

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS)

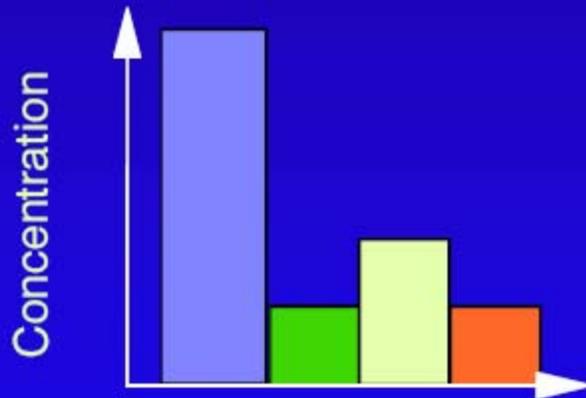
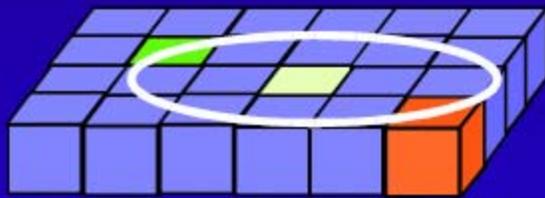
M. Tiepolo

C.N.R.-Istituto di Geoscienze e Georisorse – Sezione di Pavia

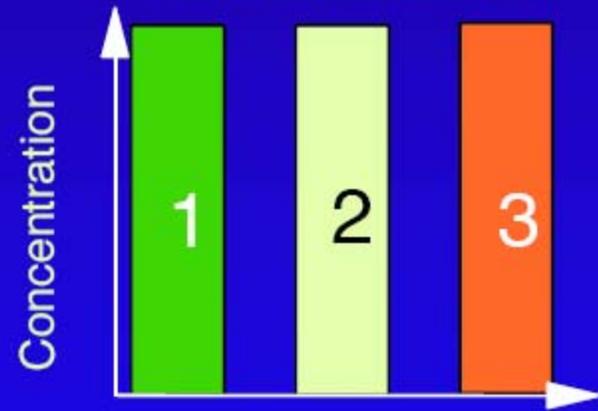
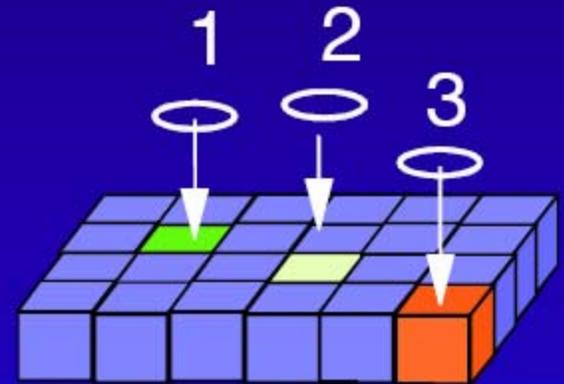


Bulk vs. Microanalysis

■ Bulk



■ Local



Solid Sampling

“Wish list”

- Submicron spatial resolution
- nm scale depth profiling
- Stoichiometric sampling
- 100 % Transport efficiency
- Quantification at attogram levels

LA-ICP-MS

(Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry)

Laser microprobe

+

ICP mass spectrometer

- Elevata risoluzione spaziale
- Capacità di campionare solidi naturali e sintetici
- Alta efficienza di ionizzazione del plasma
- Alta sensibilità

Determinazioni elementari ed isotopiche



Scienze geologiche, ambientali, biologiche, forensi,
semiconduttori

Elementi costituenti un LA-ICP-MS

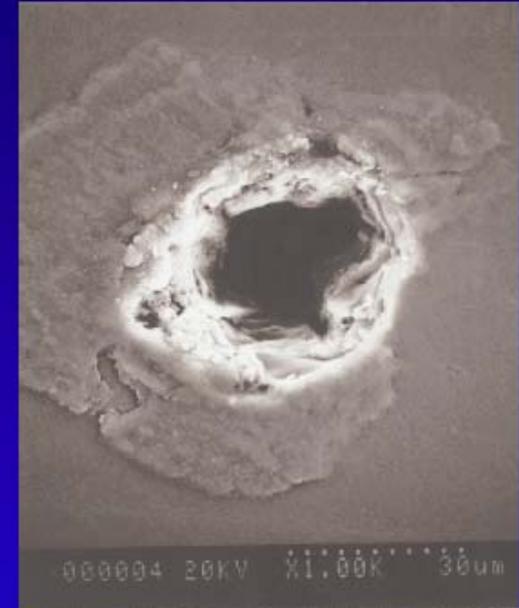
1. Sorgente laser
(Ablazione)

2. Cella di Ablazione + linea di trasferimento
(Trasporto del particolato)

3. Spettrometro di Massa ICP
(Ionizzazione + discriminazione delle masse)

Laser Ablation Systems

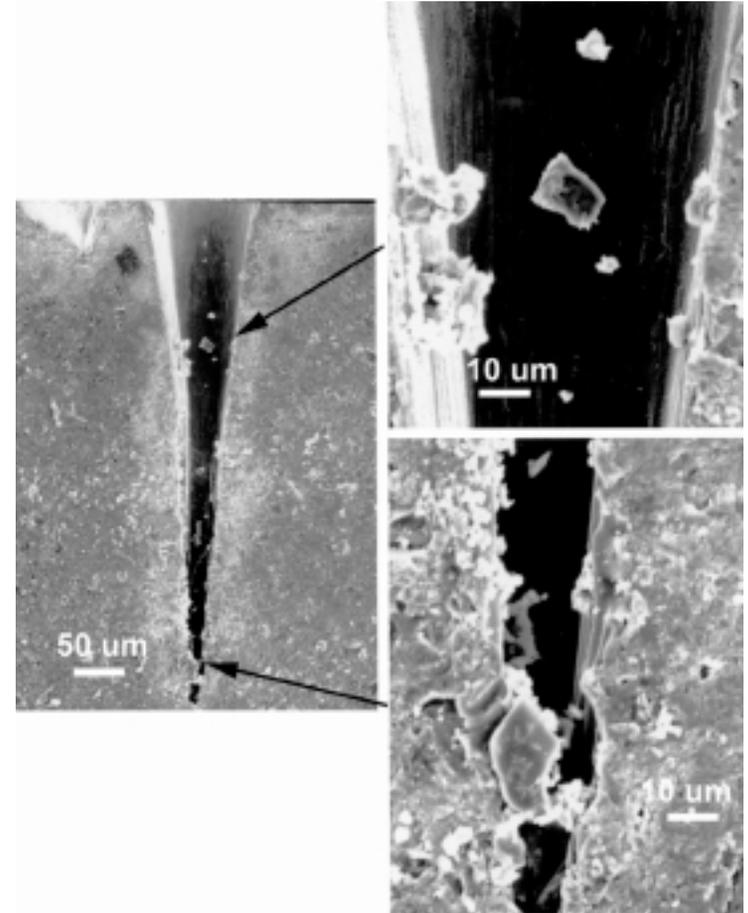
IR	1064 nm Nd:YAG
VIS	694 nm Ruby
	532 nm Nd:YAG
UV	308 nm XeCl Excimer
	266 nm Nd:YAG
	248 nm KrF Excimer
	222 nm KrCl Excimer
	213 nm Nd:YAG
	193 nm ArF Excimer
VUV	157 nm F2



Il processo di ablazione laser

L'interazione fra solido e laser produce:

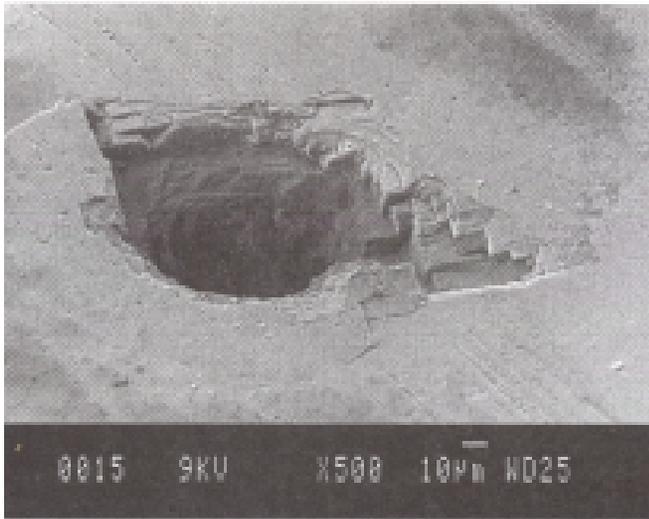
- Eccitazione elettronica all'interno del solido con espulsione di elettroni
- Trasferimento di energia al lattice del solido
- Fusione e vaporizzazione del campione
- Ionizzazione e formazione di un microplasma costituito dagli elementi del campione
- Interazione con il gas circostante ed espulsione del particolato



Da Borisov et al., 2000

Efficienza di ablazione

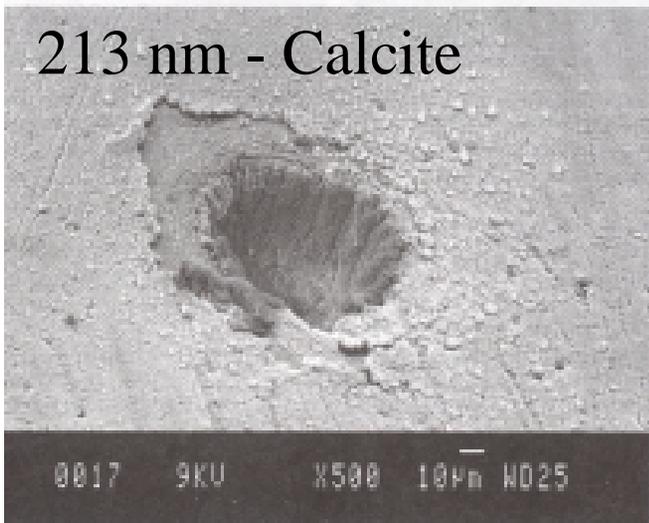
266 nm - Calcite



266 nm - Quarzo



213 nm - Calcite

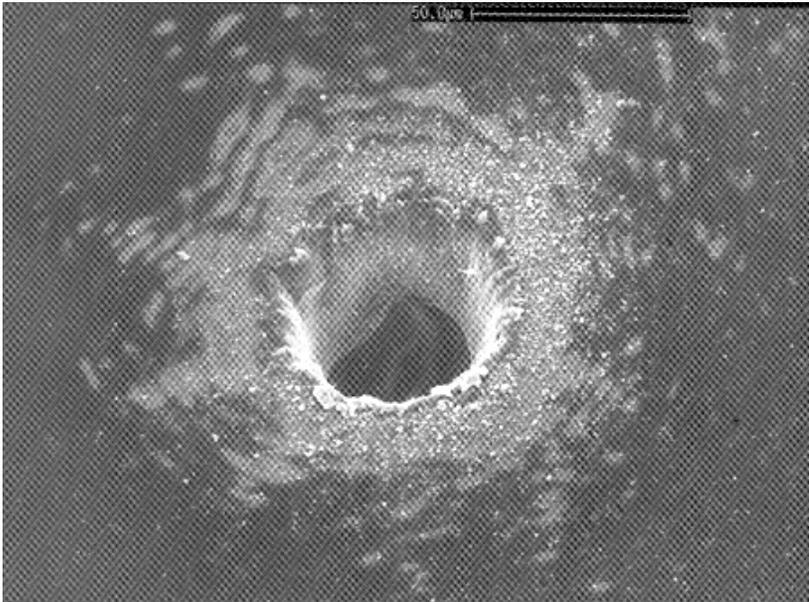


Funzione del coefficiente di assorbimento & lunghezza d'onda

Nd:YAG (266 nm) vs. Excimer ArF (193 nm)

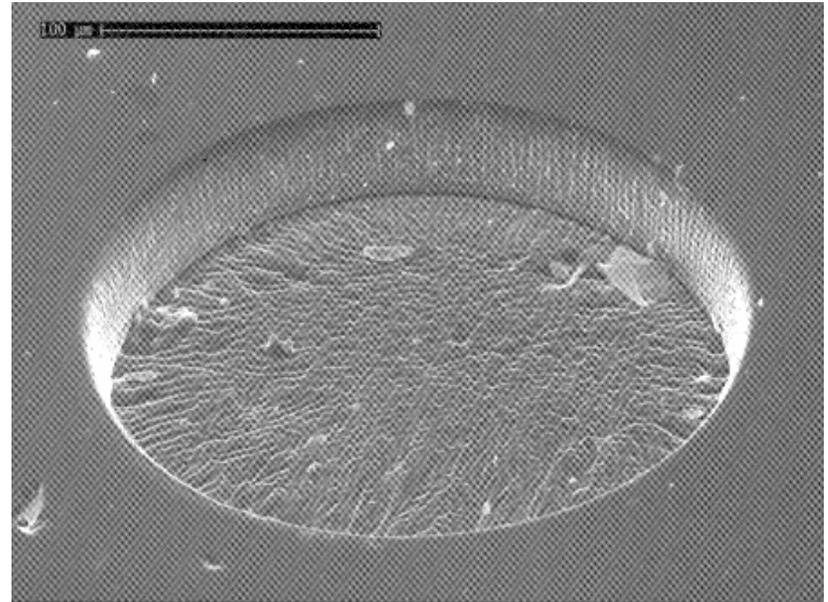
Nd:YAG-Laser

266 nm



Excimer-Laser ArF

193 nm

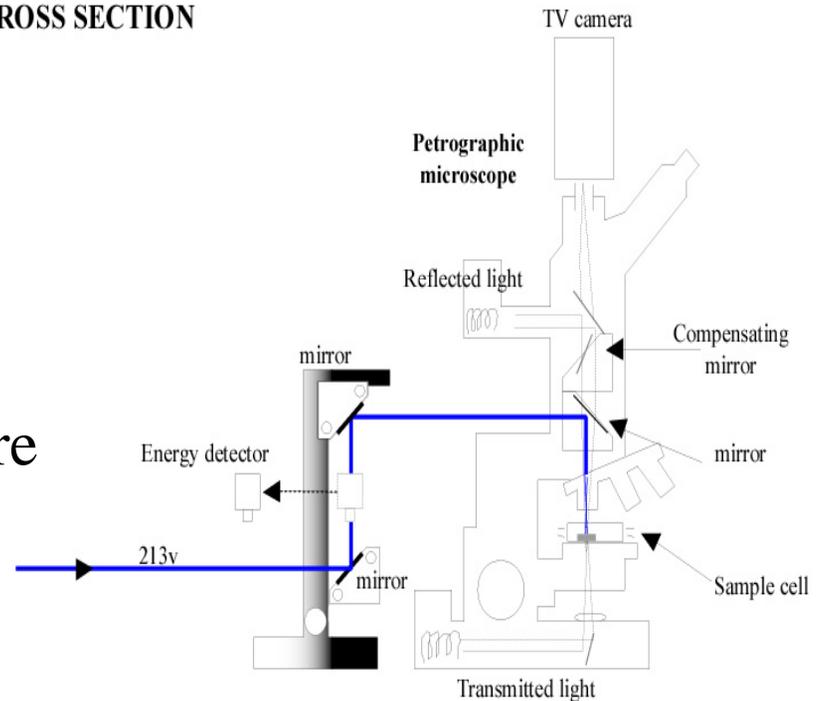
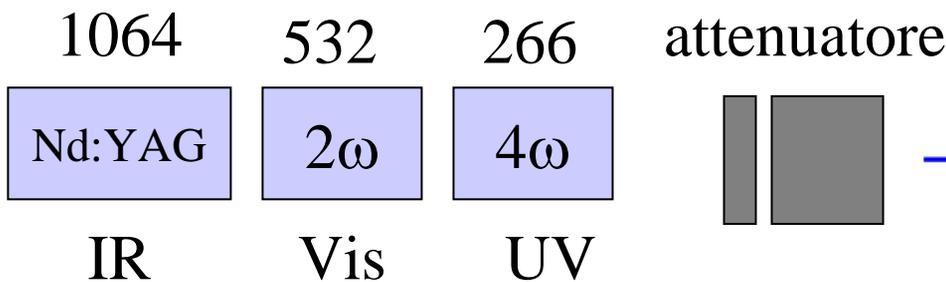


266nm laser microprobe configuration



Brilliant - Quantel pulsed
Nd:YAG laser source

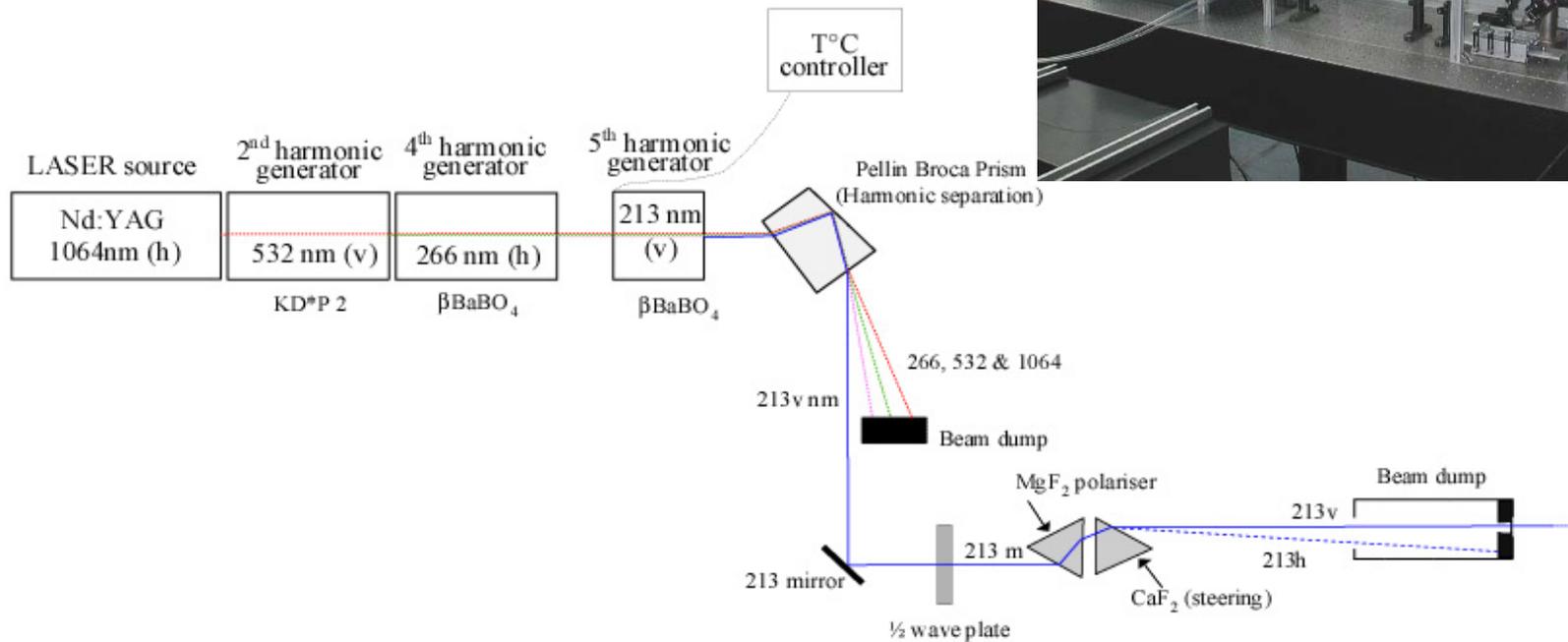
CROSS SECTION



Frequency 10 Hz – Max output energy 35.5 mJ/pulse
Spot size 10-150 μm

213nm laser microprobe configuration

PLAN VIEW



Frequency 10 Hz

Max output energy : 0.8 mJ/pulse

Spot size: 10-50 μ m

213 nm generator

5th harmonic generator

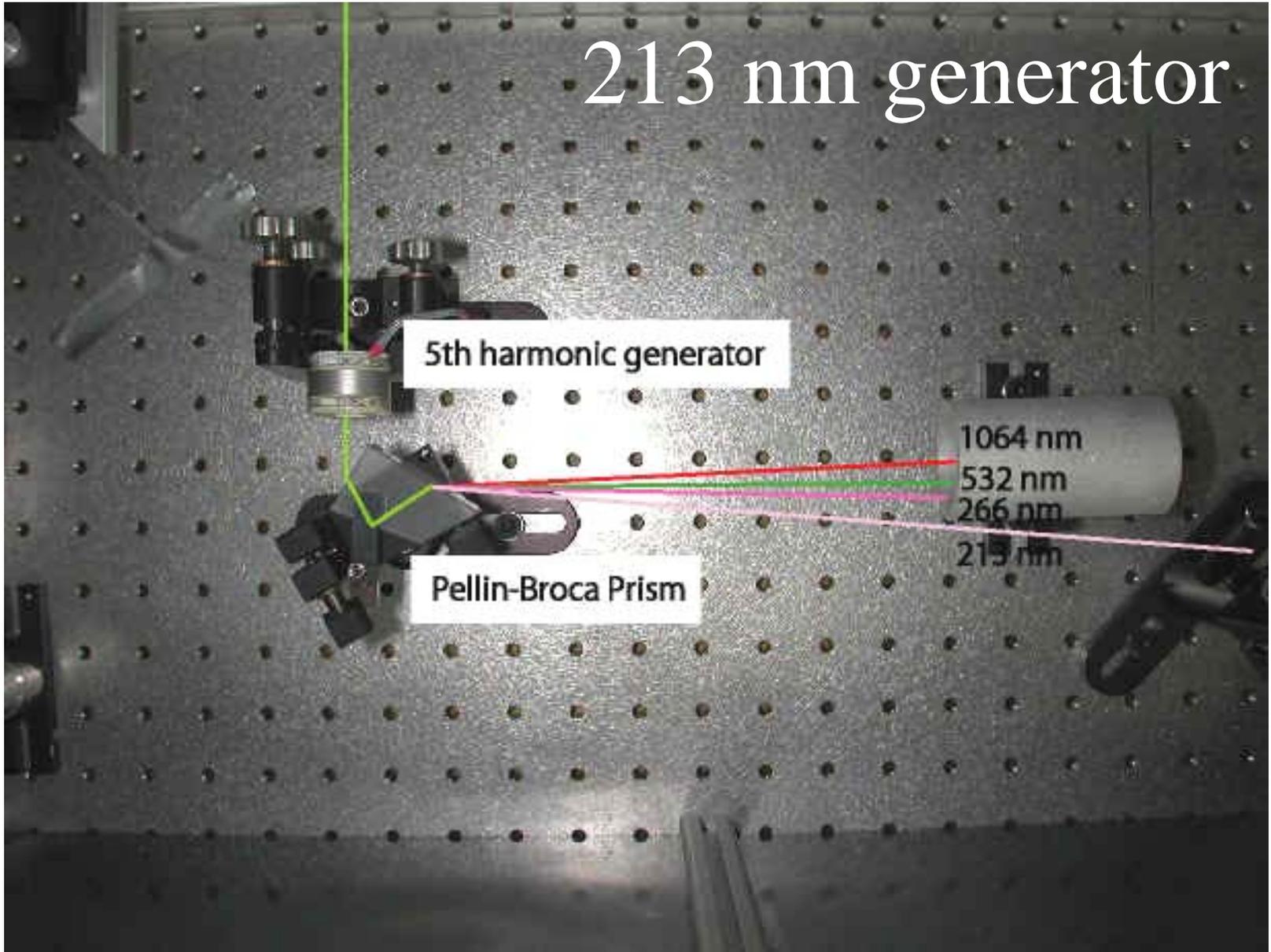
Pellin-Broca Prism

1064 nm

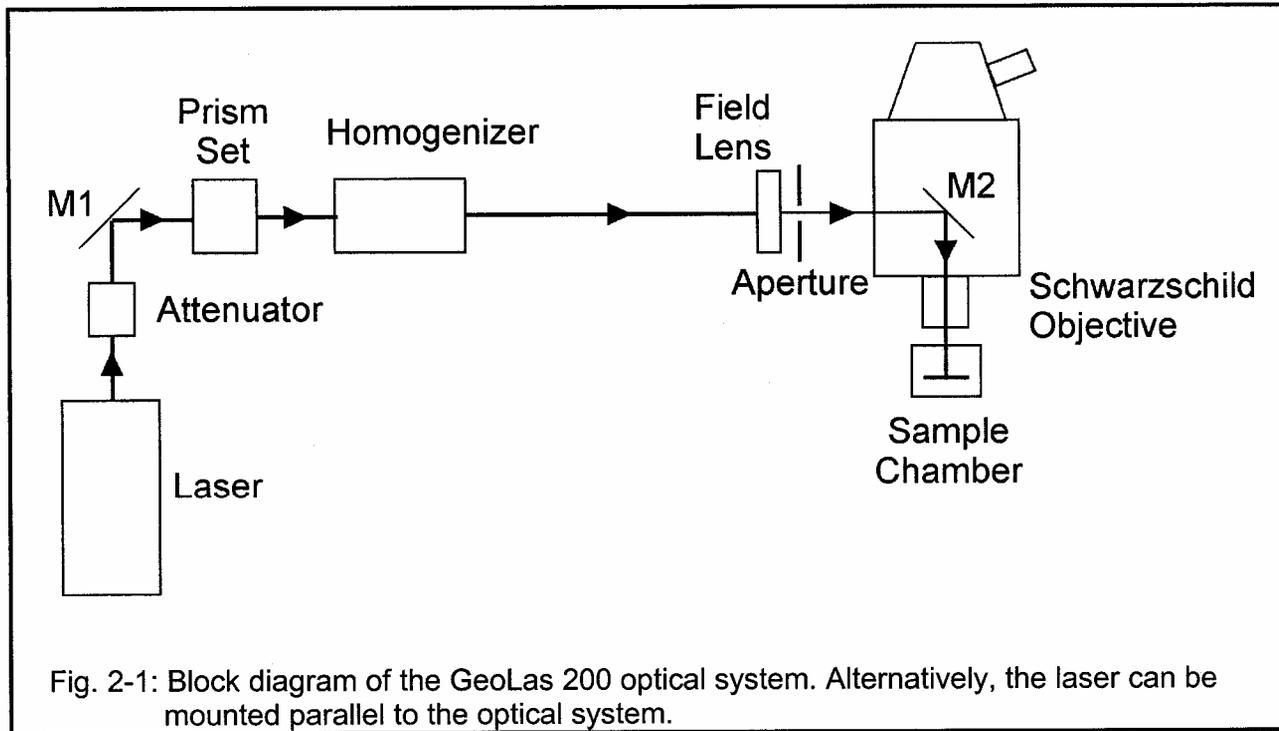
532 nm

266 nm

213 nm



Excimer Laser ArF 193 nm



ArF 193 nm Homogenizer

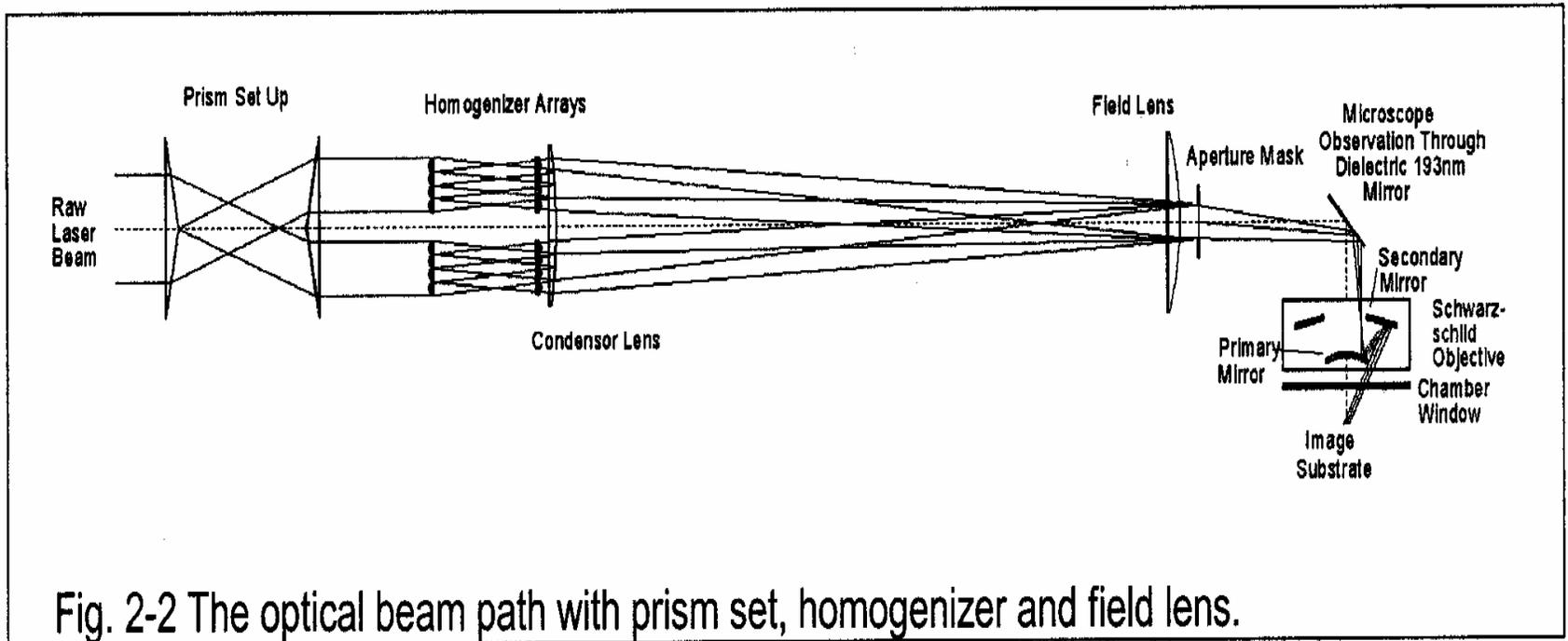
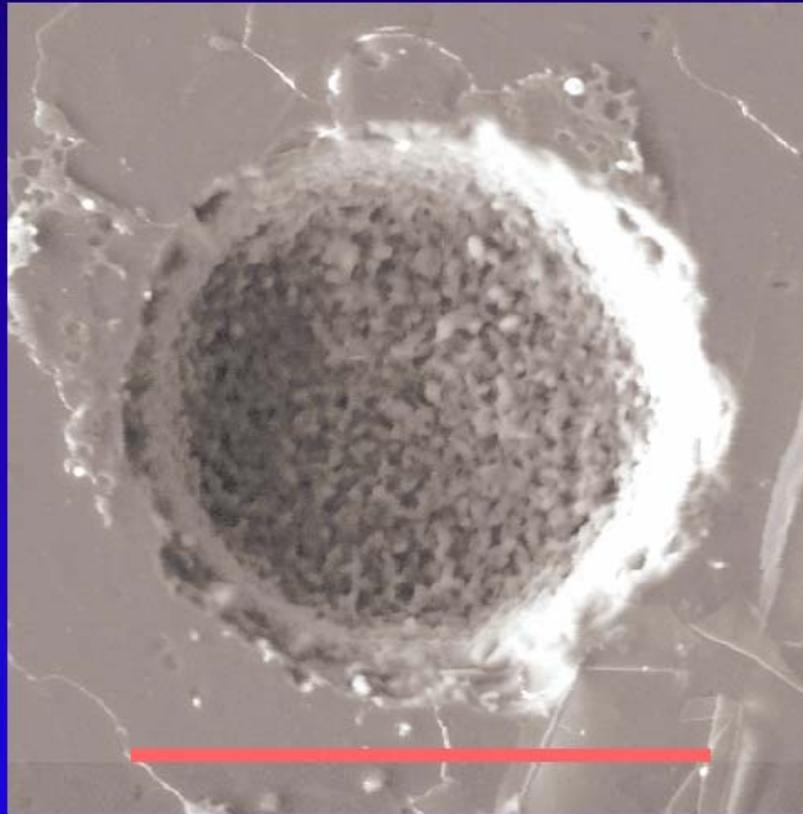


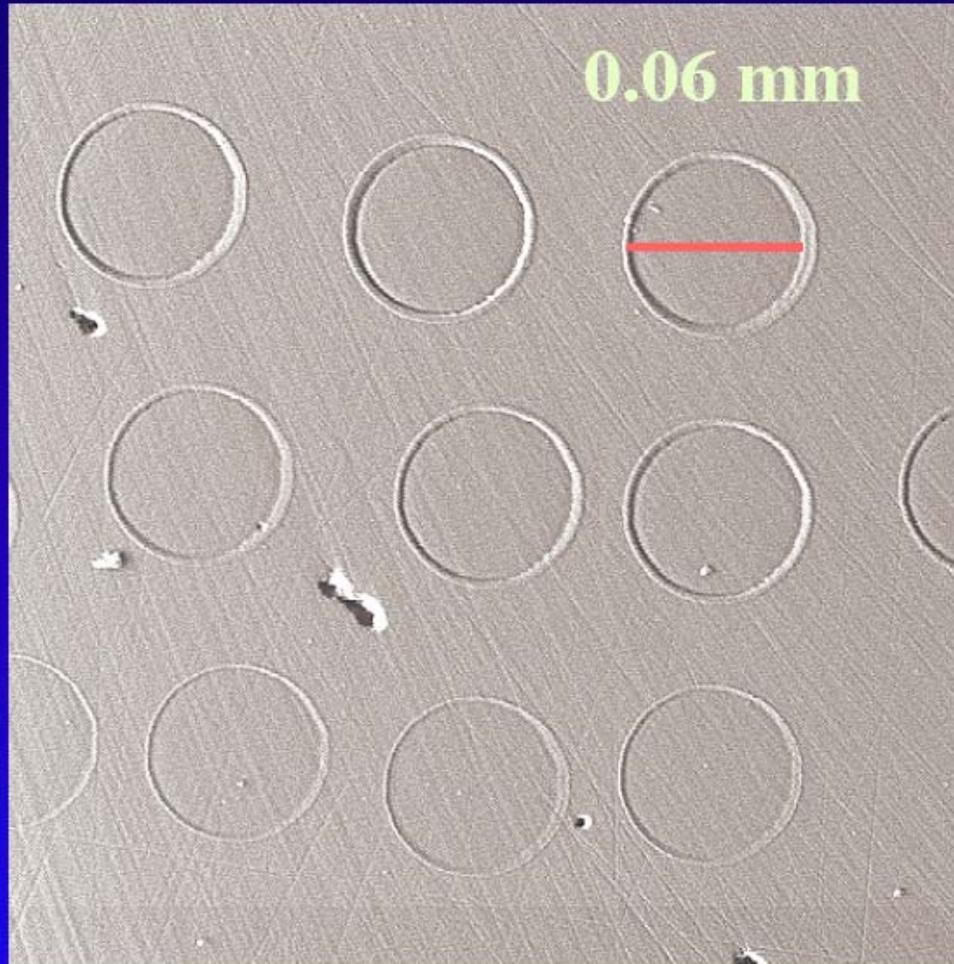
Fig. 2-2 The optical beam path with prism set, homogenizer and field lens.

Crater bottom



0.1 mm

Single shots with Excimer Laser



Il processo di ablazione

266 nm

5.0 mW

20Hz

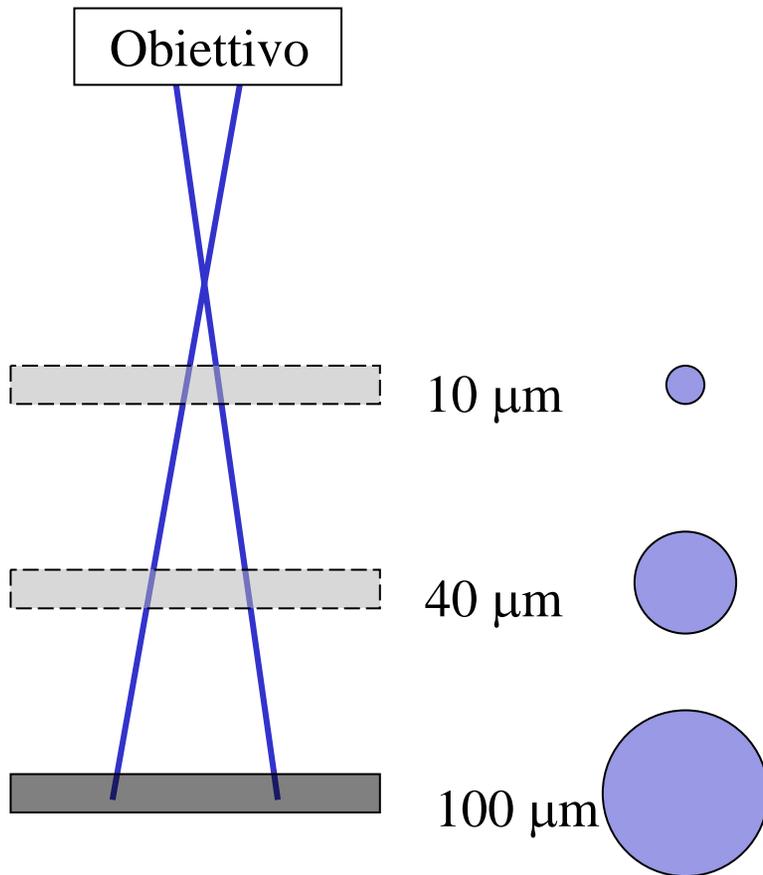
QuickTime™ e un
decompressore
sono necessari per visualizzare quest'immagine.

BCR-2
Vetro basaltico

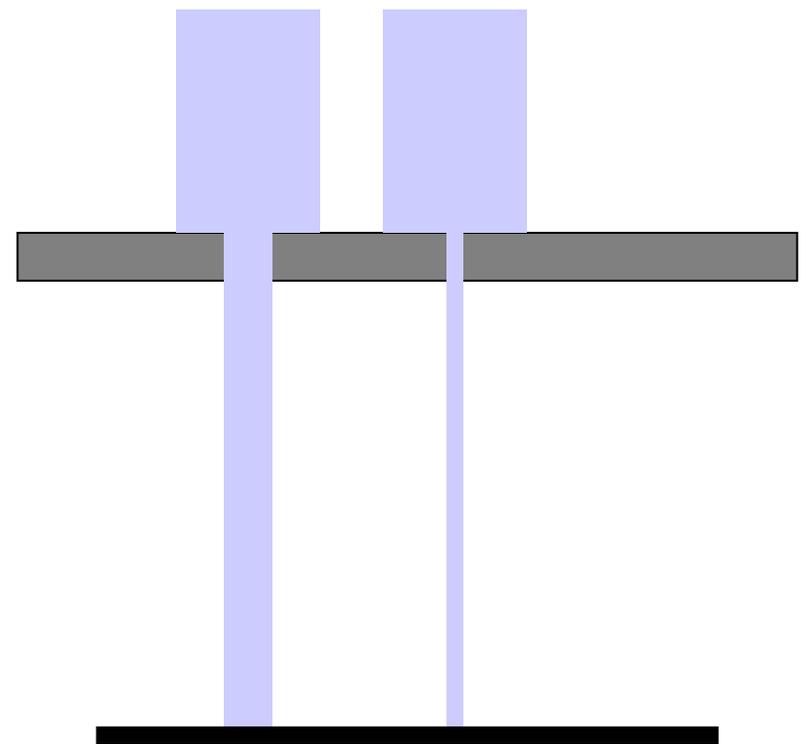
100 μm

Dimensioni dello spot

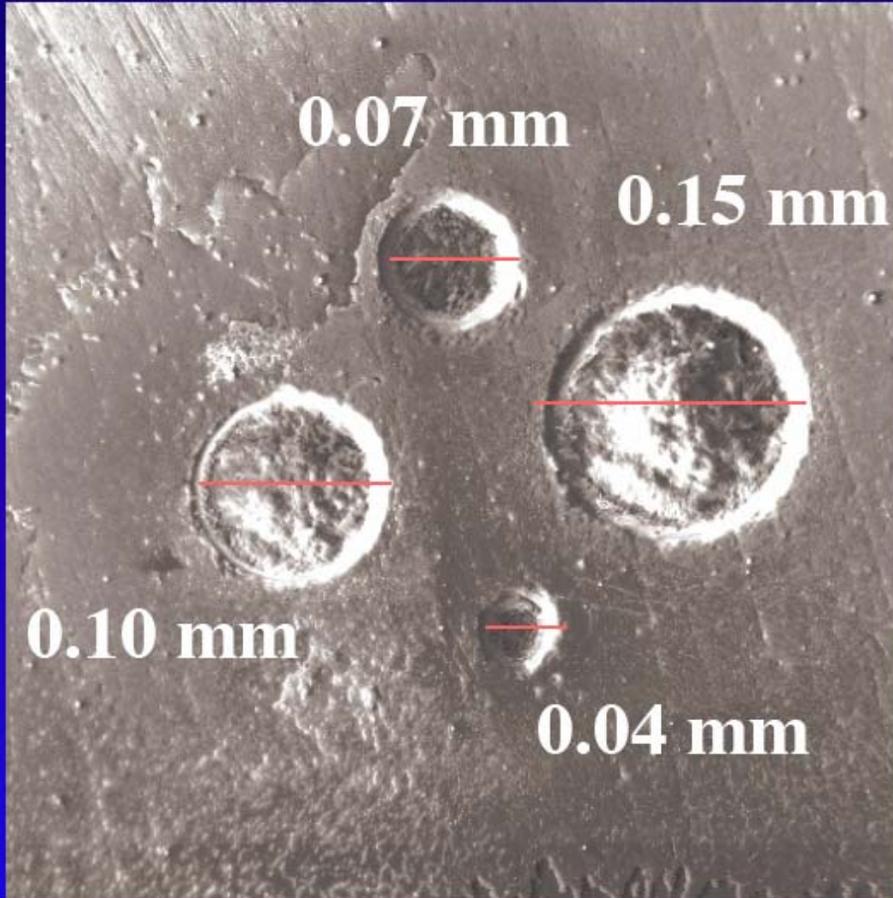
variando la posizione del campione rispetto al punto di fuoco del laser



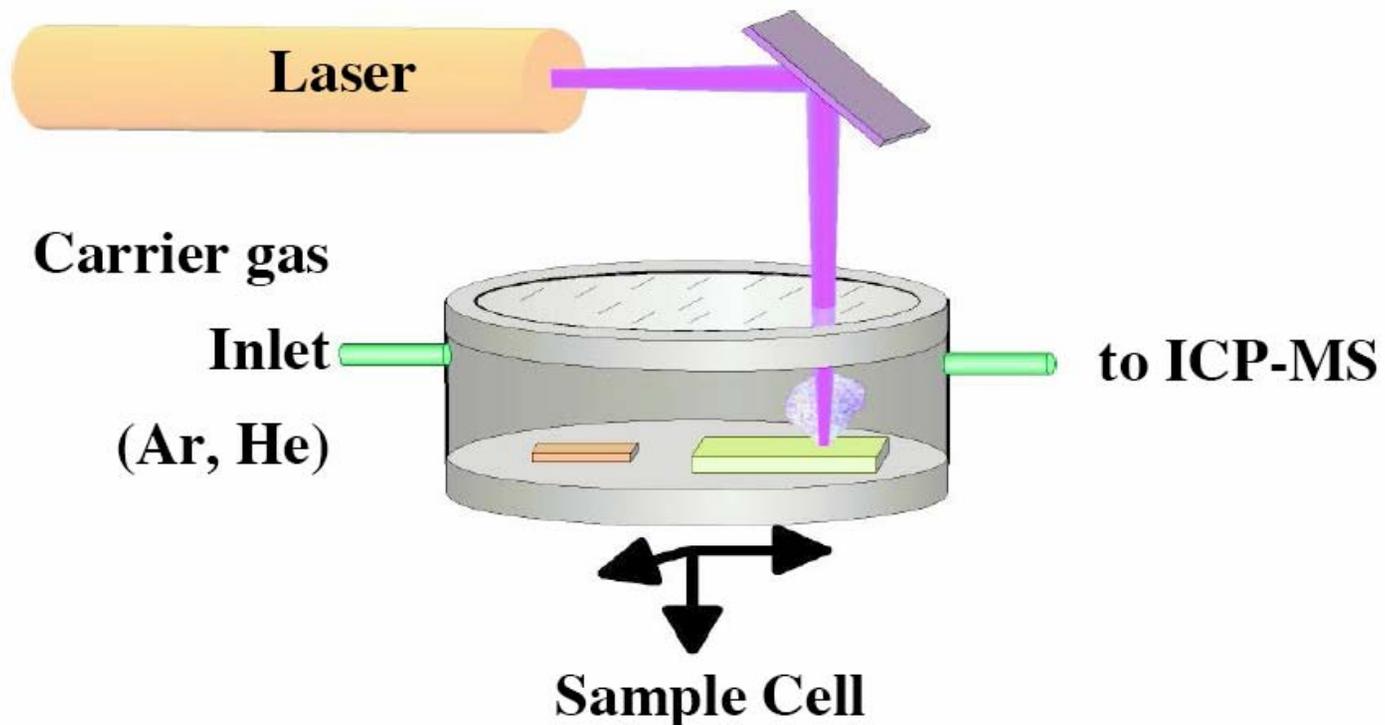
variando l'apertura del diaframma sul percorso ottico



Different crater sizes

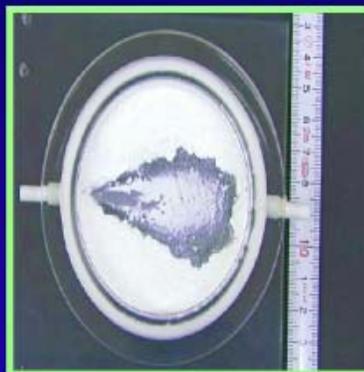


Principle of Laser Ablation-ICP-MS



Gas Flow Dynamics in the Ablation Cell

Narrow Needle
i.d. 0.15 mm



Wide Needle
i.d. 0.50 mm

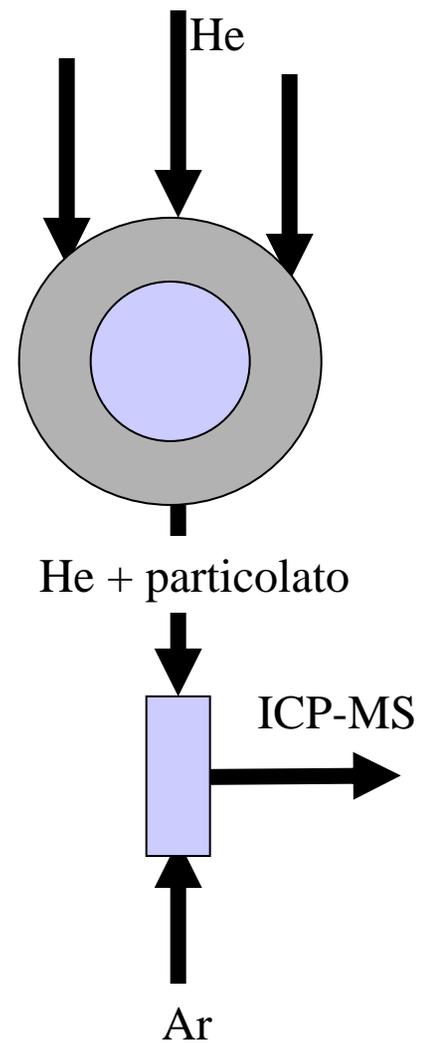
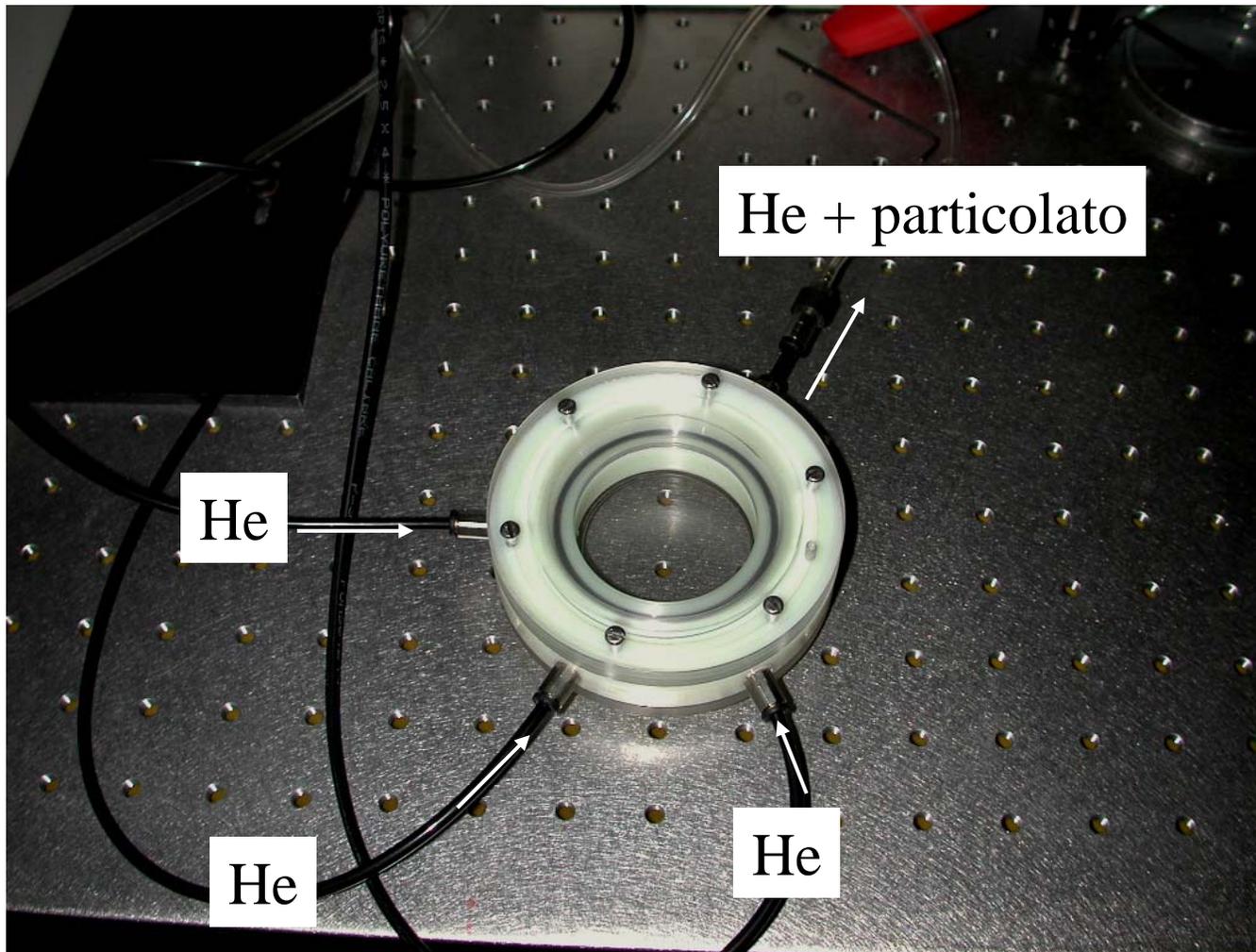


< 10 μm

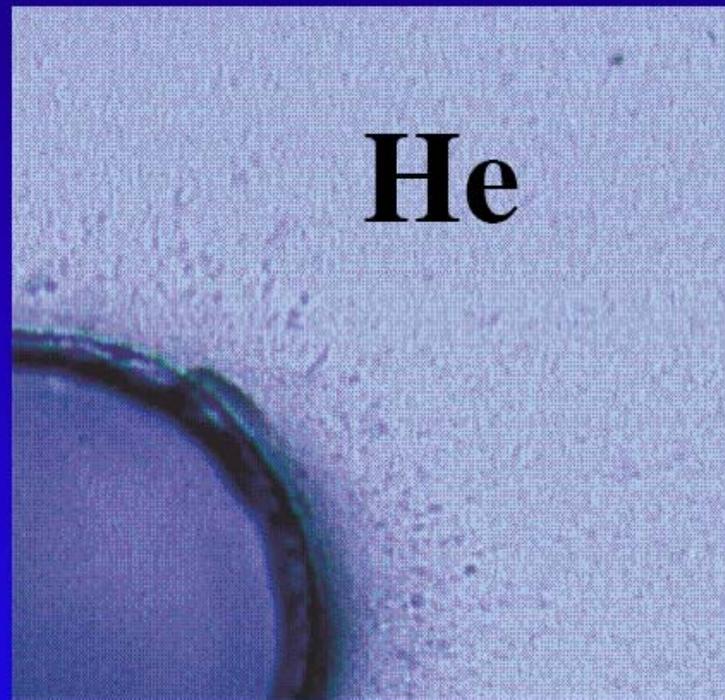
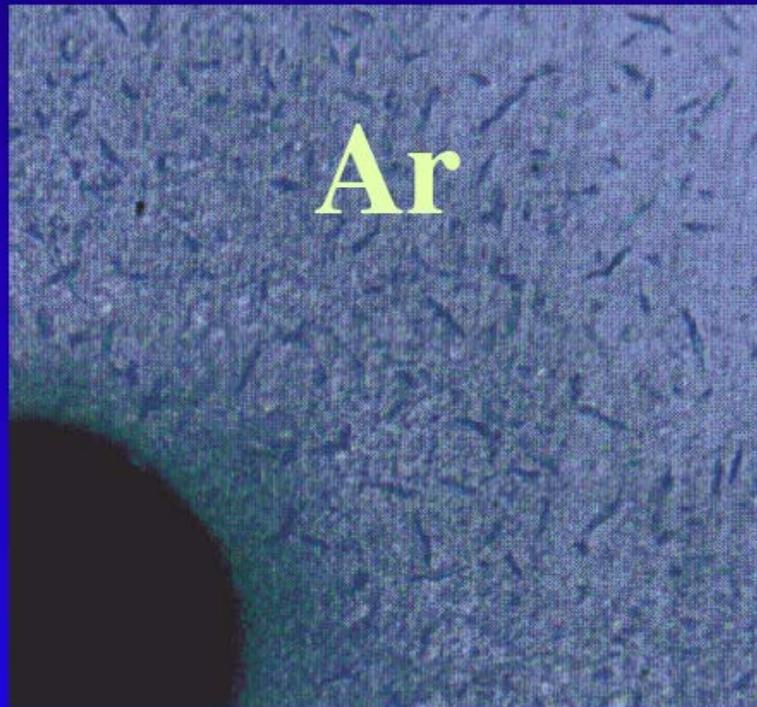
< 60 μm

Bleiner et al. , JAAS (2001)

Cella di Ablazione + linea di trasferimento

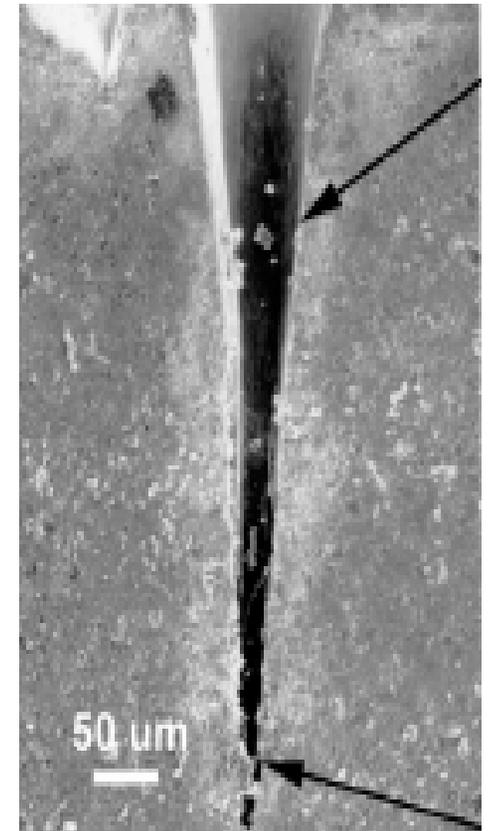
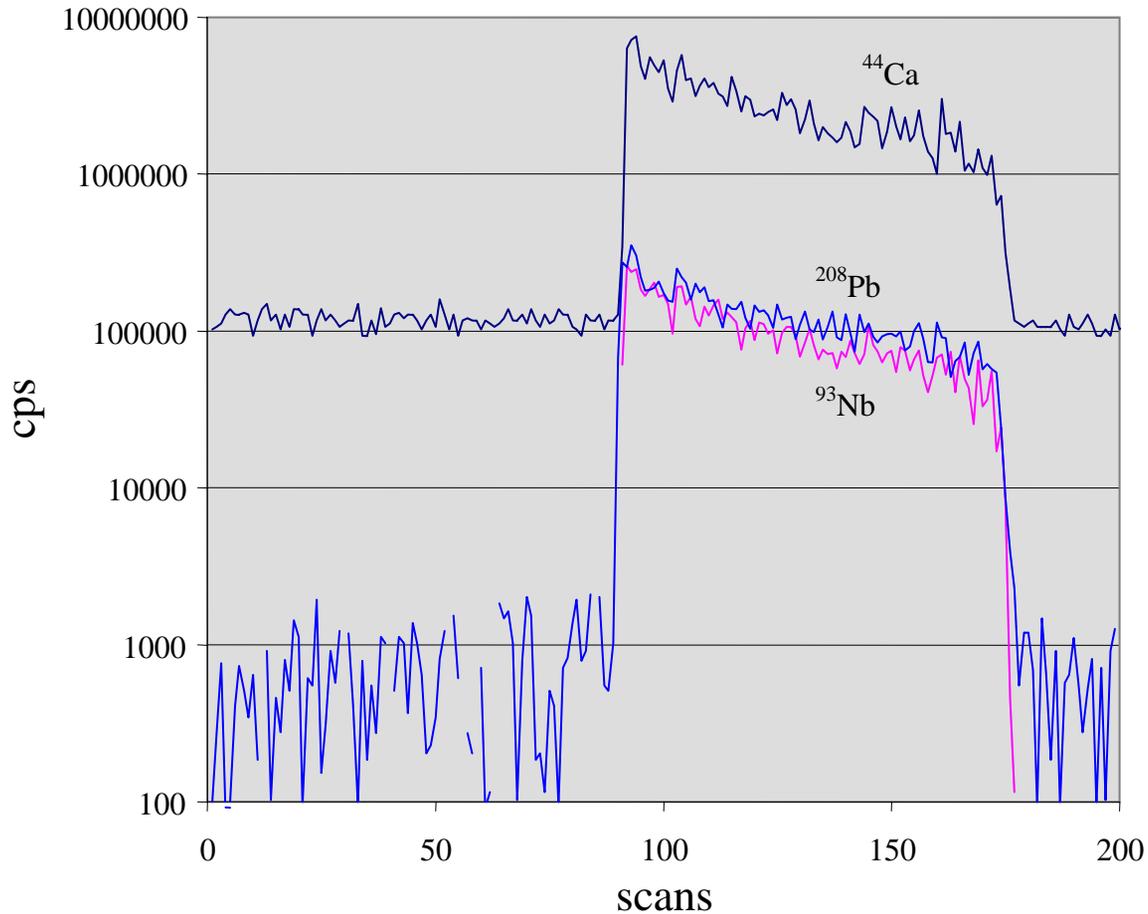


Particle Deposition in Different Gas Environments



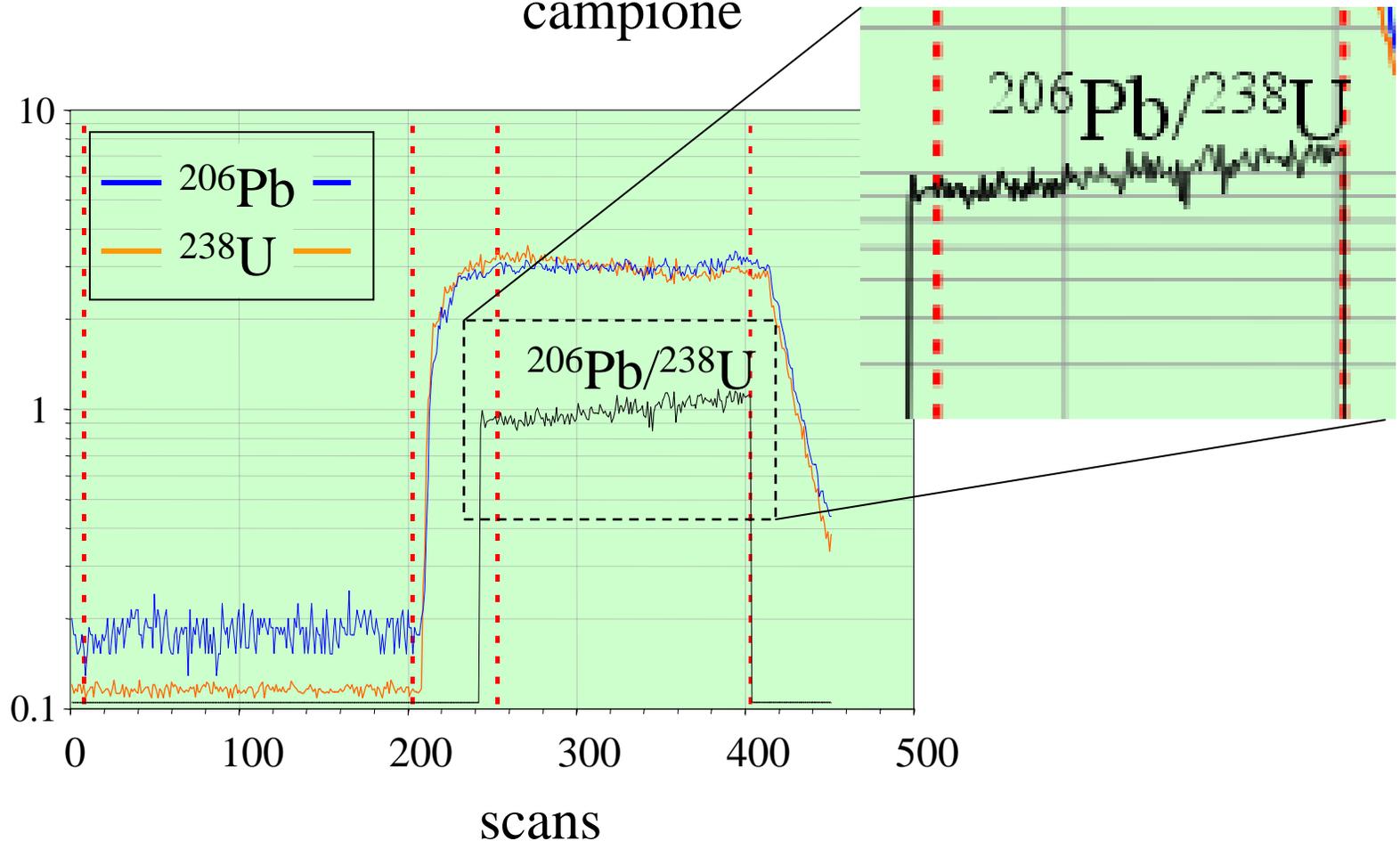
Segnale transiente

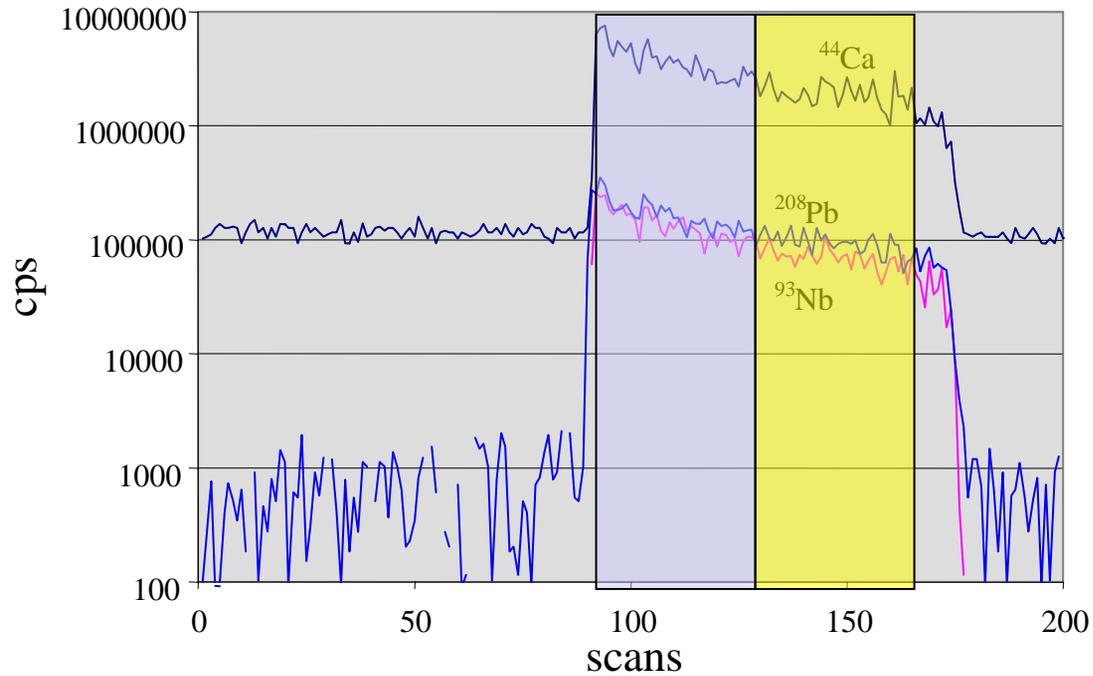
Diminuzione dell'intensità del segnale nel tempo



Frazionamento elementare (ablazione non stechiometrica)

Cambiamento dell'intensità dei segnali nel tempo indipendente dal
campione



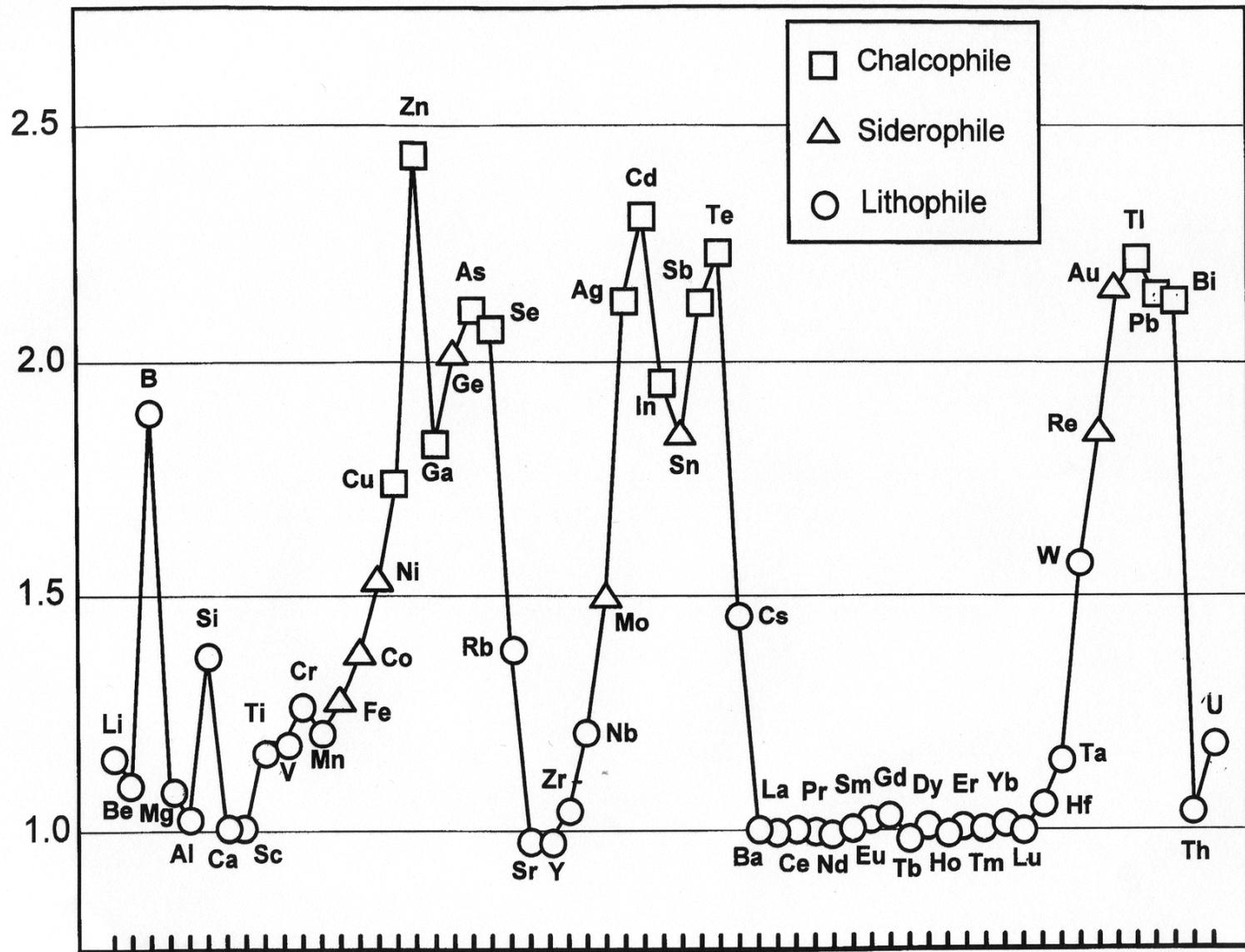


FRACTIONATION INDEX =

MEAN SIGNAL M^+ (min 2-4)/MEAN SIGNAL Ca^+ (min 2-4)

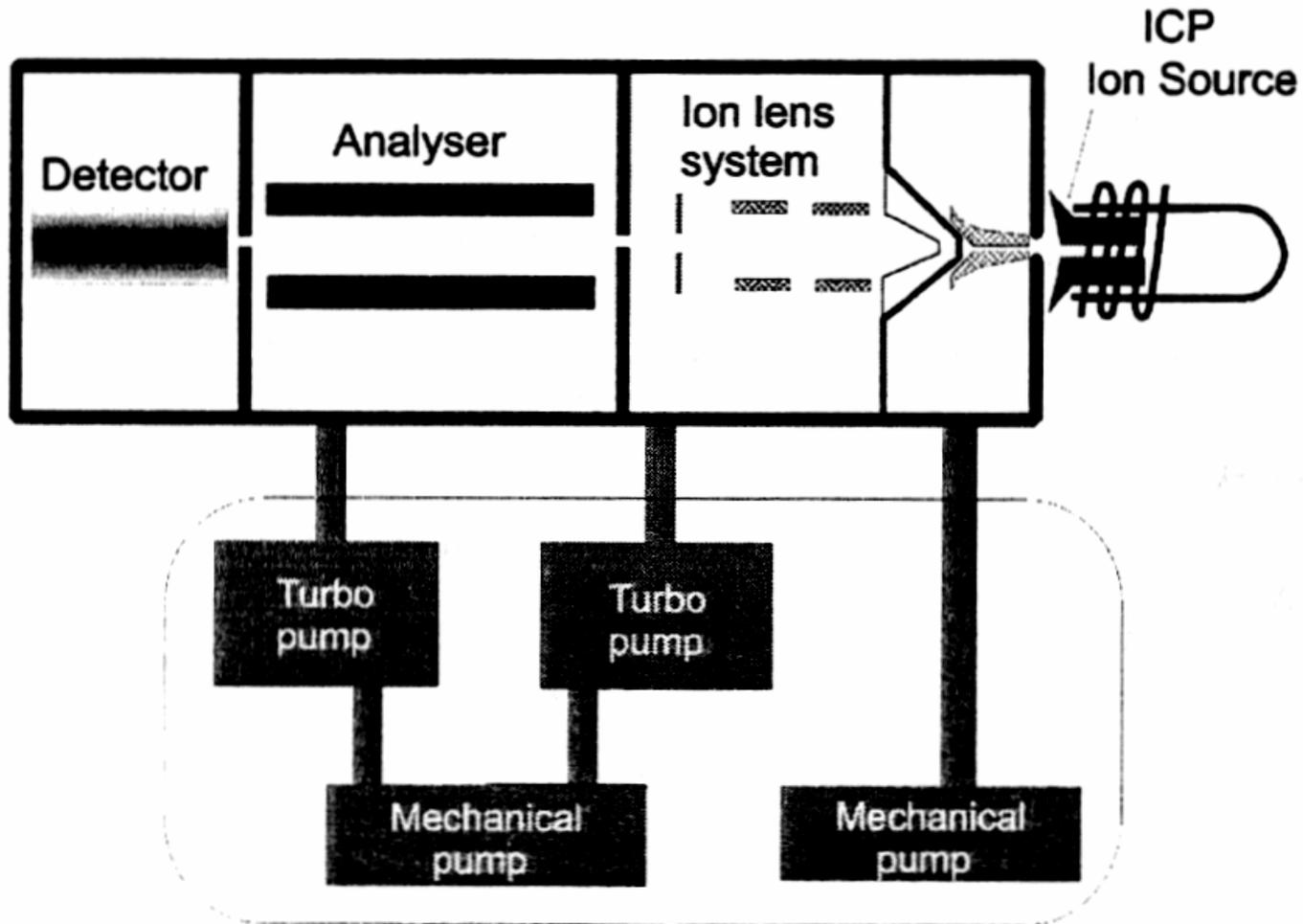
MEAN SIGNAL M^+ (min 0-2)/MEAN SIGNAL Ca^+ (min 0-2)

FRACTIONATION INDEX



Li B Al Ca Ti Cr Fe Ni Zn Ge Se Sr Zr Mo Cd Sn Te Ba Ce Nd Eu Tb Ho Tm Lu Ta Re Tl Bi U
 Be Mg Si Sc V Mn Co Cu Ga As Rb Y Nb Ag In Sb Cs La Pr Sm Gd Dy Er Yb Hf W Au Pb Th

Spettrometro di Massa



ICP-MS systems

improved acquisition speed

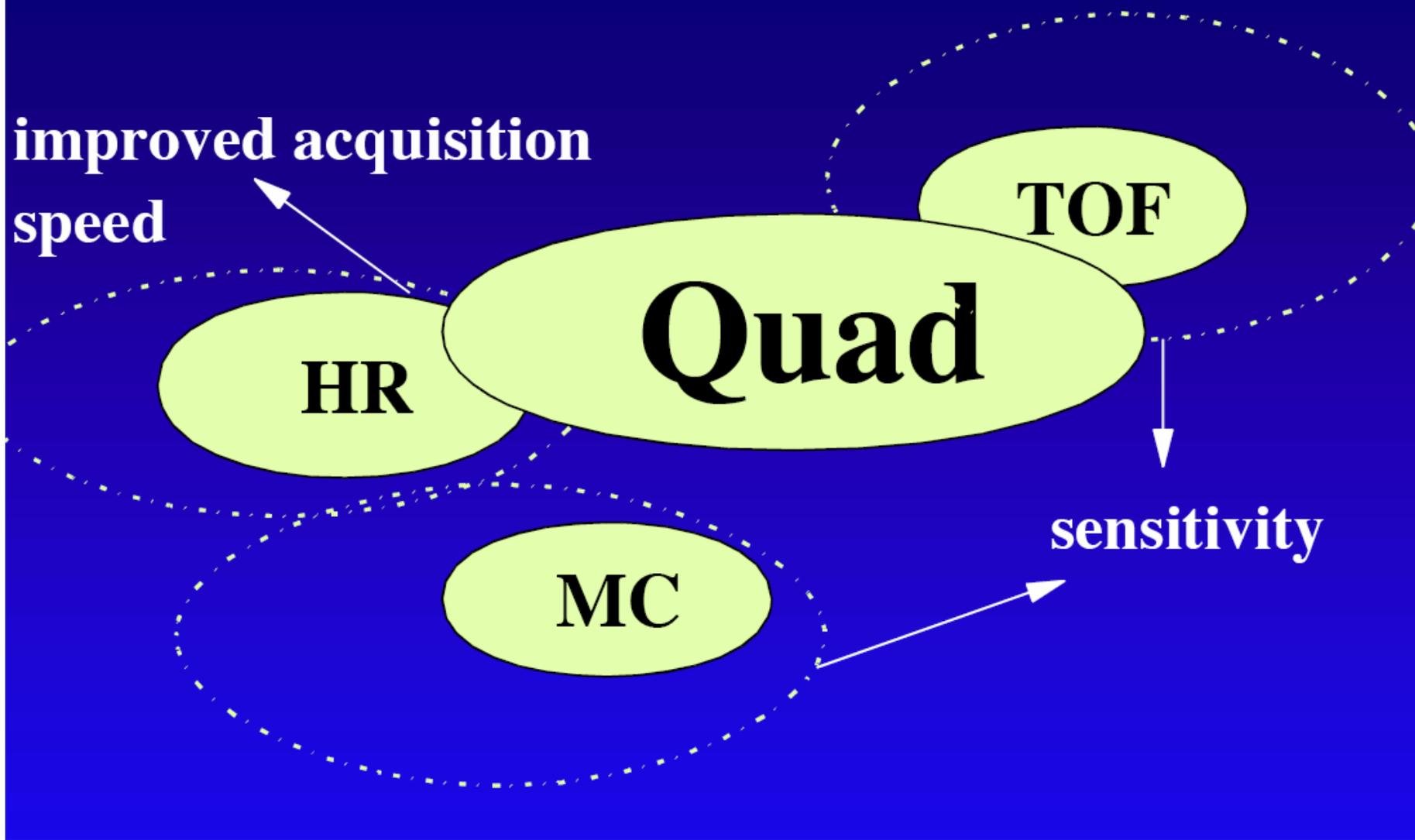
HR

Quad

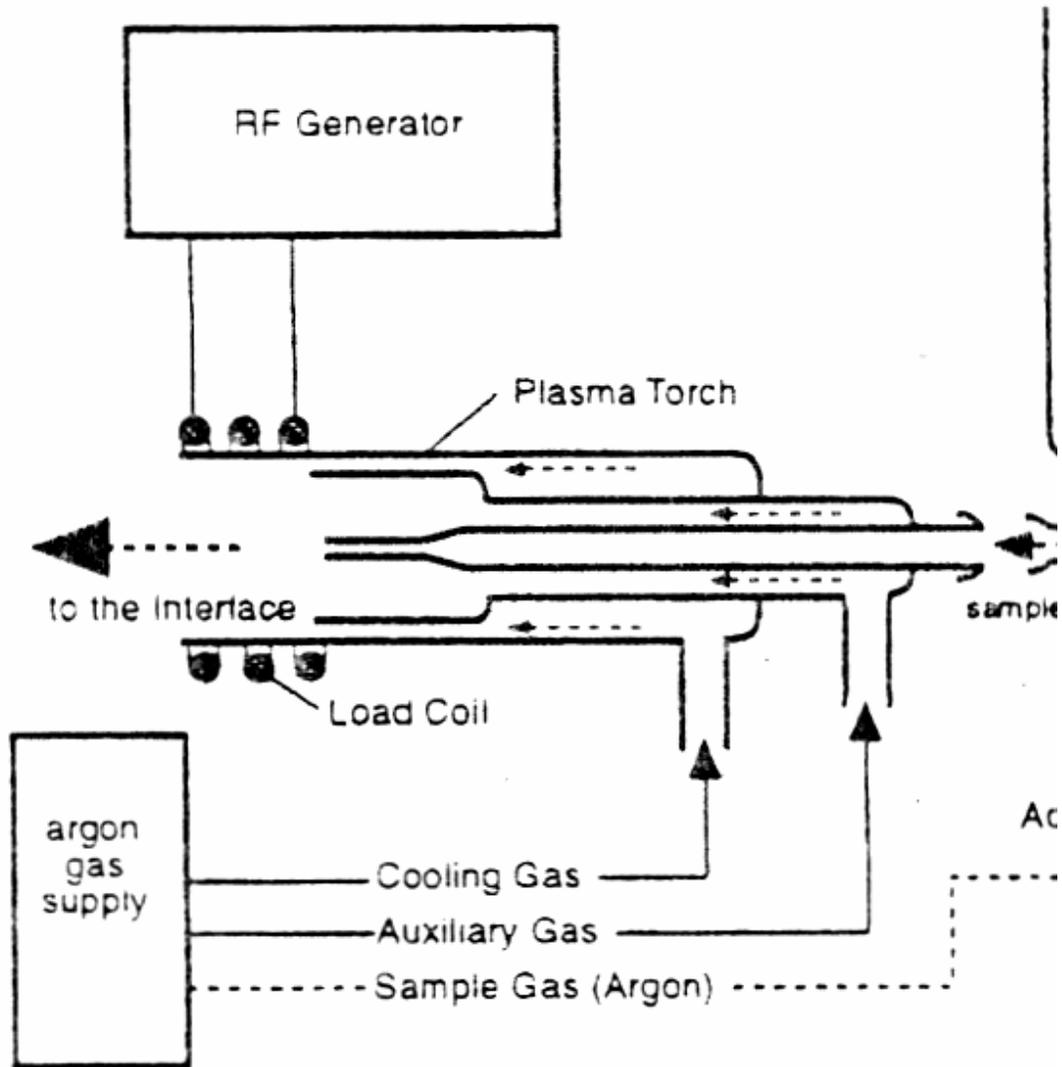
TOF

MC

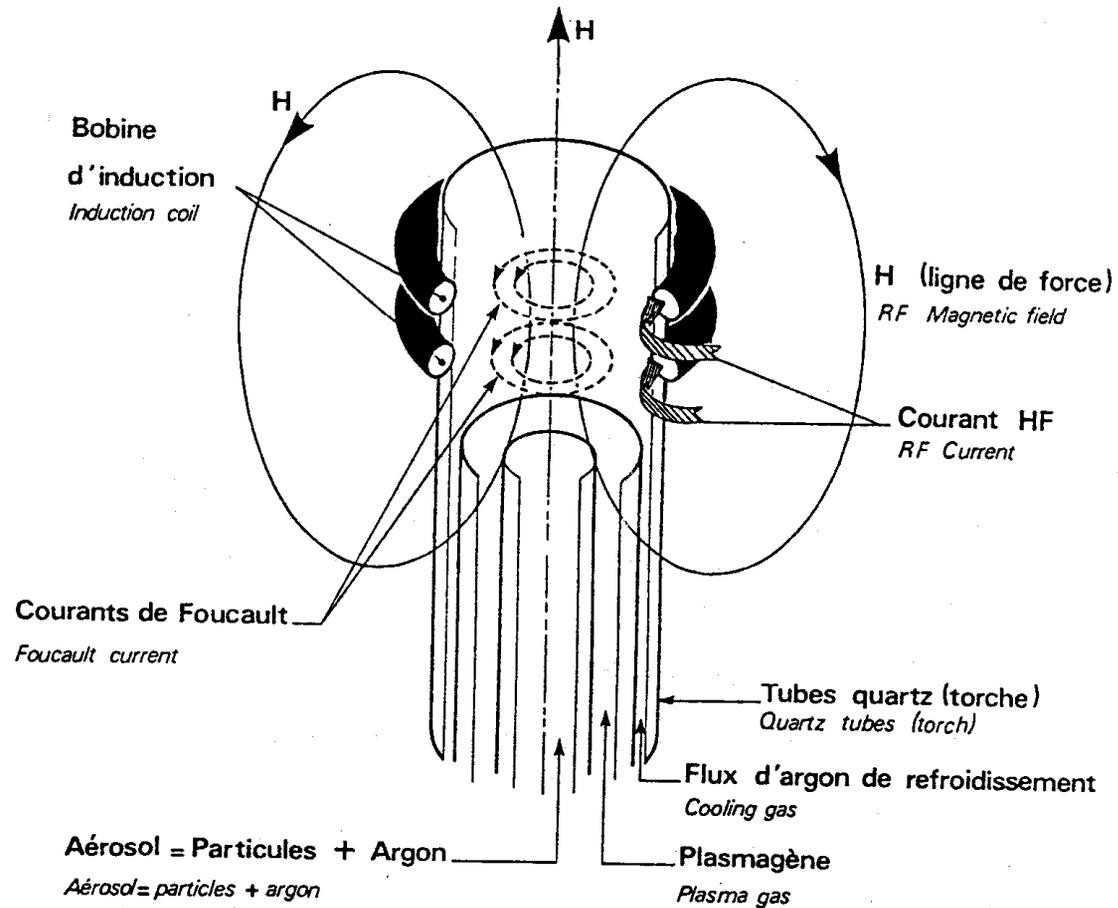
sensitivity



Sorgente ICP (1) - ionizzazione



Sorgente ICP (2) - ionizzazione

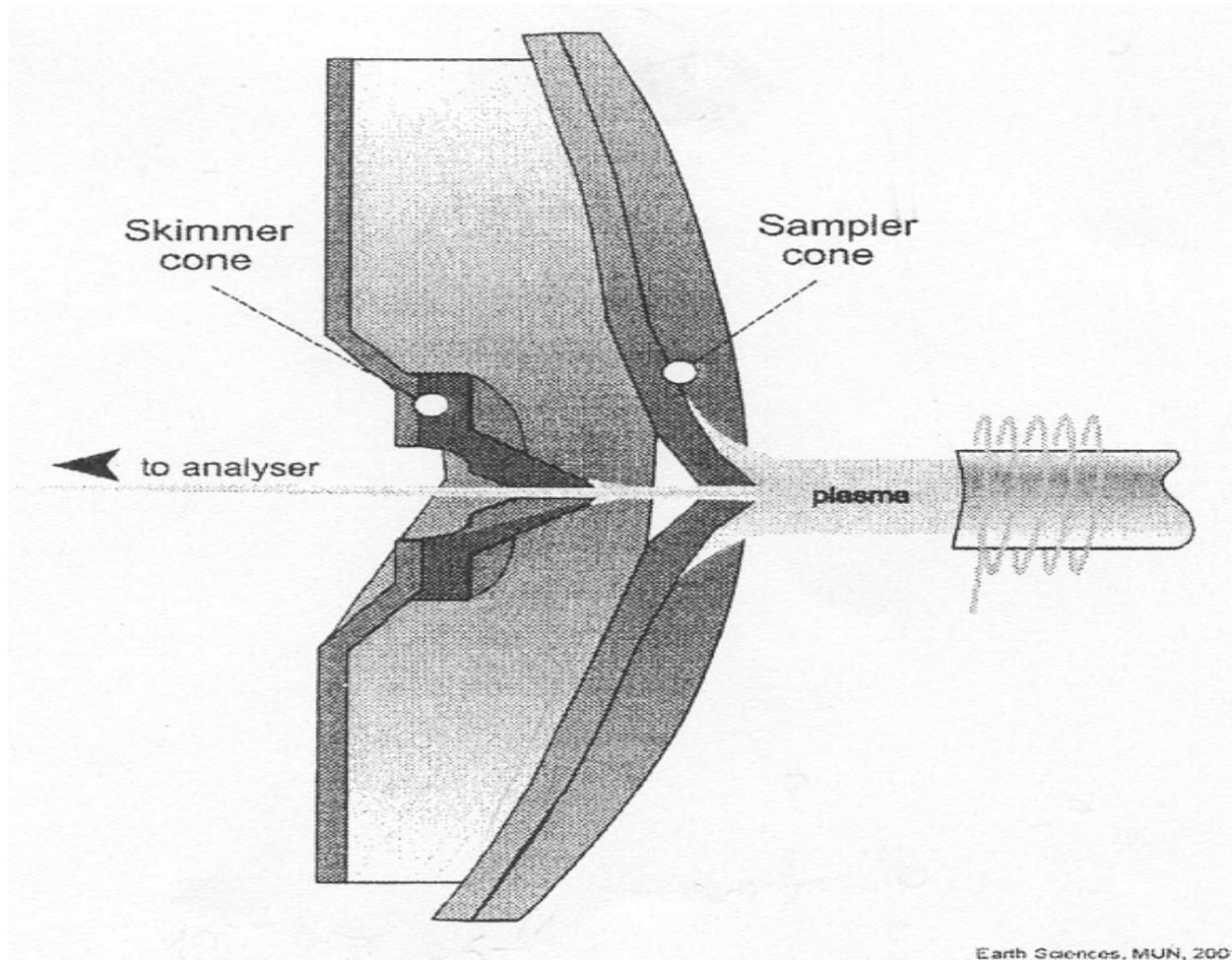


Mean Free Path

Pressione (torr)	“Mean Free Path”
760 (1atm)	0.1 μm
1	0.05 mm
0.05	1 mm
10^{-5}	5 m
10^{-6}	50 m
10^{-7}	500 m
10^{-8}	5000 m

Affinché gli ioni si possano muovere è richiesto un determinato grado di vuoto all'interno dello strumento

Ingresso nello spettrometro

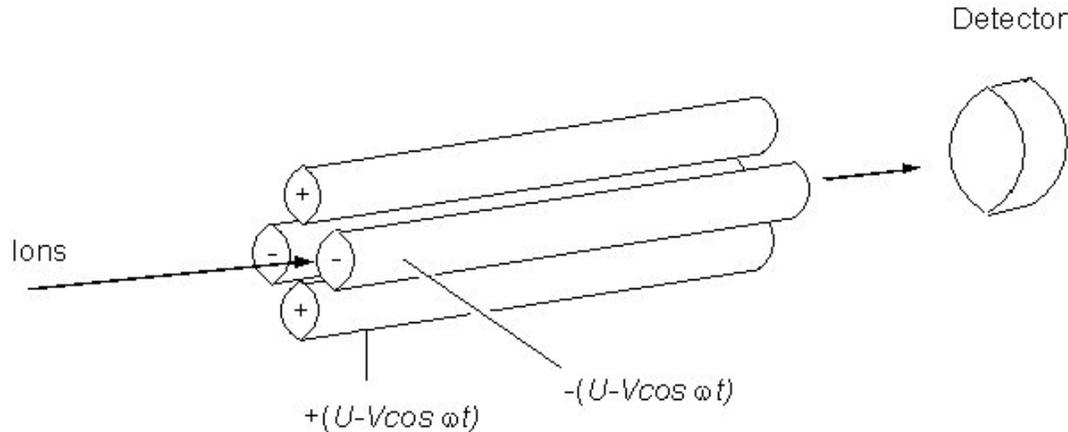


Analizzatore

- Ha la funzione di discriminare le masse
- I principali tipi di analizzatori sono:
 - Quadrupolo
 - Settore magnetico (+ESA)
 - TOF (Tempo di volo)

Quadrupole analyser

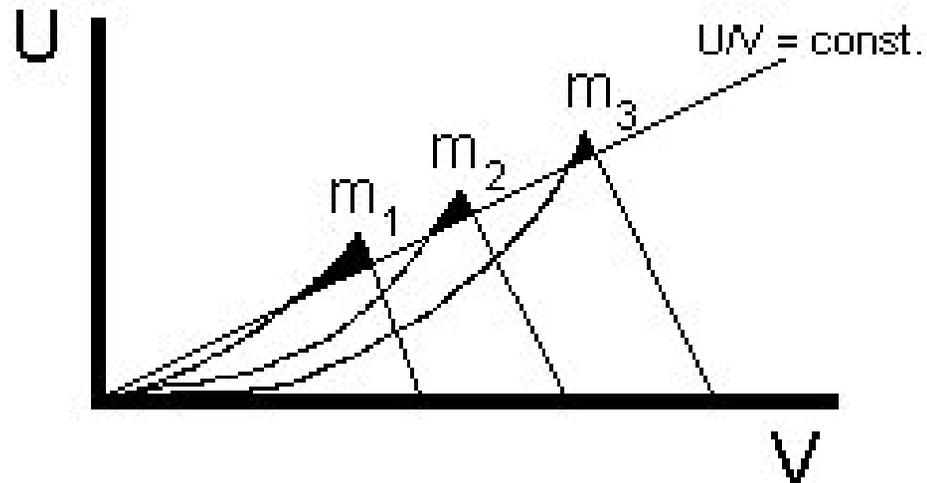
The quadrupole analyser consists of four parallel rods to which a varying voltage is applied, resulting in a fluctuating electric field. The potential applied to the rods is made up of a DC (U) and RF ($V\cos \omega t$) component:



The key result is that for an ion with a particular m/z ratio to pass through the quadrupole (and on to the detector), certain combinations of U and V must be obtained.

Thus, if U and V are scanned such that $U/V = \text{const.}$ then successive detection of ions of different mass will be achieved. The following figure illustrates the principle graphically. The three stability curves represent values of U and V for which the three masses m_1 , m_2 and m_3 have stable trajectories through the quadrupole. Only those values which lie within the black shaded regions allow ion transmission.

Notice that resolution of the mass analyser can be increased by increasing the slope of the curve $U/V = \text{const.}$, and that if $U = 0$ then ions of all m/z are transmitted.



Features of ICP-SFMS

+ **High sensitivity**

2. **Low DLs**

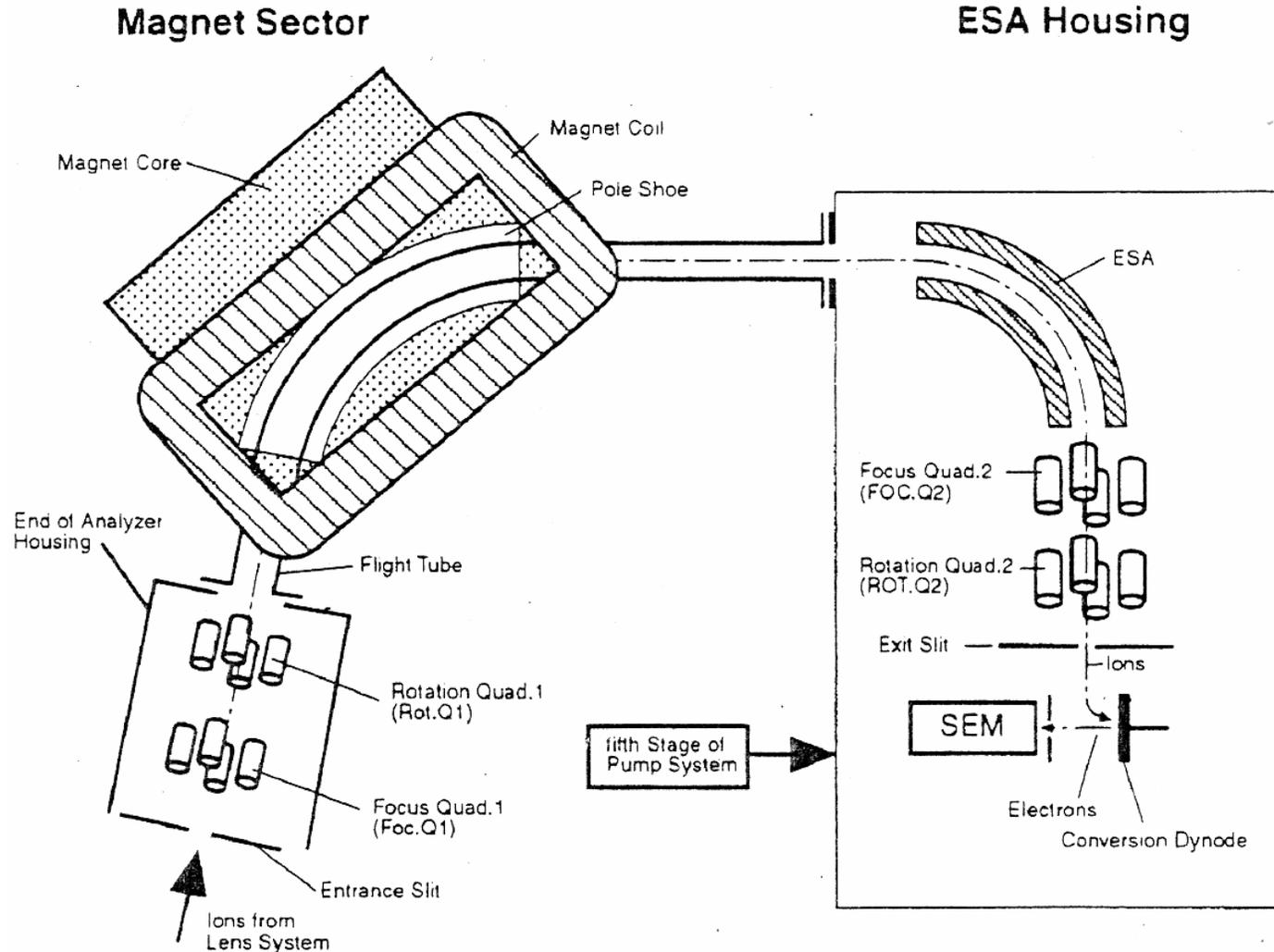
3. **Resolving Power**

4. **Linear Dynamic Range**

- **Slow acquisition speed**

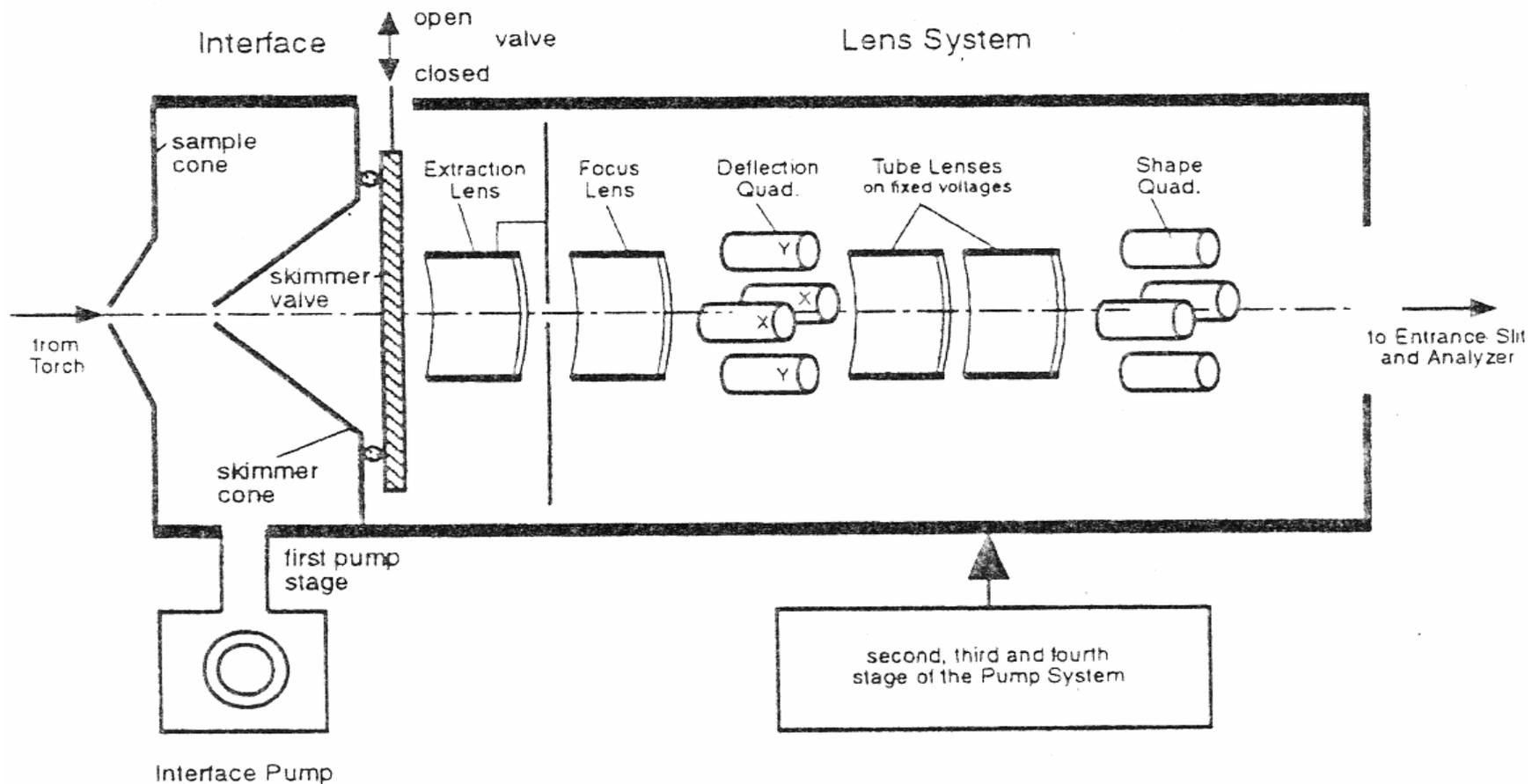
2. **High background for the lower mass region**
(Na, Mg, Al, Si, K, Ca,...)

Settore magnetico a doppia focalizzazione

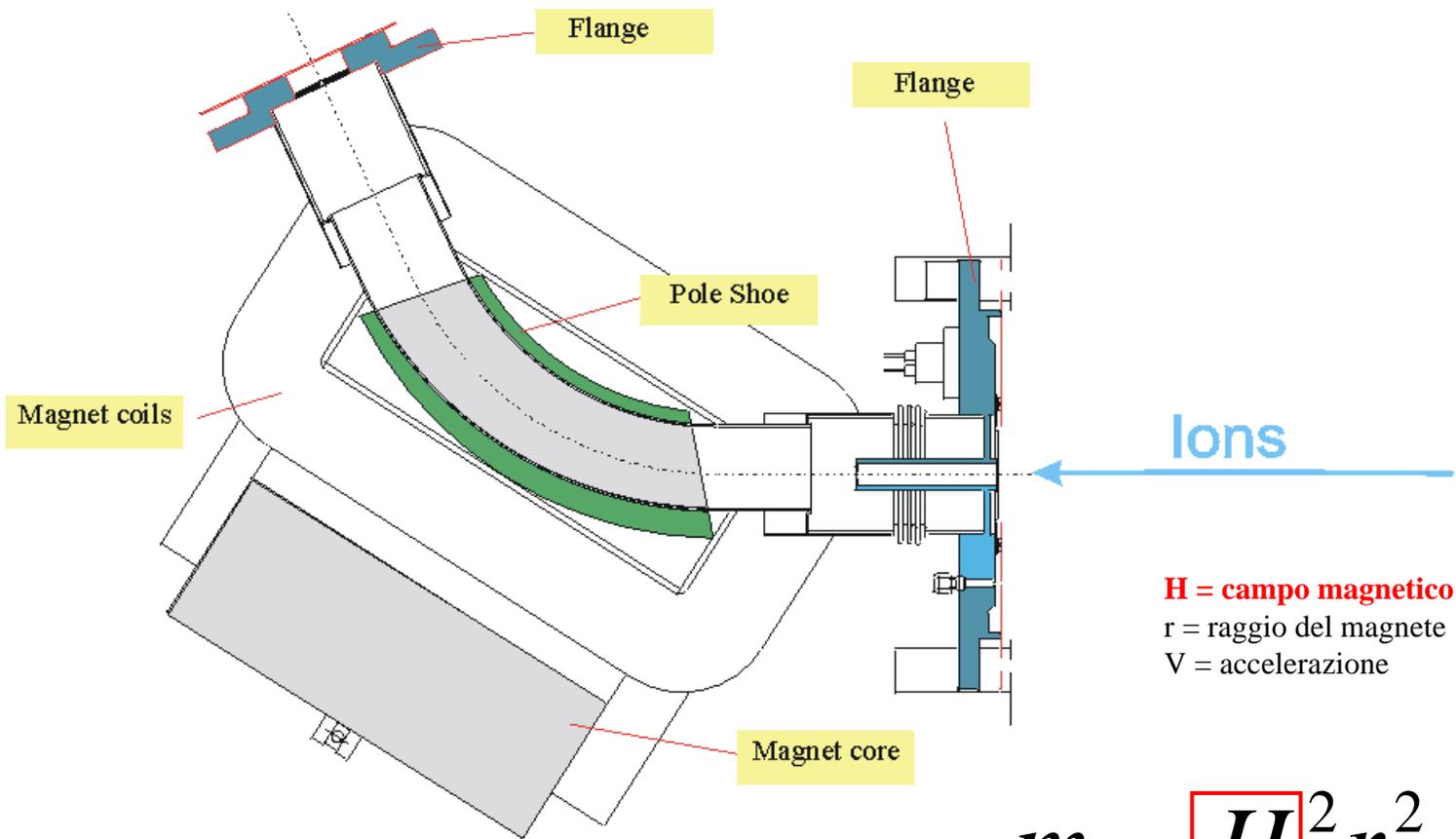


Reversed Nier-Johnson geometry

Lenti di trasferimento



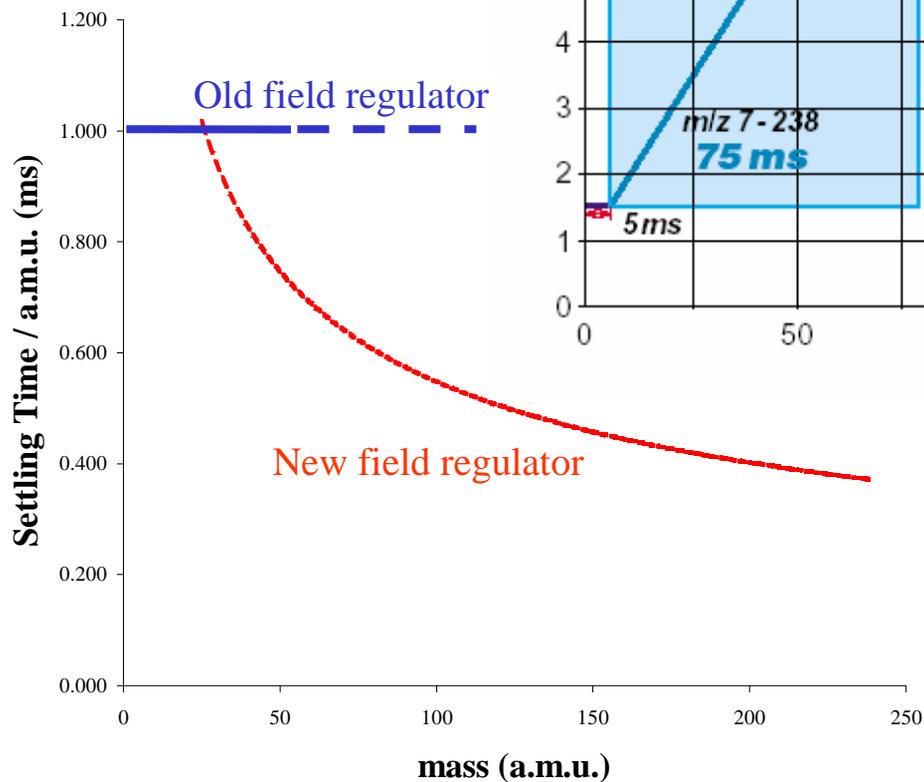
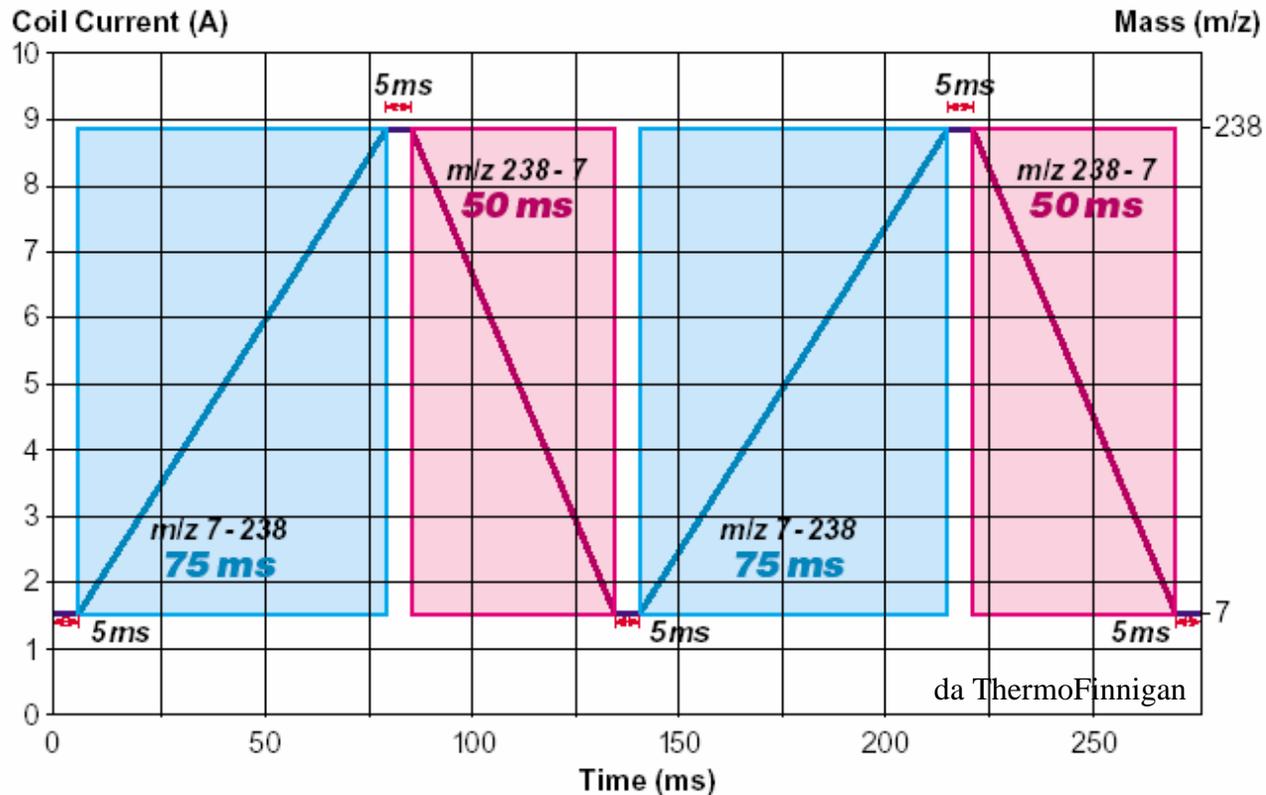
Magnetic sector



Settling time $\propto \Delta(m/z)$

$$\frac{m}{e} = \frac{H^2 r^2}{2V}$$

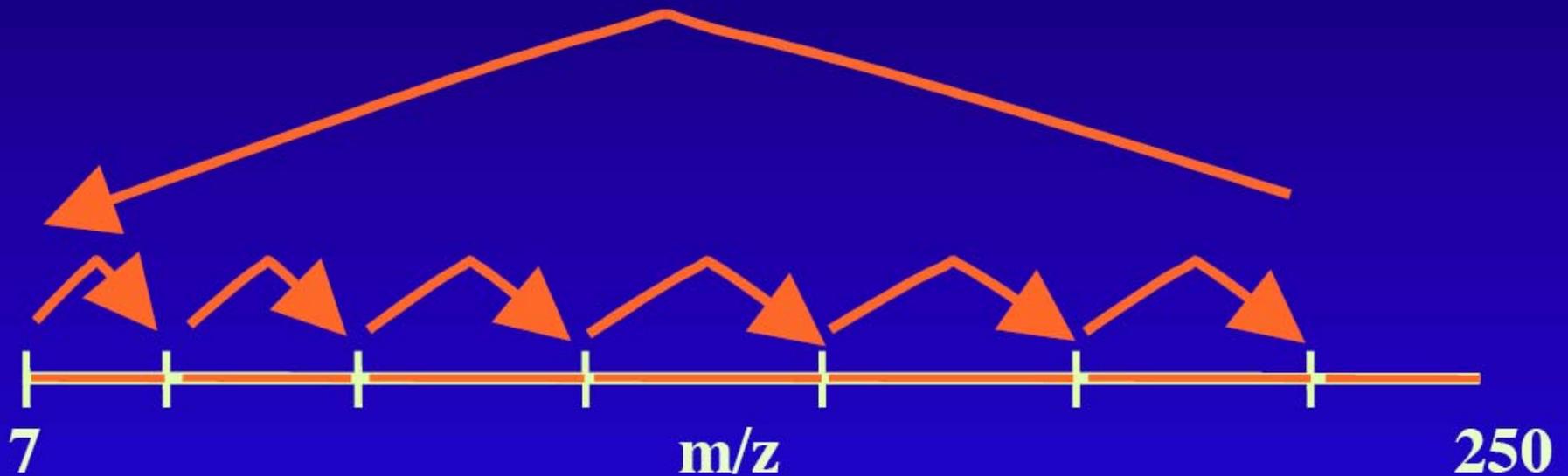
“High power magnet field regulator”



m/z 7-238 **230 ms**

m/z 7-238 **75 ms**

Scan Speed



**Multi-Element Approach
with 6 Magnet Jumps across the whole mass range**

Comparison Scan Speed

Multi-Element Method: 35 isotopes (10 ms each)

Na, Mg, Al, Si, Ar, K, Ca, Ti, Mn, Fe, Co, Cu, Zn, Ga, Sn, I, Cs, Ba, La, Ce, Eu, Tb, Ho, Tm, Lu, Hf, Ta, W, Au, Tl, Pb, Bi, Th, U, ThO

Standard Technology

- 35 x 10 ms
- 29 x 0.001 s (E-Scan)
- 6 x 0.1 s (Magnet Jump)

979 ms total time / cycle

→ 35.8 % measurement cycle

Fast Scanning Technology

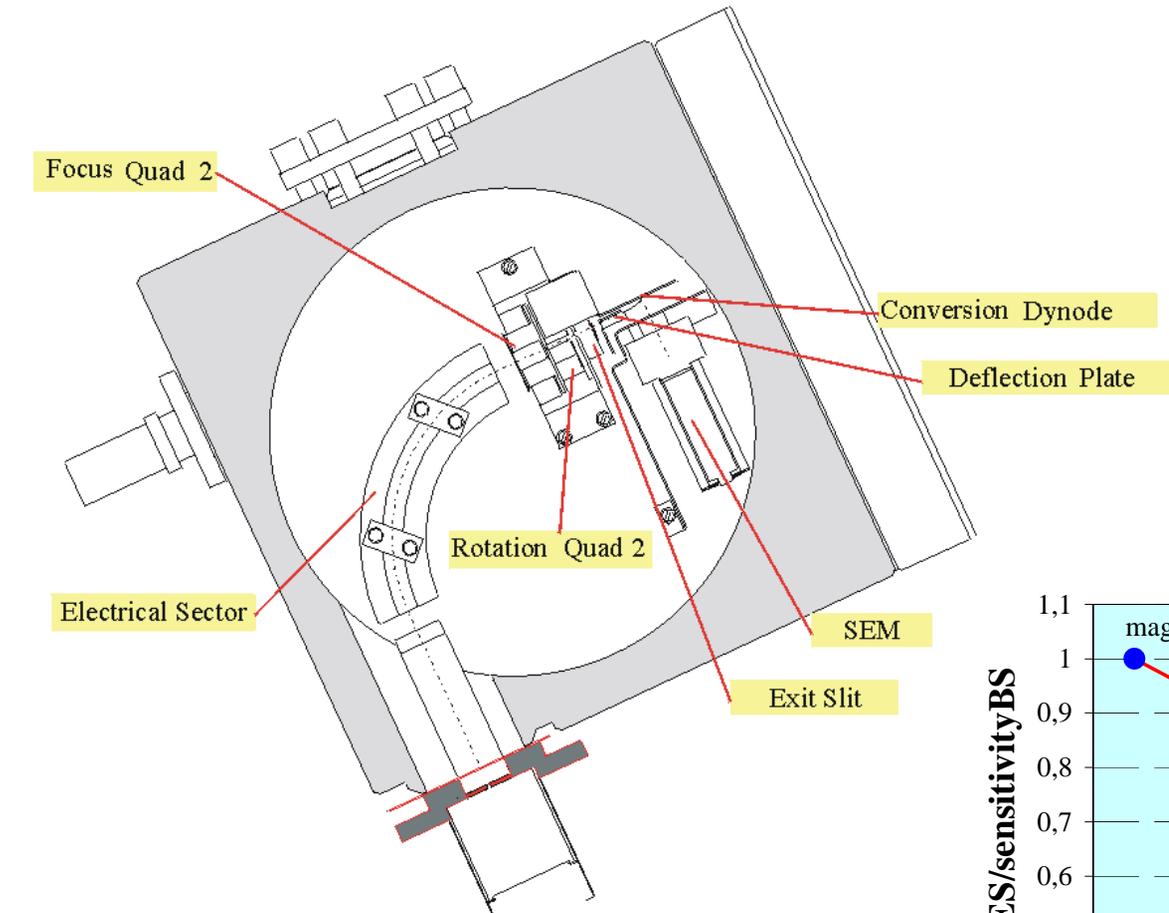
- 35 x 10 ms
- 29 x 0.001 s (E-Scan)
- 6 x 0.022 s (Magnet Jump)

511 ms total time / cycle

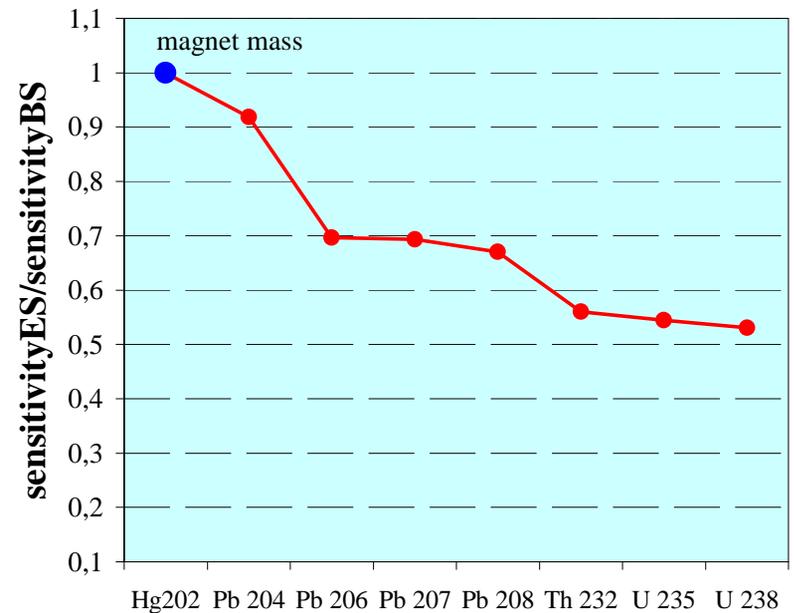
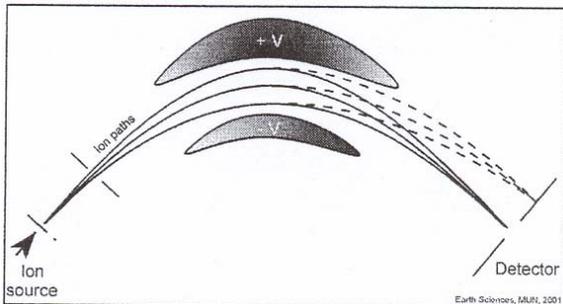
→ 68.5 % measurement cycle

Settore elettrostatico

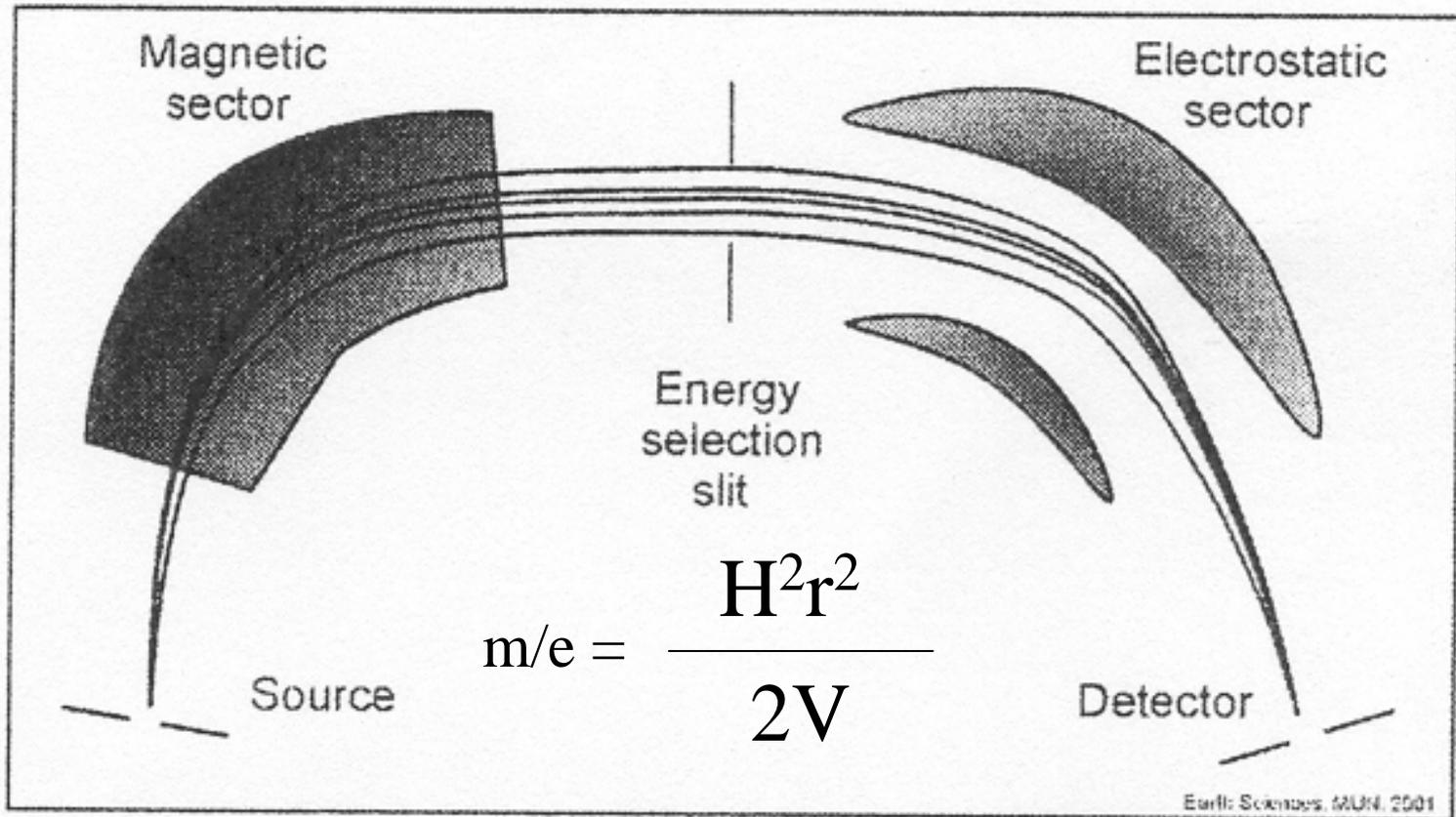
Electrostatic sector
Scan speed: 1 ms/jump



$$\frac{m}{e} = \frac{H^2 r^2}{2V}$$



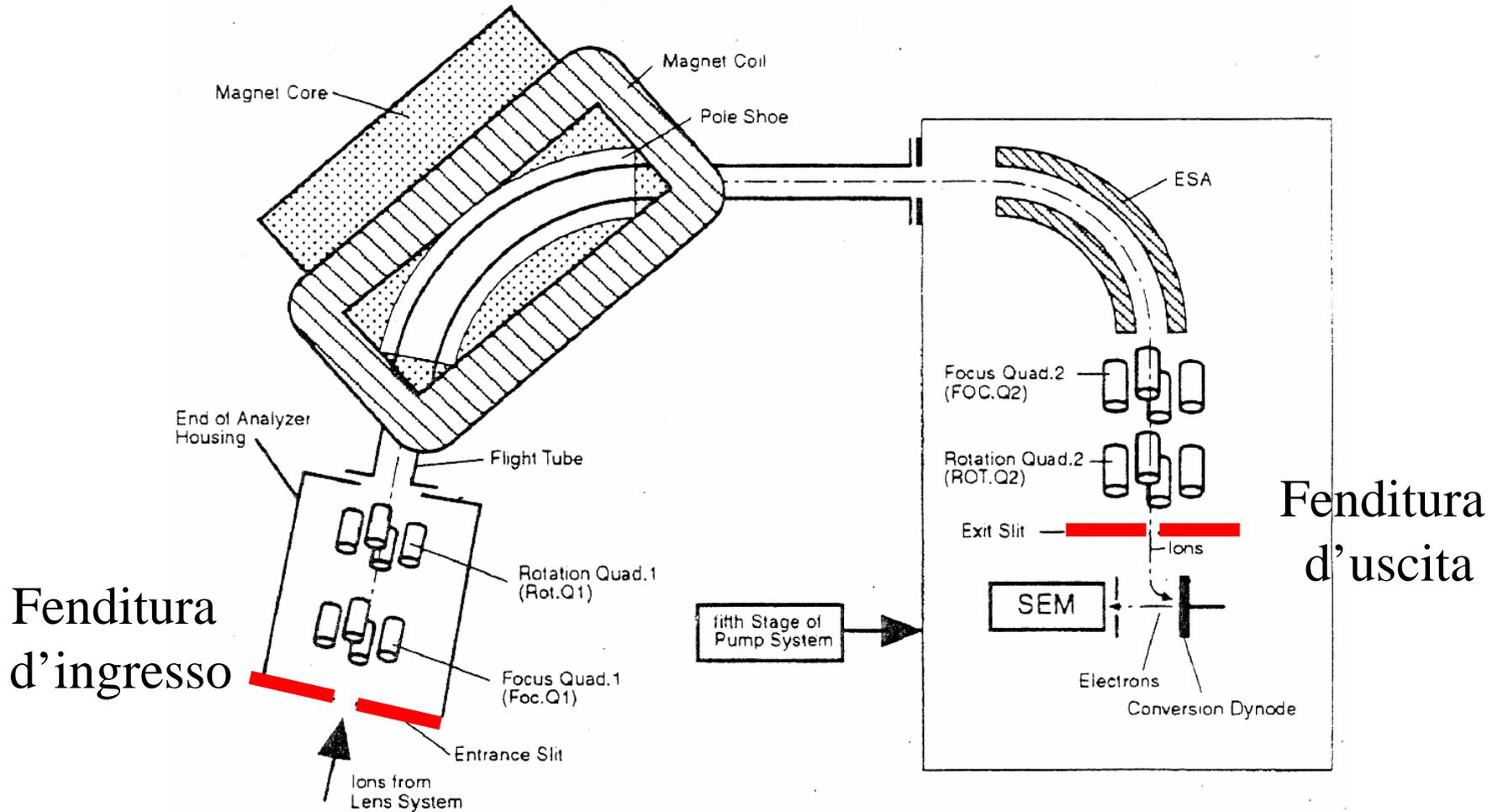
MSA + ESA (doppia focalizzazione)



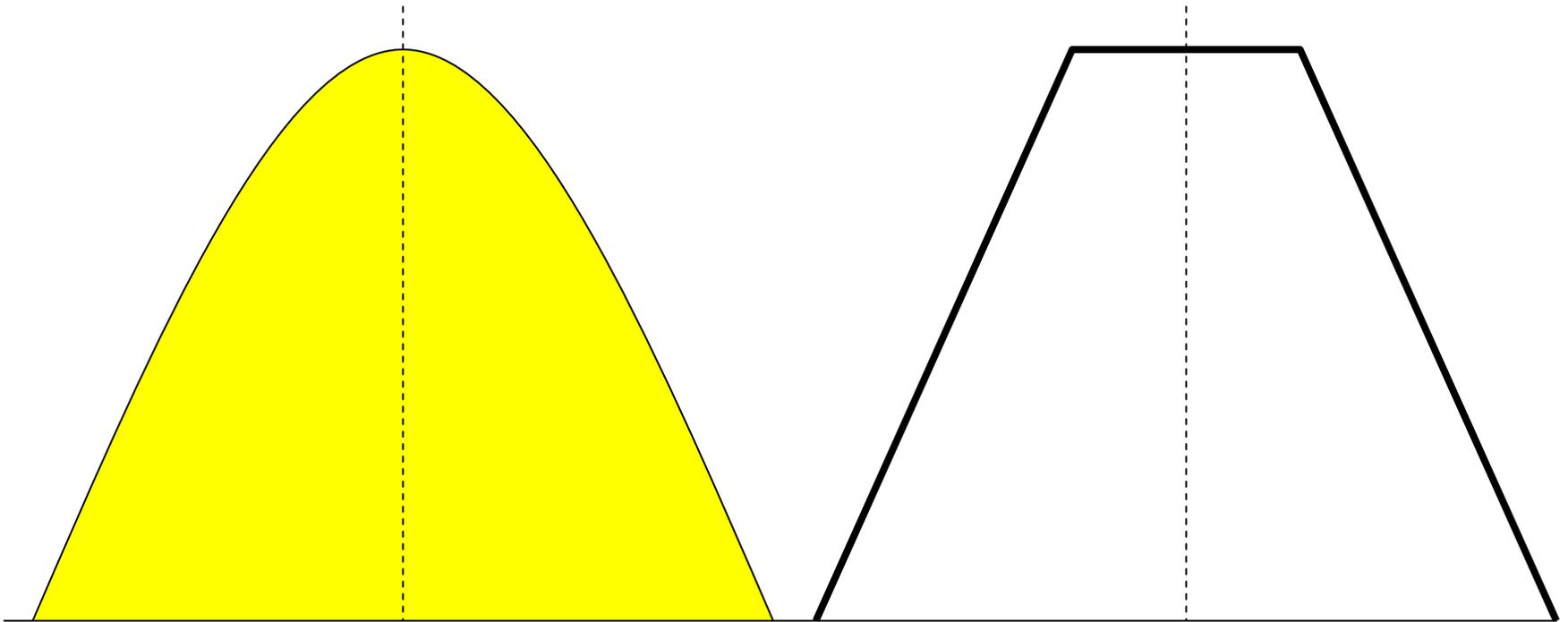
Fenditure ingresso/uscita

Magnet Sector

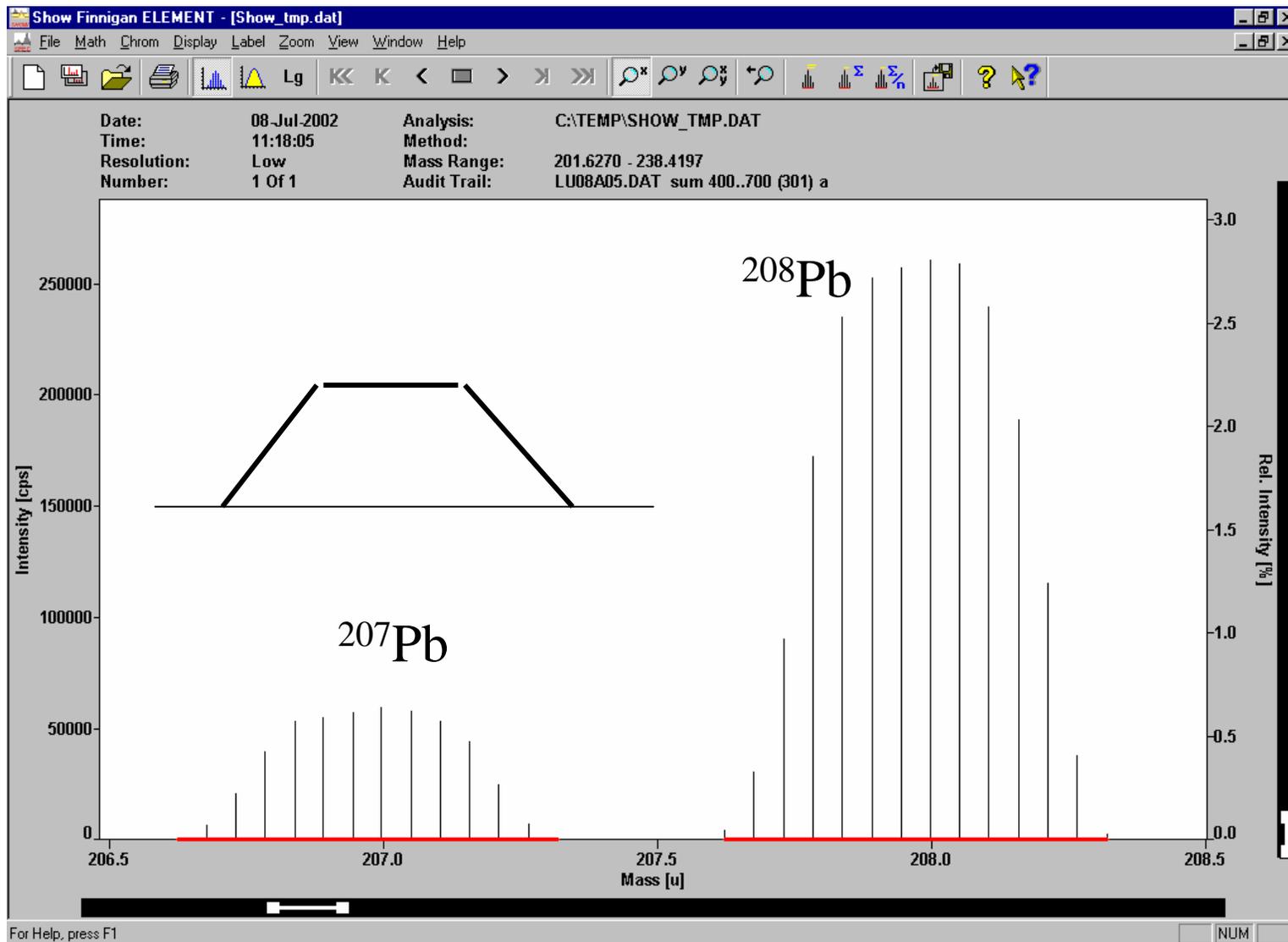
ESA Housing



Peak shape quad vs. sector field

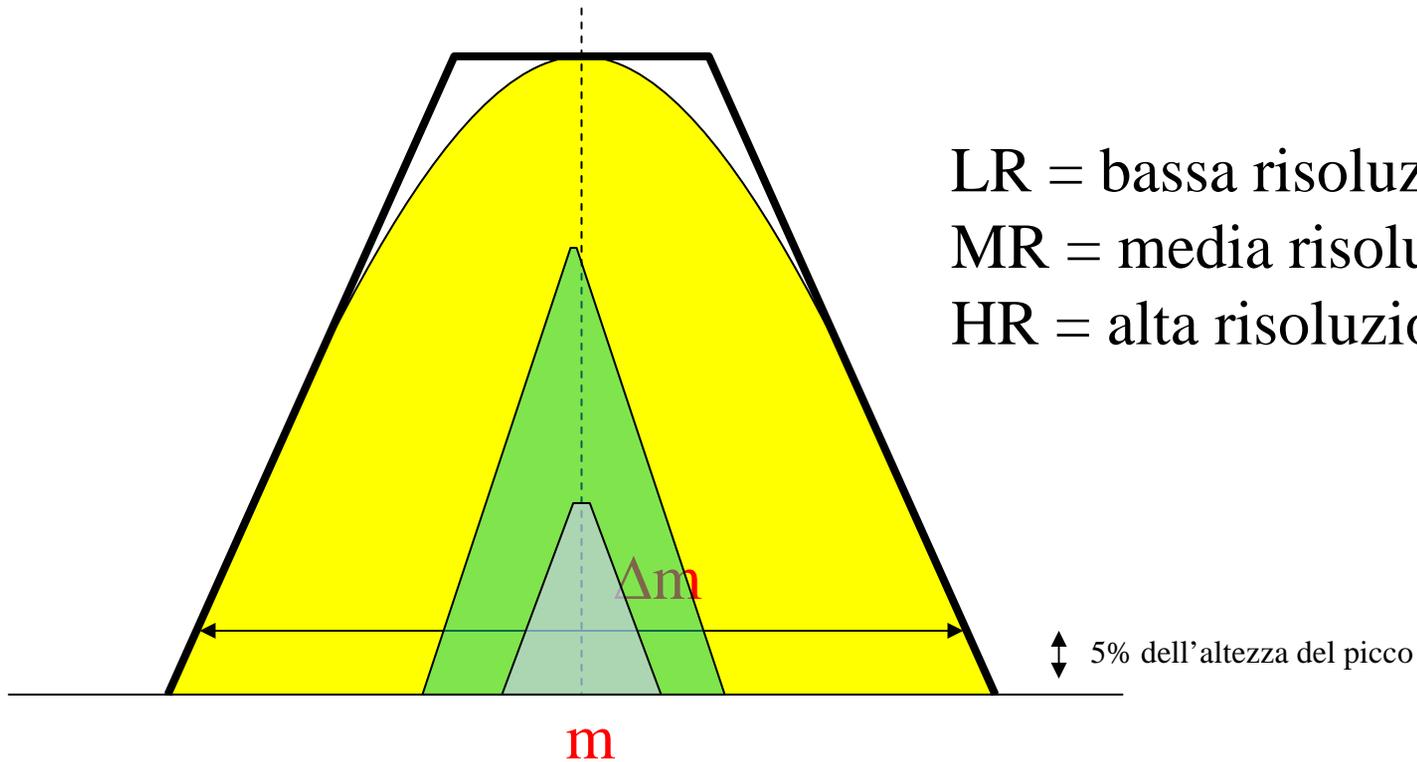


“Flat top” peaks

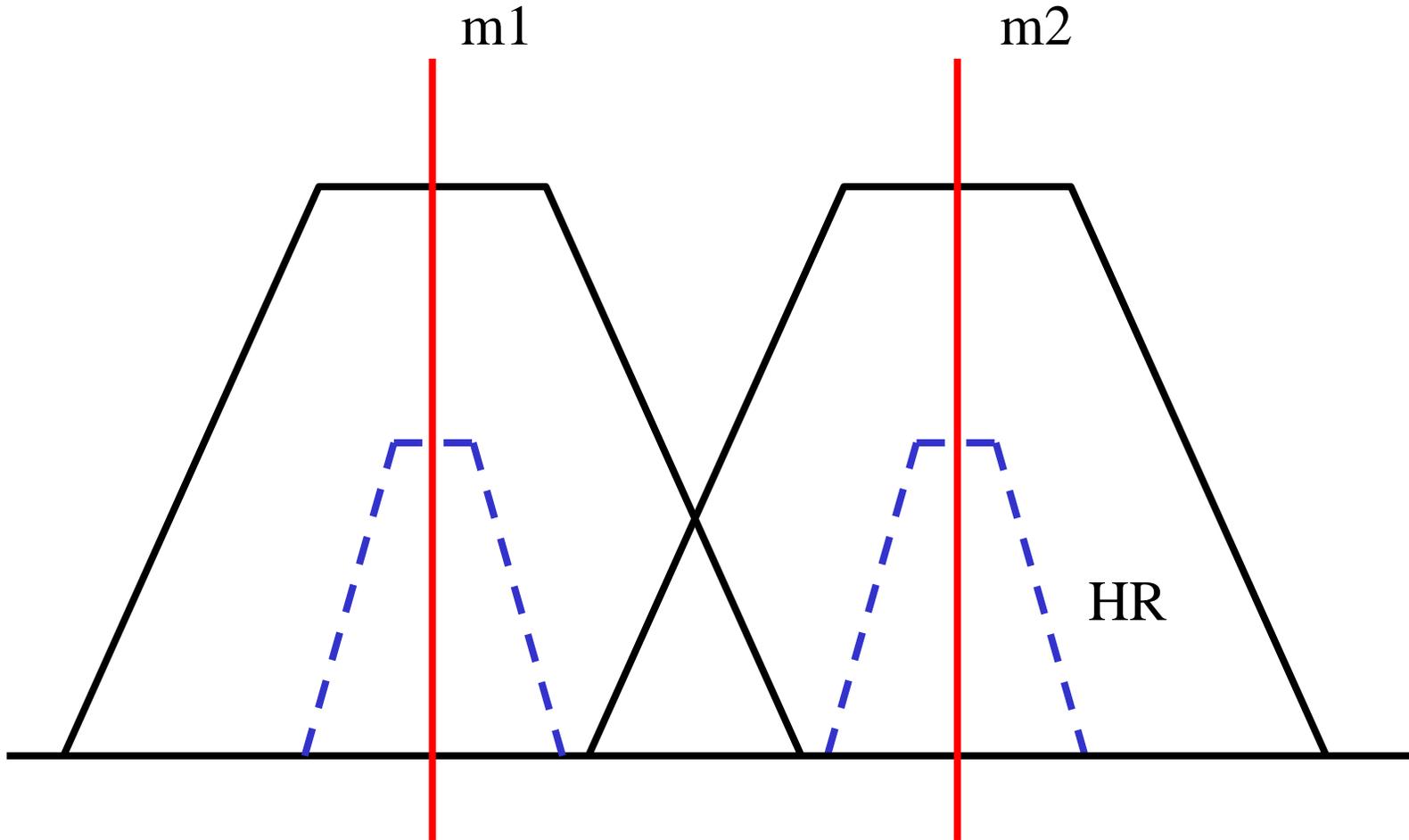


Risoluzione

$$\text{MRP (Mass Resolving Power)} = m/\Delta m$$

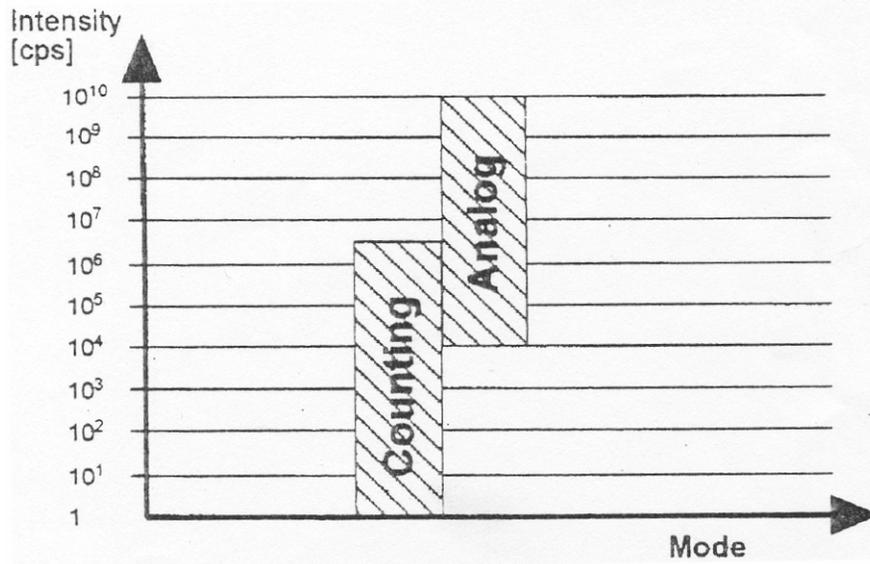
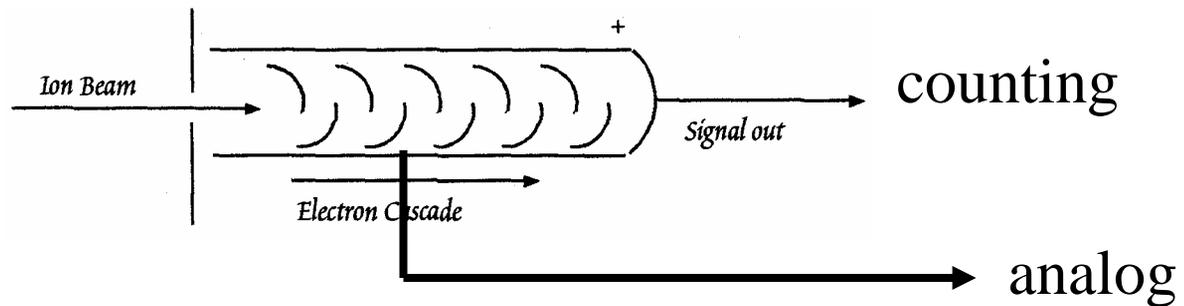


Interferenze

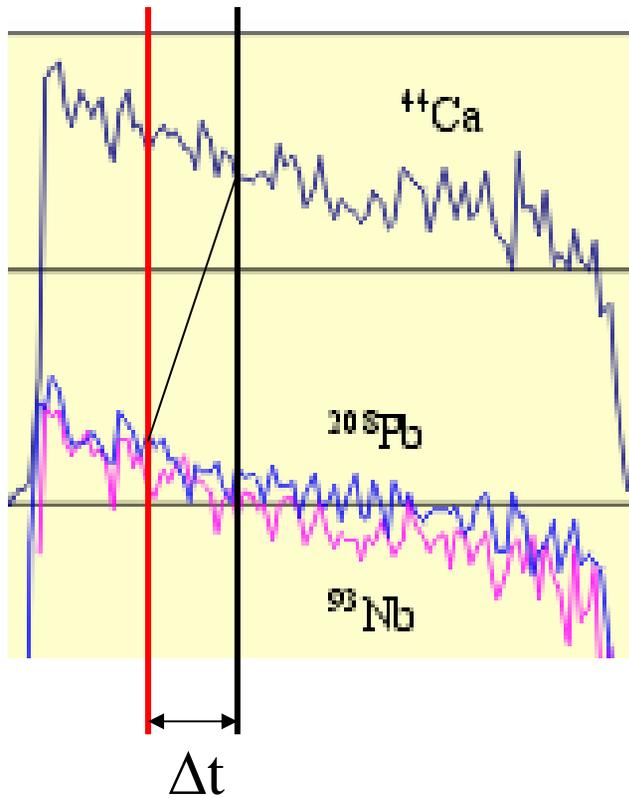


Detector (contatore)

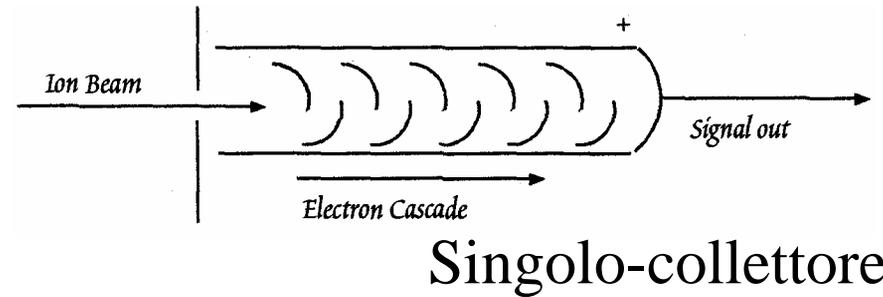
Responsabile del conteggio degli ioni



Acquisizione simultanea vs. Acquisizione sequenziale



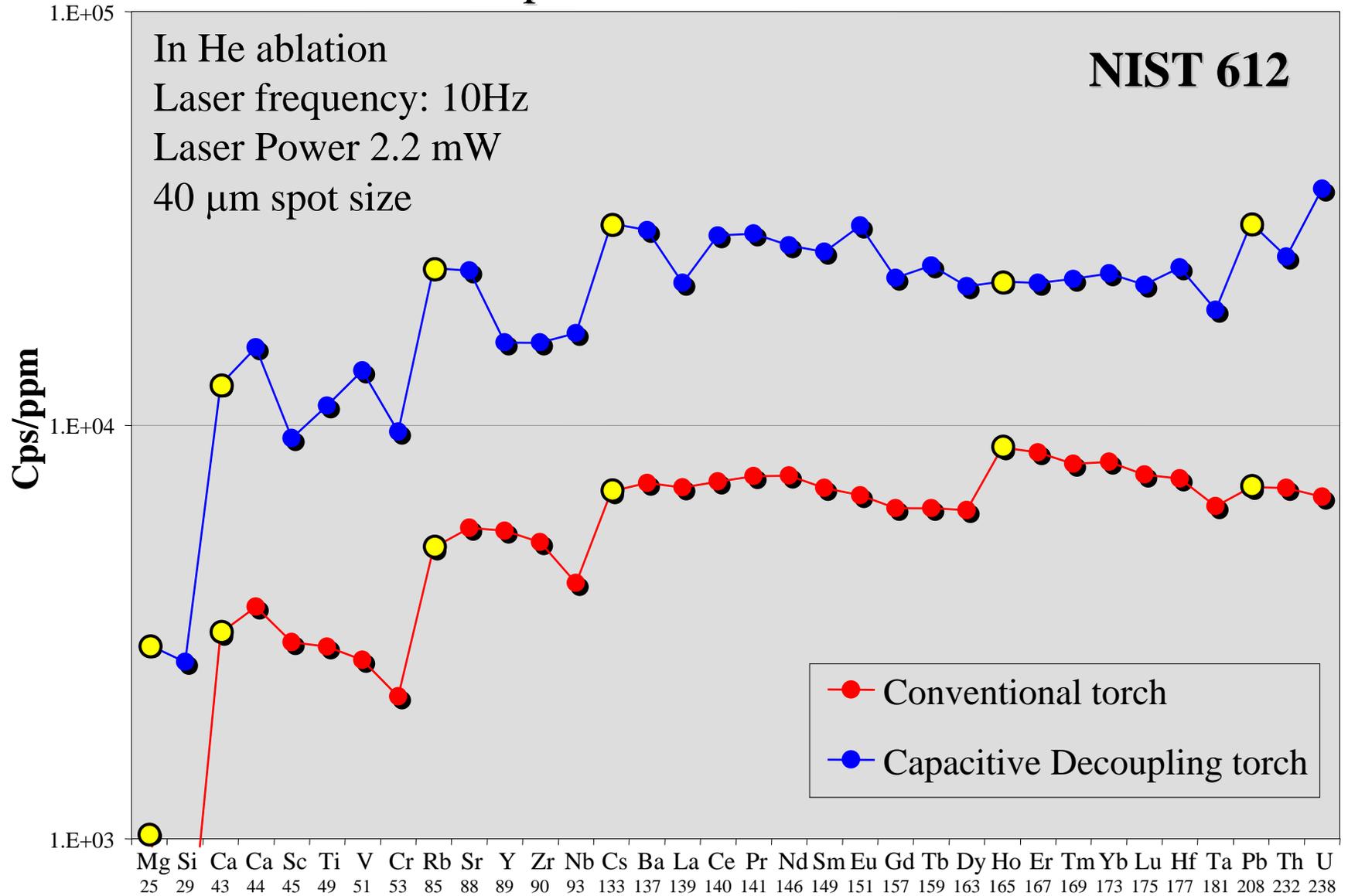
Multi-collettore



$$\left(\frac{^{44}\text{Ca}}{^{208}\text{Pb}}\right)_m = f \left[\Delta t ; \left(\frac{^{44}\text{Ca}}{^{208}\text{Pb}}\right)_s \right]$$

Response curve

Isotopic abundance normalized



Determinazioni elementari

Quantification Strategies

Analytical Task	Possible Solutions
Quantitative	External Standards: Reference Material Samples Matrix Matched (Synthetic) Samples ¹⁾ Dried Aerosol Standard Solutions ²⁾ (Aerosol) Standard Solutions Standard Addition
Semi-Quantitative	External Standards: Reference Material Samples Matrix Matched (Synthetic) Samples Dried Aerosol Standard Solutions (Aerosol) Standard Solutions
Isotope Dilution	Standard Addition
Isotope Ratio	External Standards: Reference Material Samples Dried Aerosol Standard Solutions (Aerosol) Standard Solutions
Signal Ratio	Internal Standardization only

Analisi quantitativa

$$C_i^{SAMP} = \frac{C_i^{STD} \cdot I_i^{SAMP}}{I_i^{STD} \cdot RSF}$$

RSF è uguale per tutti gli elementi in una singola analisi

$$RSF = \frac{C_{is}^{STD} \cdot I_{is}^{SAMP}}{I_{is}^{STD} C_{is}^{SAMP}}$$

Elemento maggiore (livello %)

Elemento presente sia nello standard che nel campione

Elemento multi-isotopo che permetta la scelta di quello a minore abbondanza (segnale meno intenso)

^{43}Ca , ^{29}Si , ^{25}Mg , ^{49}Ti

Limits of detection ($3\sigma_{R_{net}}/S$)

1 ppm

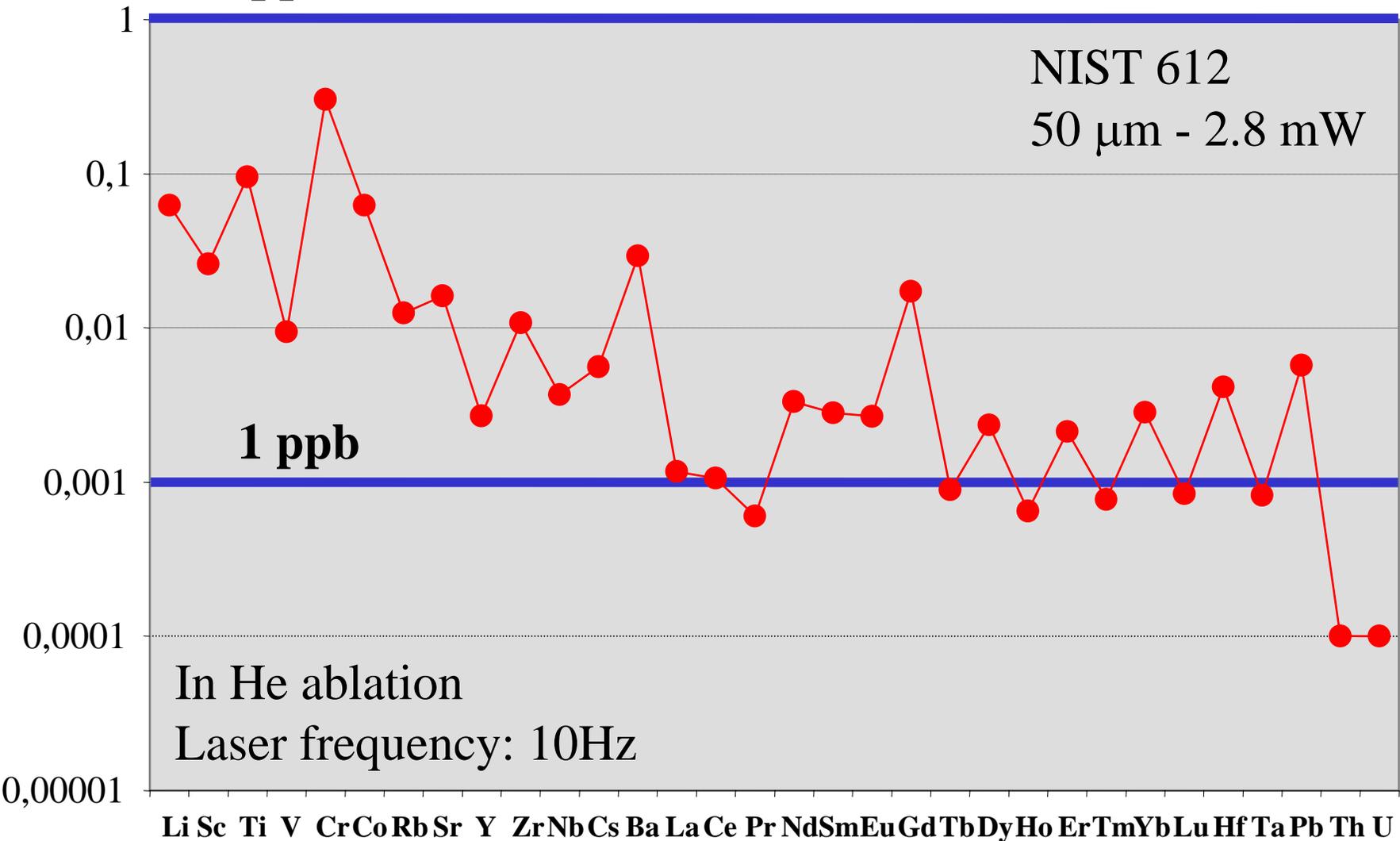
NIST 612

50 μm - 2.8 mW

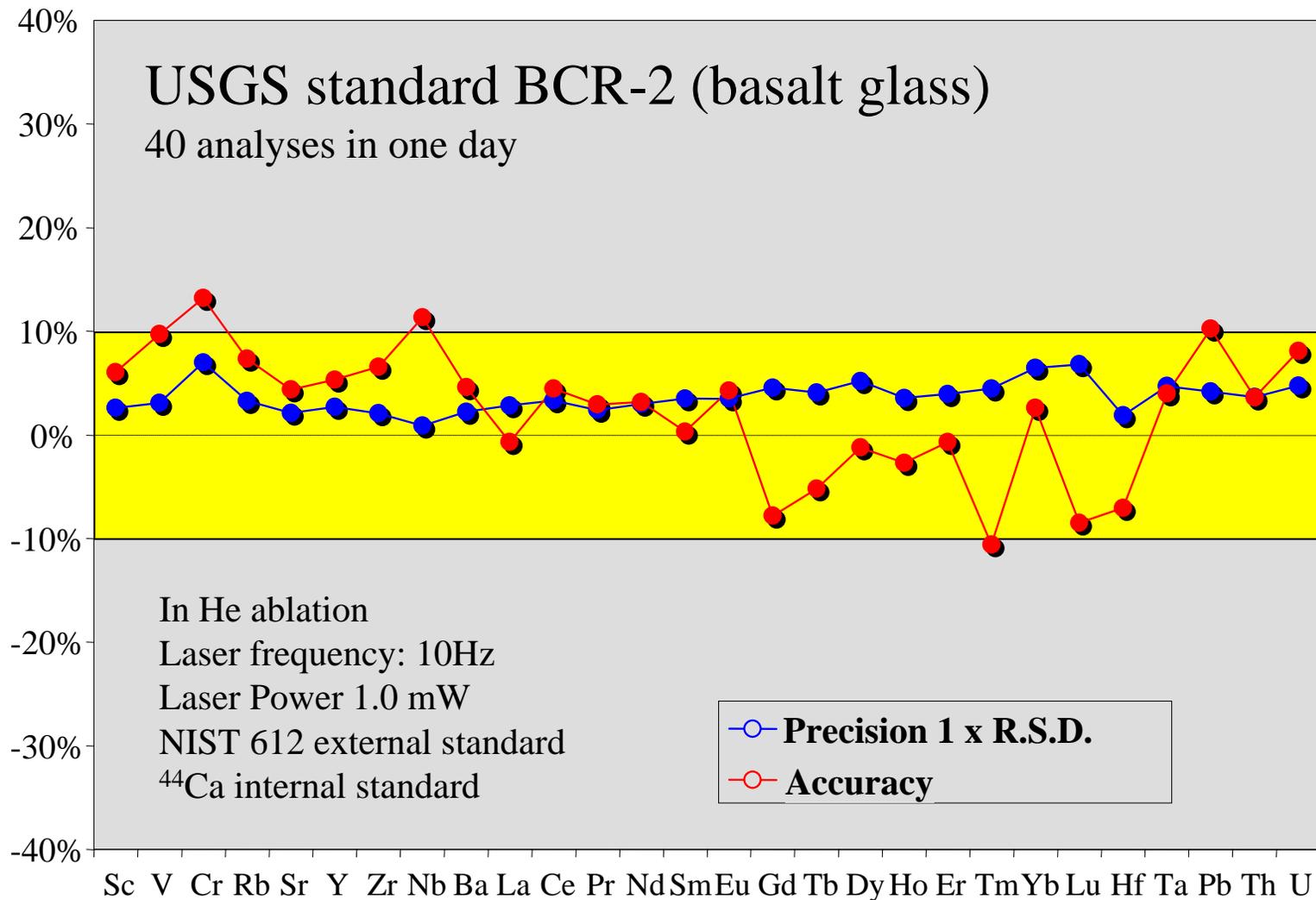
1 ppb

In He ablation

Laser frequency: 10Hz

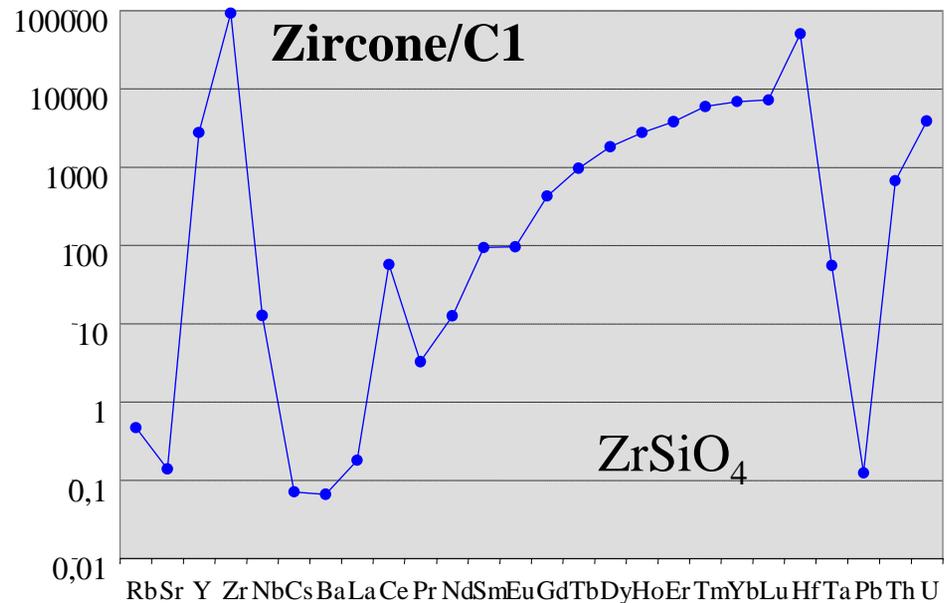
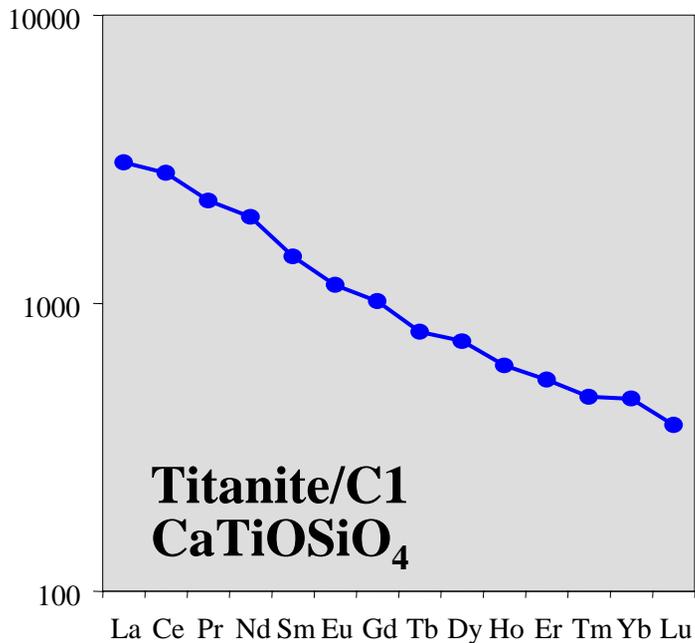
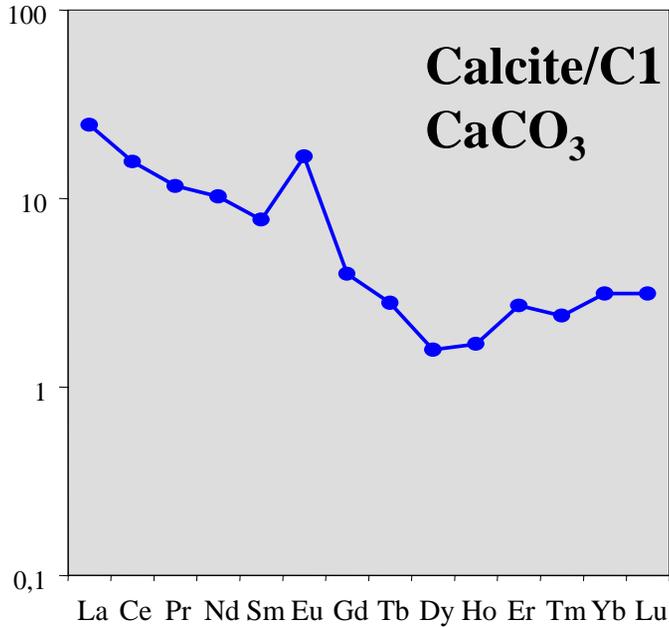


Precision and accuracy at 40 μm spot size

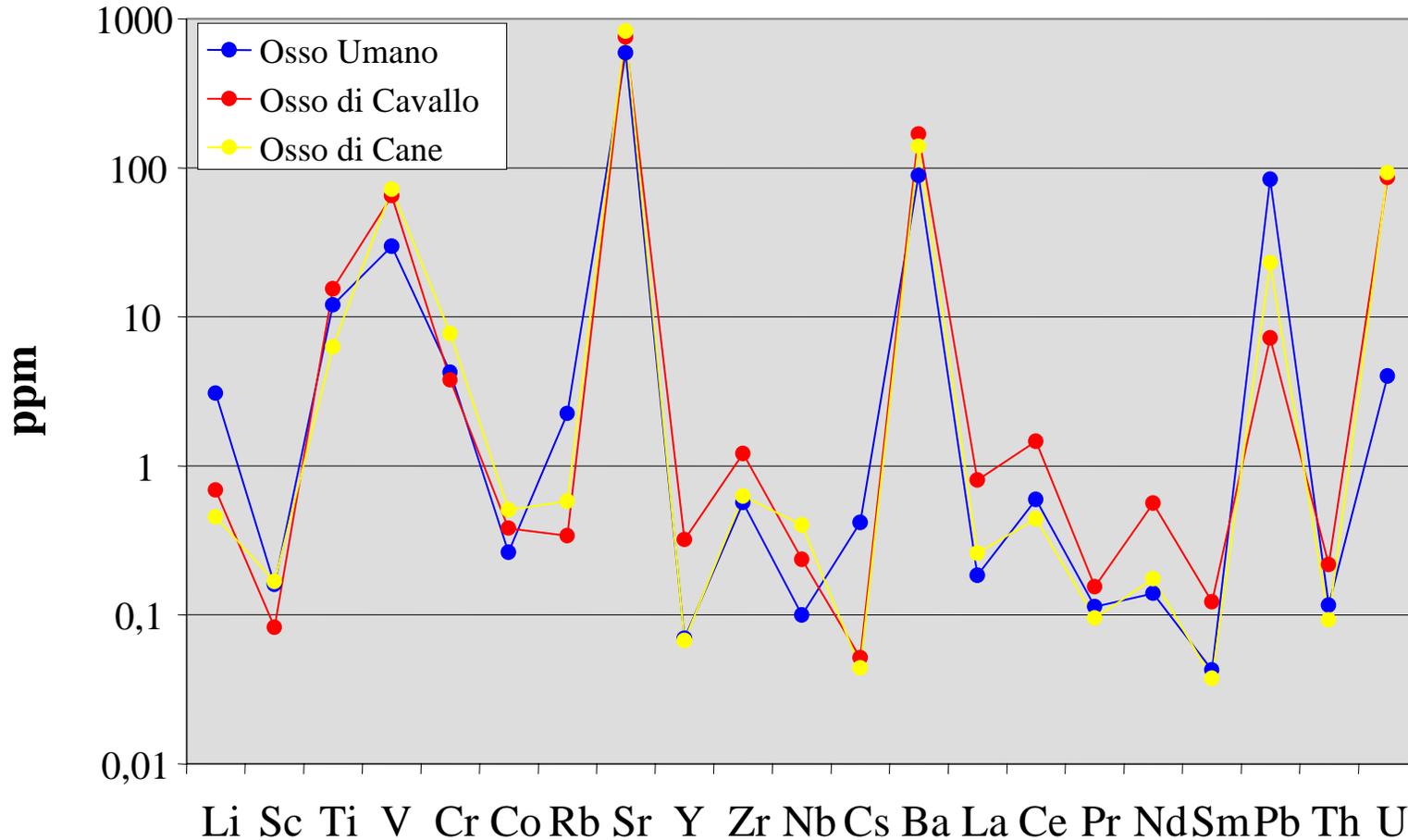


Determinazioni elementari su fasi mineralogiche

Anfibolo – Clinopirosseno –
 Ortopirosseno – Titanite – Calcite –
 Ossidi – Plagioclasio.....

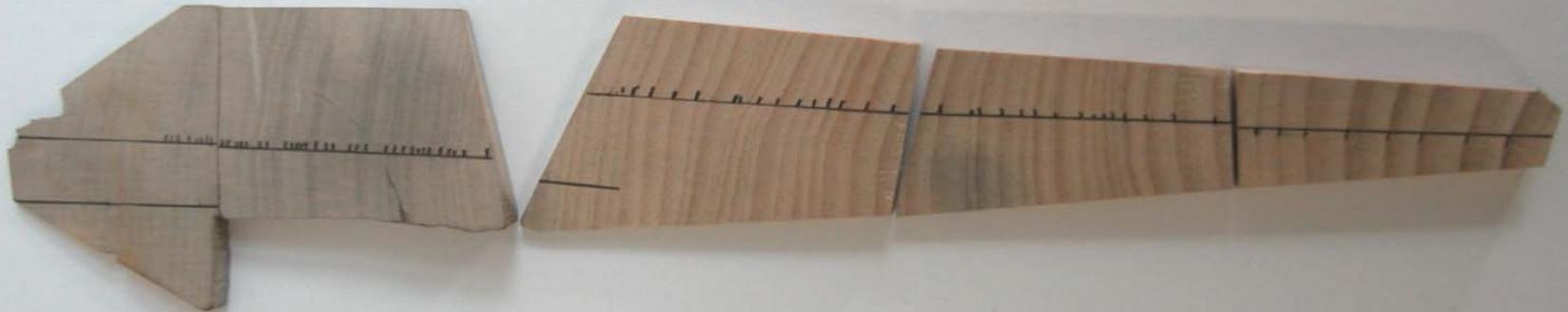


Reperti ossei di età romana



Determinazioni elementari su matrici di interesse ambientale

Quercia centenaria del Parco del Ticino abbattuta nel 2001



2000

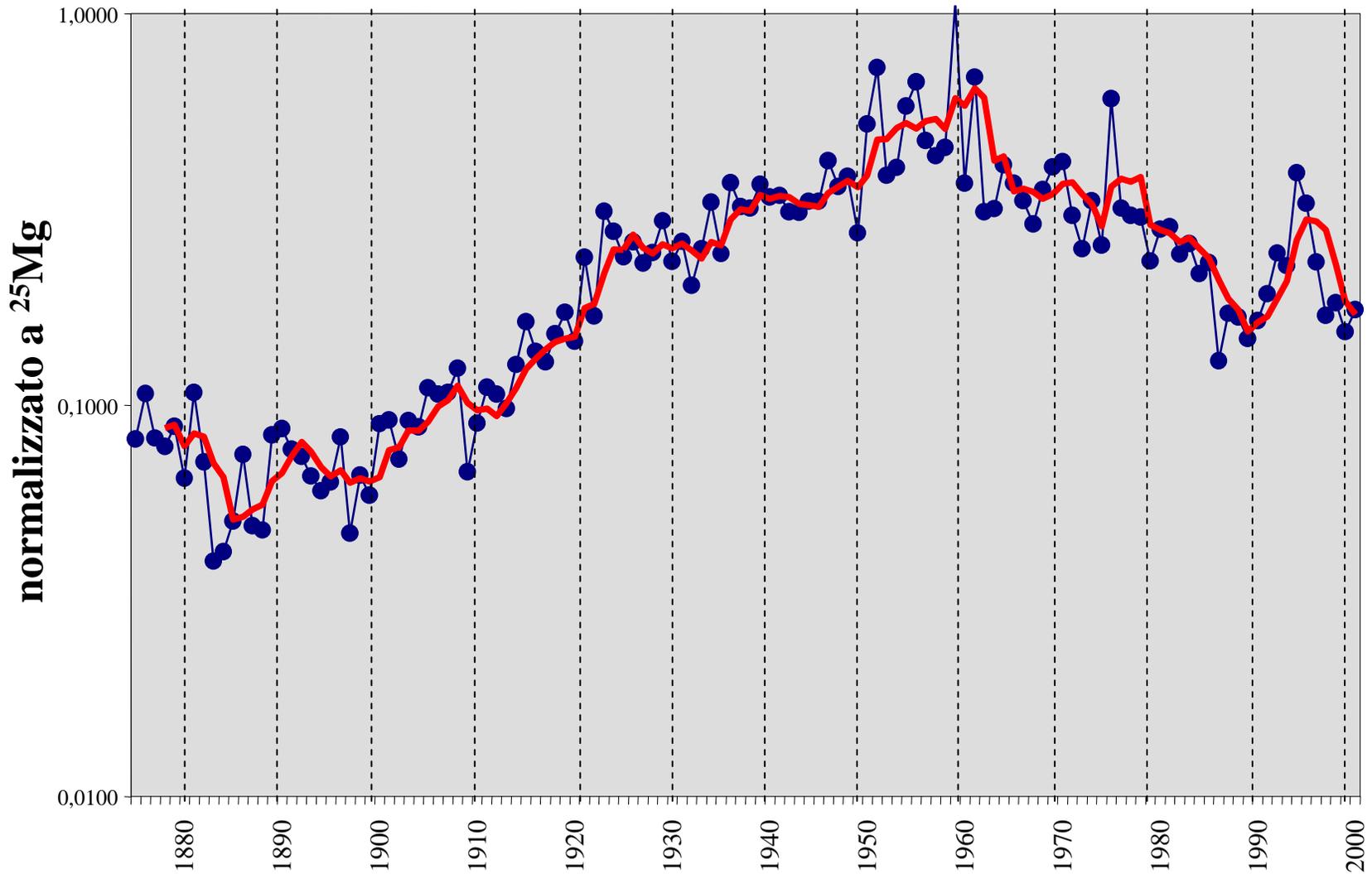
1 spot di 60 μm a cerchio di crescita

1880

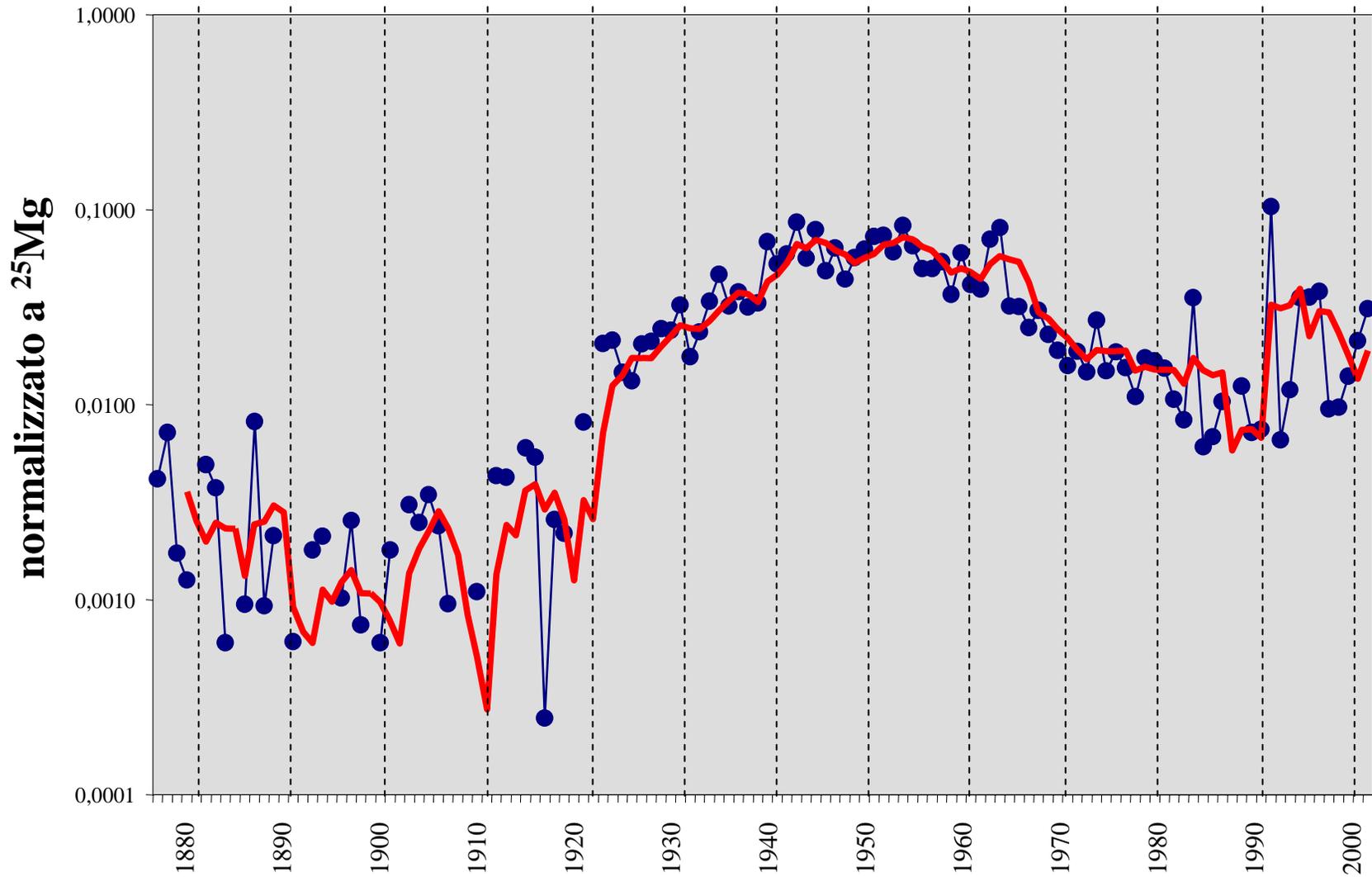


Assenza di standard interno – tutti elementi rapportati al Mg

Pb



V



Rb

