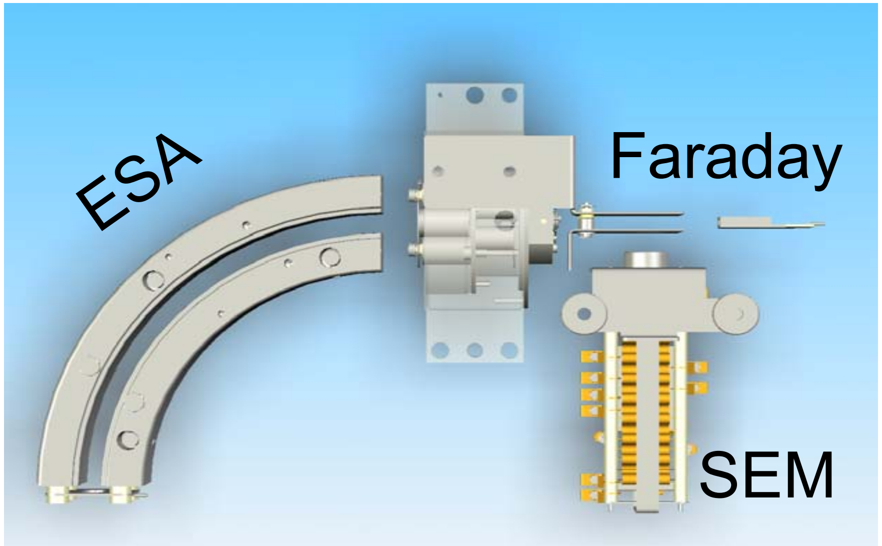
Automatic switch to Faraday Detector



‘Triple’ Detector Mode: ^{36}Ar (LR, log scale)



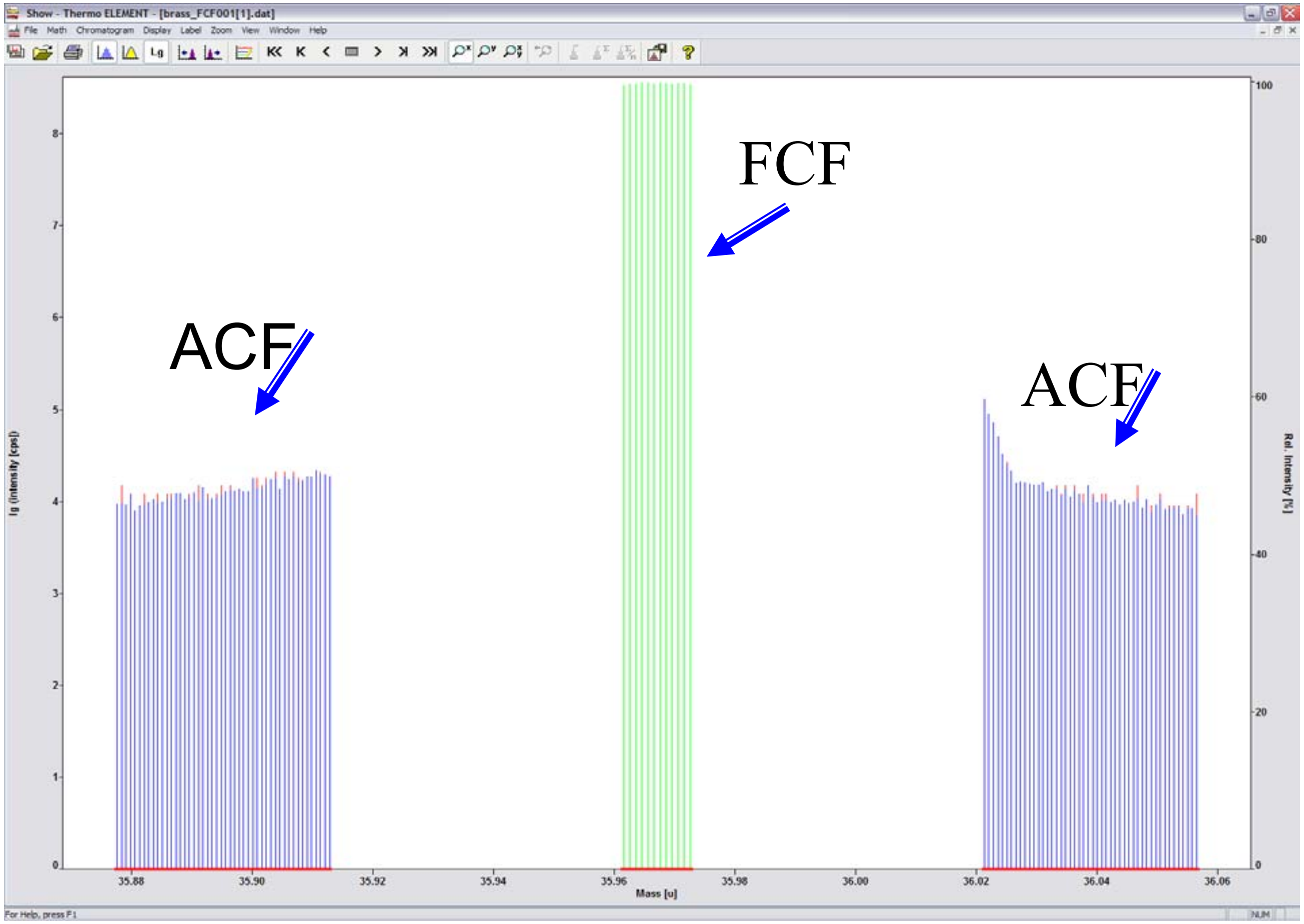
Finnigan ELEMENT XR : Triple Mode Detection system



Matrix and ultra-traces in one analysis

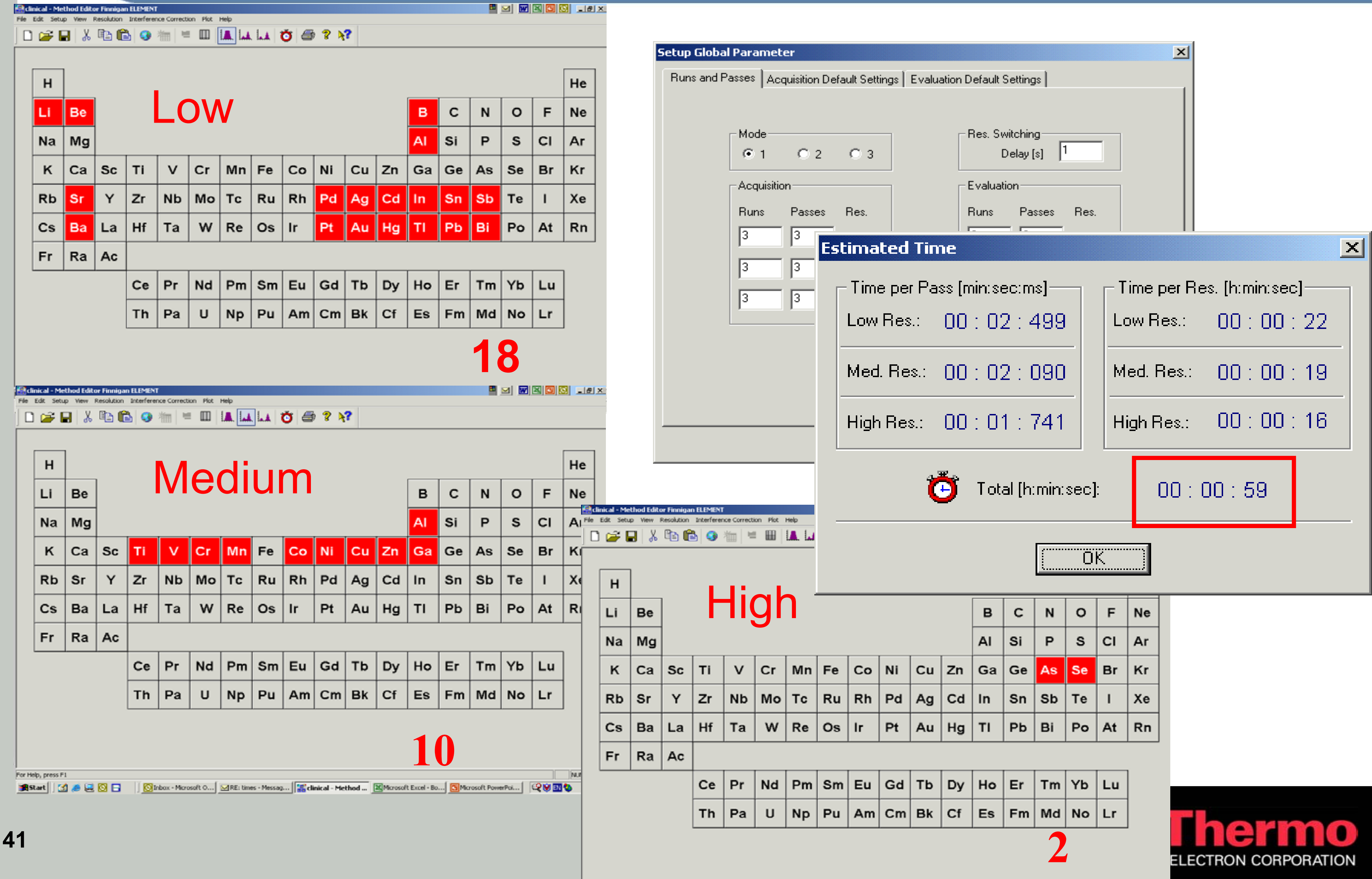
- 0.2 cps to 1×10^{12} cps
  - complete analysis from 0.1 ppt to 0.1% in LR (solution)
- Minimum integration time:
  - counting: 0.1 ms
  - analog: 1 ms
  - Faraday: 1 ms
- *No decay time with Faraday detection system*
  - Due to integration circuit
- Automatic switching between detection modes
  - *no preset*
  - *< 1 ms to Faraday detection*
- Automatic cross calibration

Finnigan ELEMENT XR Cross Calibration



- Mass independent cross calibration
  - *e.g. Argon*
- Fast
  - *3 s for ACF and FCF determination*
- Reliable
  - *automatic*
  - *user independent*

Finnigan ELEMENT2 Analysis Time



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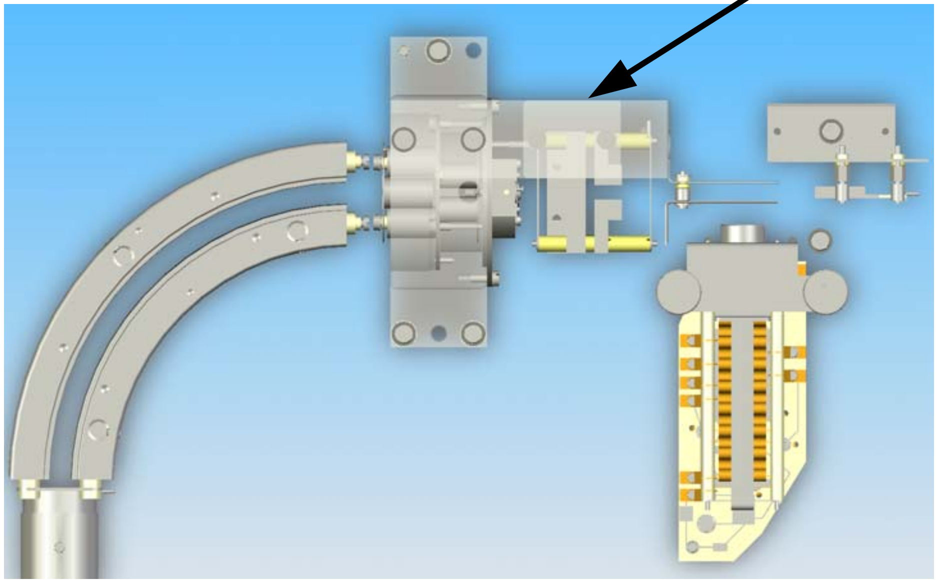
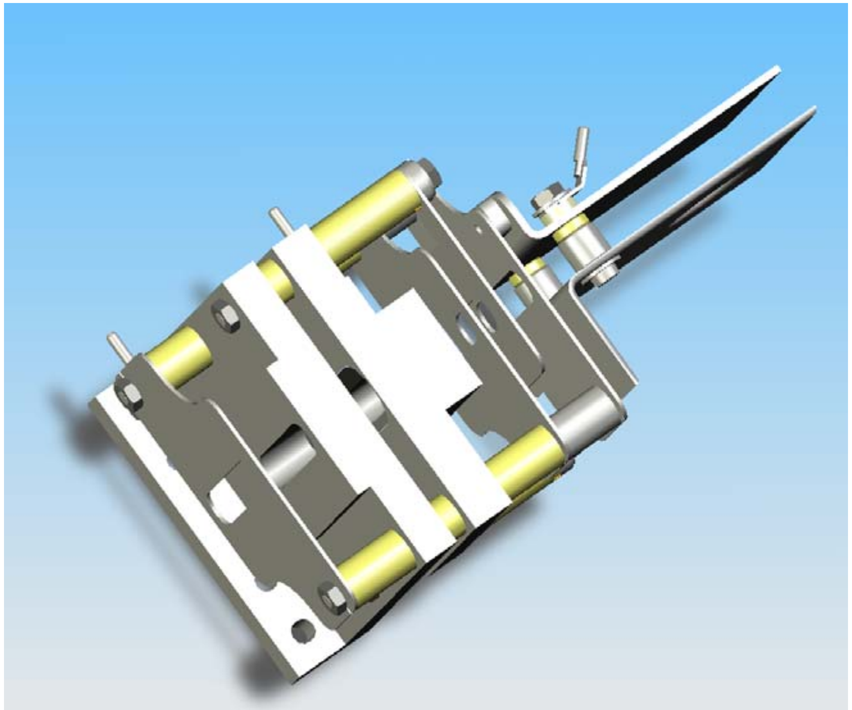
Element XR Detection System – Filter Lens

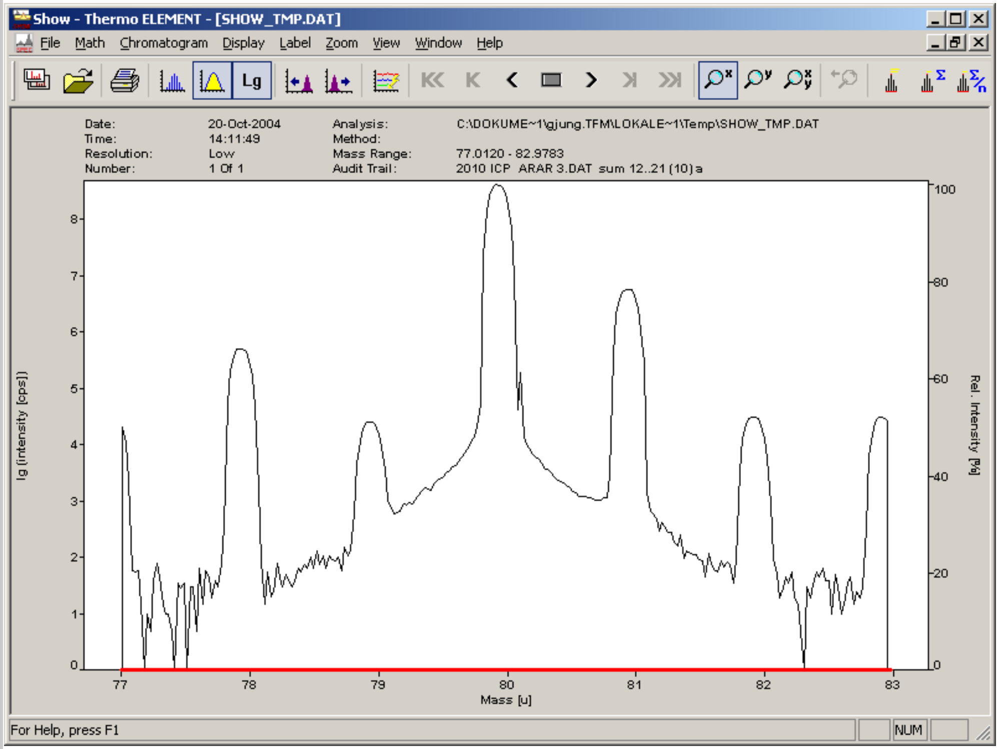
Filter Lens



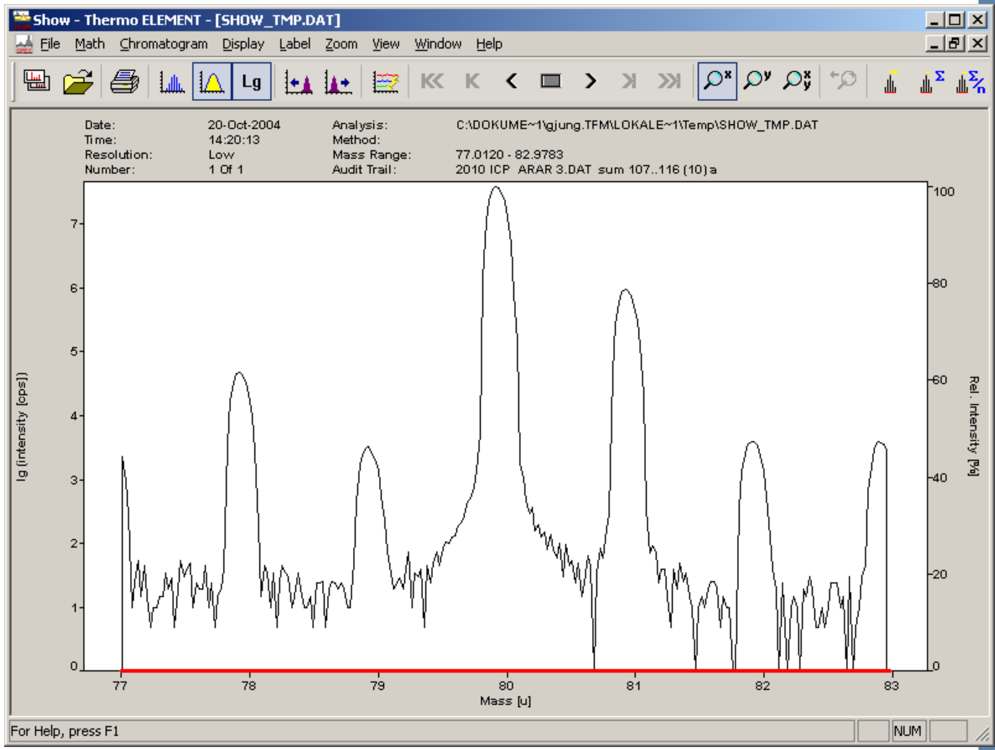


Filter Lens: ICP at $^{40}Ar^{40}Ar$

-20 V



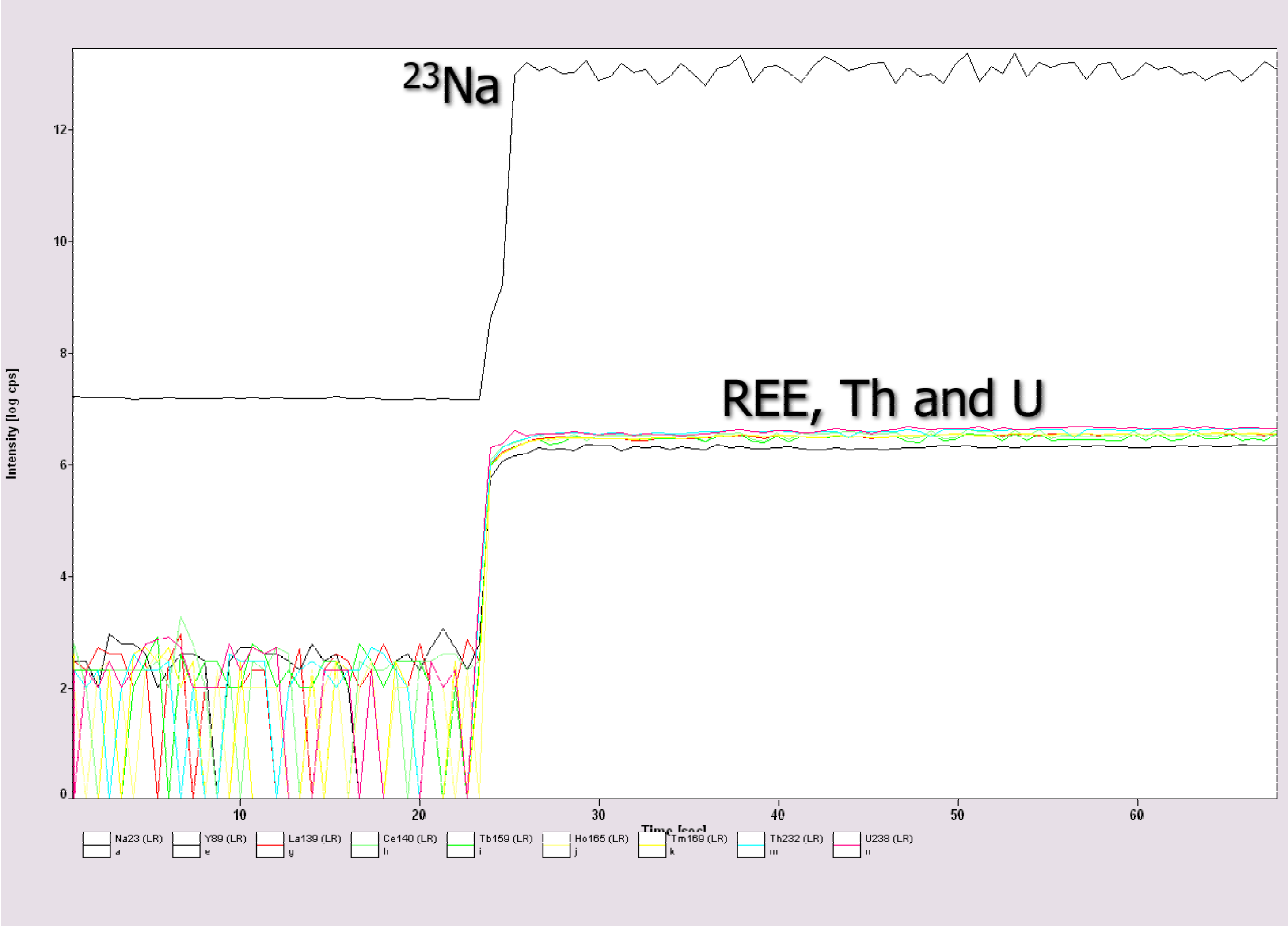
7 V



Applications of ELEMENT XR

- Geological:
  - *Determination of majors, traces and ultra-traces in survey analyses, replacing complimentary analysis techniques (e.g. AAS or ICP-AES).*
  - *Use of the matrix element as internal standard in laser ablation analysis:*
    - Na in fluid inclusions.
    - Al in melt inclusions.
    - Ca in bone / corals / otoliths etc.
    - C in diamond analyses
    - Large isotope ratios
  - *Concentration determination in minerals by laser ablation.*
  - *Elemental ratios by laser ablation (e.g. Ca / Sr etc).*

Finnigan ELEMENT XR with Laser Ablation



Summary

- Finnigan ELEMENT XR
  - *All of the advantages of the ELEMENT2:*
    - High sensitivity
    - High resolution for reliable interference removal
    - Dark noise independent of resolution
    - Fast scanning
  - *Faraday Detector*
    - Increased linear dynamic range ($>10^{12}$)
    - No decay time
    - 1 ms integration time
    - Automatic switching
    - Automatic cross calibration