

# Challenges in localized high precision isotope analysis by SIMS

- General context
- IMF, definition and physical meaning
- Sources of isotopic fractionations
  - Collection of secondary ions
  - Ion detection with an EM
  - Potential stabilization at insulating surfaces and ion collection
- Concluding remarks

# Instrumental Mass Fractionation "IMF"

Sample (A,B)

A isotopes  $^1A, ^2A, ^3A$  with  $M_1 < M_2 < M_3$

$C_A = N(A)/[N(A)+N(B)]$  atomic concentration

$C_1 = N(^1A)/N(A), \dots$  bulk isotopic abundances

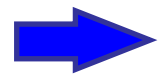
$R_T = C_2/C_1$ , true bulk isotopic ratio

$N_1^-$ : mean number of monatomic secondary ions  $A_1^-$  collected within given angular and energy ranges.

$R_M = N_2^-/N_1^-$  measured ratio  $\longrightarrow R_M \neq R_T$

$$\longrightarrow \text{IMF} \left( ^2A / ^1A \right) = \text{IMF} (2 / 1) = \left( \frac{R_M^{\text{St}}}{R_T^{\text{St}}} - 1 \right) \times 1000$$

IMF( ${}^2A/{}^1A$ ), ... are **matrix dependent** in general



- 1) Experimental determination of IMF on a standard of the same type as the unknown sample
- 2) Measurement of  $R_M^S$  on the unknown sample and determination of the true bulk ratio  $R_T^S$  by

$$R_T^S(\text{unknown}) = \frac{R_M^S}{1 + \text{IMF}(\textit{standard})/1000}$$

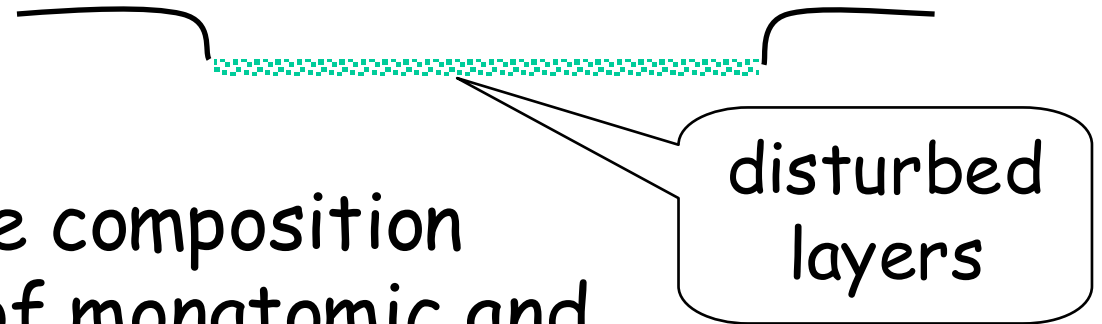
# Where are the problems ?

- ◆ Need of a large set of standards with same chemical state
- ◆ Reproducibility is not always good,...
- ◆ Better precision and accuracy are highly desirable  $10^{-4}$  (0.1‰) instead of  $10^{-3}$  (1‰)
- ◆ ...

# " Rewriting " IMF

$N_p$  impacts of primary ions remove  $N_T$  target atoms

Dynamic Steady State



$N_T$  atoms reproduce sample composition  
**Sputtered phase** is made of monatomic and polyatomic species: A, B,  $A_n$ ,  $B_m$ ,  $A_pB_q$ ,....

$N^*(^1A)$  mean number of isotopes  $^1A$  sputtered as **monatomic species in given angular and energy ranges.**

$$N_1^* = N^*(^1A) = N_1^0(^1A^0) + N_1^-(^1A^-) + N_1^+(^1A^+)$$

**Ionization Probabilities**  $P_1(^1A^-) = \frac{N_1^-}{N^*(^1A)}, \dots$

Isotopic ratio  $\rightarrow R_M = \frac{P_2 N^*(^2A)}{P_1 N^*(^1A)}$

For a given element a first order approximation may be :

$$P_2 = P_1 + dP \rightarrow \frac{P_2}{P_1} \cong \left( 1 + \frac{dP}{P} \right) \text{ with } \frac{dP}{P} \ll 1$$

*Limited expansion of  $P(En, Ang, M, Q)$  with  $M/M$*

En: energy, Ang: angle, Q: matrix

$$\frac{dP}{P} \cong h(En, Ang, Q) \frac{\Delta M}{M} \quad \frac{P_2}{P_1} \cong \left( 1 + h \frac{\Delta M}{M} \right)$$

*How much different from  $C_2/C_1$  are ratios like  $N^*(^2A)/N^*(^1A)$ ?*

Similarly

$$\frac{N^*(^2A)}{N^*(^1A)} \cong \frac{C_2}{C_1} \left( 1 + g(\text{En, Ang, Q}) \frac{\Delta M}{M} \right)$$

$$R_M = \frac{P_2}{P_1} \frac{N^*(^2A)}{N^*(^1A)} \rightarrow R_M \cong \left( 1 + (h + g) \frac{\Delta M}{M} \right) \frac{C_2}{C_1}$$

$$\text{IMF}(2/1) = \left( \frac{R_M}{(C_2/C_1)} - 1 \right) \times 1000 \rightarrow \text{IMF}(2/1) \cong (h + g) \frac{\Delta M}{M}$$

*In the case of 3 isotopes*

If  $M_2 = M_1 + 1$  and  $M_3 = M_1 + 2$   IMF(3/1) 2·IMF(2/1)

*Comparing samples  $S^a, S^b, S^c, \dots$  with known*

$$R_T^a(2/1), \dots, R_T^b(2/1), \dots, R_T^c(2/1), \dots$$

$$\Rightarrow \delta_a^b(2/1) = \left( \frac{R_T^b(2/1)}{R_T^a(2/1)} - 1 \right) \times 1000, \dots$$

*If  $S^a$  and  $S^b$  belong to the same isotopic reservoir:*

$$\delta_a^b(2/1) \cong f \frac{\Delta M}{M} \quad \Rightarrow \quad \delta_a^b(3/1) \cong 2 \cdot \delta_a^b(2/1)$$

*Taking sample  $S^a$  as a reference:*

$$\Delta_{(a)}^b(2/1) \cong \left( \frac{R_M}{R_T^a} - 1 \right) \times 1000$$

*If  $S^a, S^b, S^c, \dots$  are of the same type:*

$$\text{IMF}(a; 2/1) = \text{IMF}(b; 2/1) = \text{IMF}(c; 2/1), \dots$$



# Secondary Ion Beam Definition

- ◆ Magnetic Sector Spectrometer

- Entrance Diaphragm (or slit) ED
- Aperture Stop FA
- Energy Slit ES

Mass  
Resolving  
Power

- ◆ Collection Optical System

- Immersion Lens + Transfer Lens

- ◆ ED and FA :

- determine collection angles and analyzed areas

# Immersion Lens Highlights

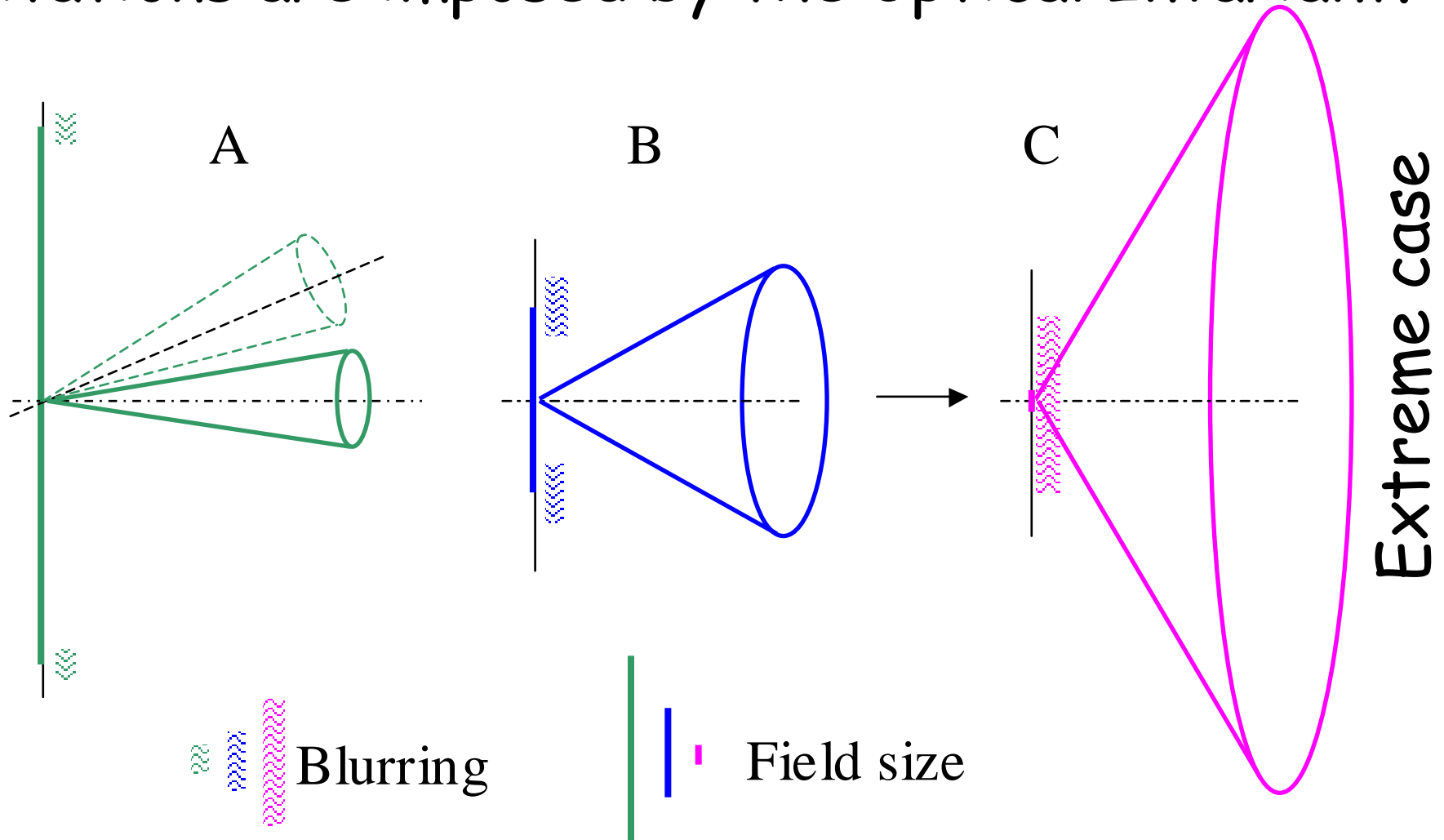
- ◆ High Extraction Voltage
  - ↑ Reduction of angular divergence of emitted ions and relative energy dispersion
- ◆ Direct ion images of the sample surface
- ◆ Exit pupil or Crossover, which is also a rotation center
  - ↑ Collection solid angle, same for all image points
  - ↑ Aberration control on image points

## Warning

The sample surface is the first "electrode". Any local geometry or potential change will modify the potential distribution and therefore the optical properties.

# Transfer Optical System

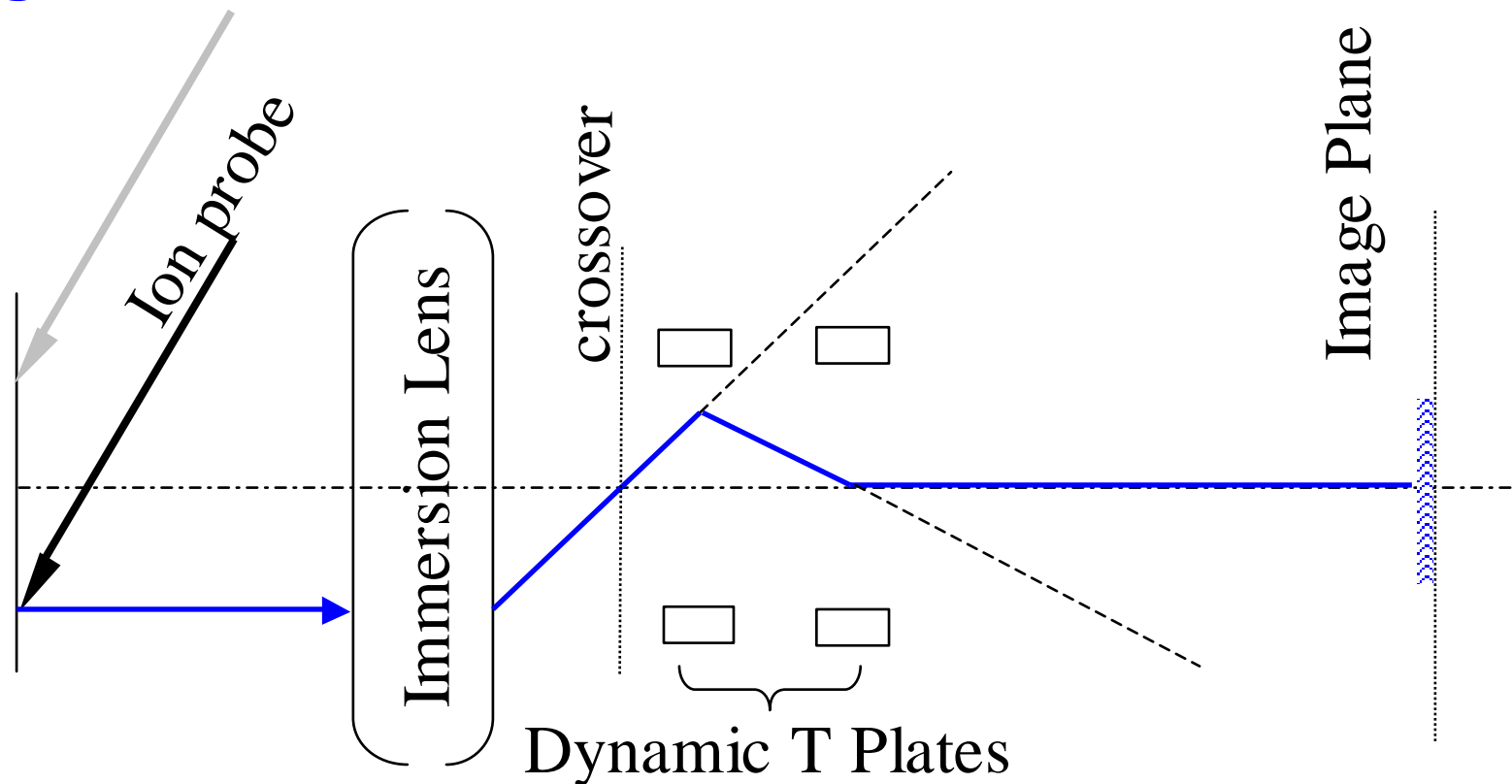
- Transport of crossover and image on ED and FA with adjustable magnifications. ED and FA are fixed for a given MRP.
- Limitations are imposed by the Optical Invariant.



**Intrinsic Collection Efficiency "ICE"** is referred to a point, ICE increases with the collection solid angle.

ICE ↗ Blurring ↗ Field size ↘

**Dynamic transfer** allows to extend high ICE values to large fields and high MRP with an ion probe (**scanning ion imaging**)



- ◆ Each time a diaphragm edge cuts the secondary beam there is a risk for isotopic fractionation because of changes in collection parameters.
- ◆ **Weak permanent magnetic fields** may mass disperse the secondary beam before its definition by ED and FA and produce insidious isotopic fractionation.
- ◆ The increase of ICE, useful for local analysis, may emphasize **Quasi Simultaneous Emission of ions, QSE**

# QSE and direct ion yield K

$K = (\text{number of collected ions}) / (\text{primary ion impact})$

$K = 1$

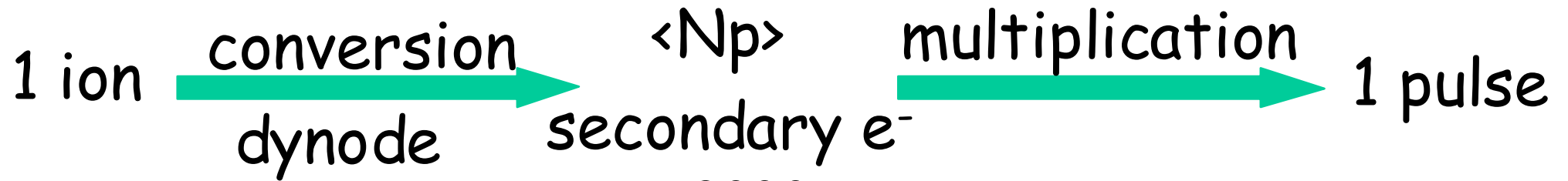
Number of ions/ impact	0	1	2	3	4
Probability (Poisson) (%)	36.8	36.8	18.4	6.1	1.5

1 Event 1, 2, 3,... ions ejected per impact ( 1ps)

$1 - P(0)$ , probability for 1 Event to occur 63.2%

Ions/ Event	1	2	3	4
Probability (%)	58	29	9.7	2.4

# Detection with an electron multiplicateur



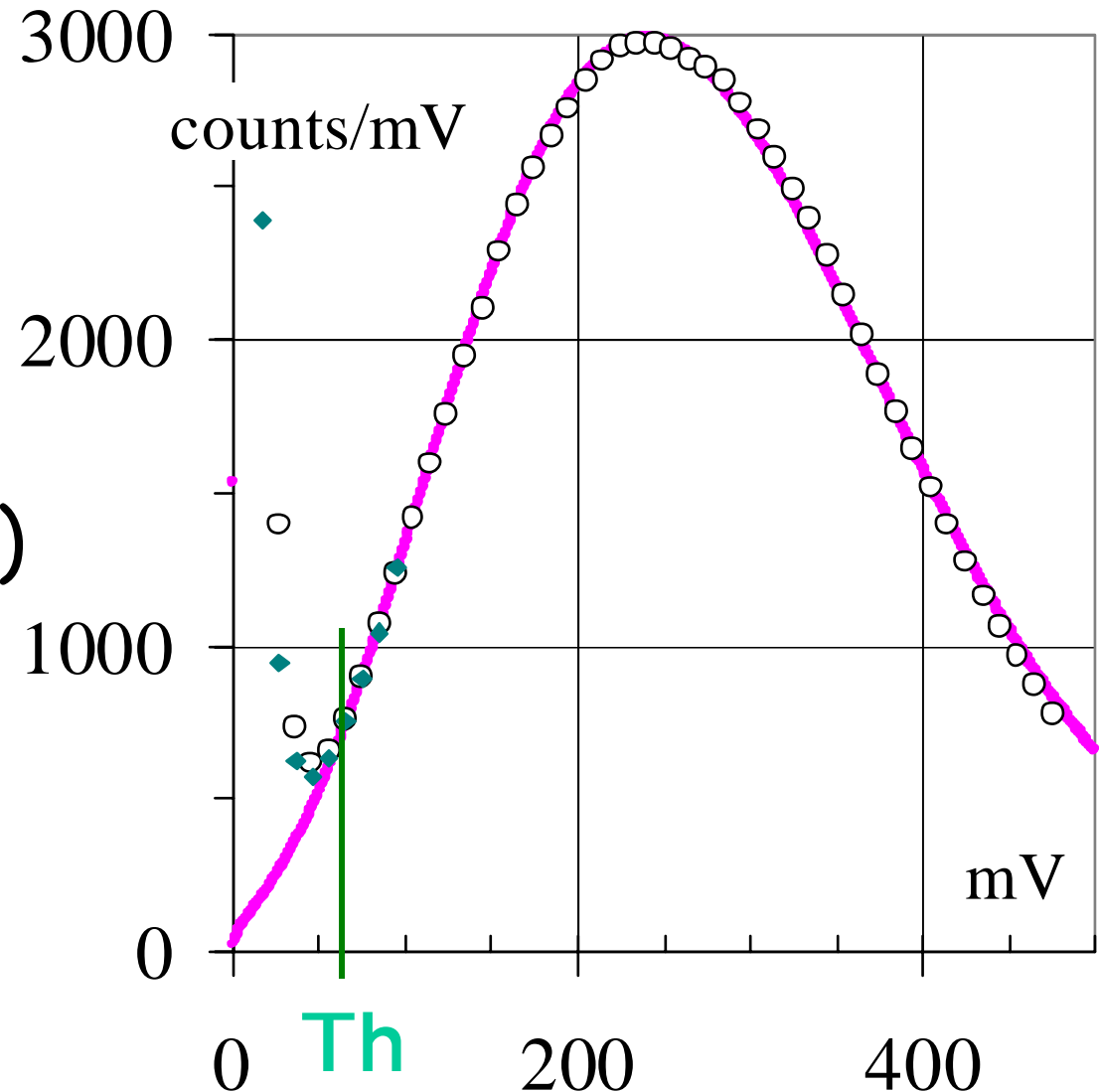
## Pulse Height Distribution PHD

Experimental points  
(o: 5mV,  $\diamond$ : 1 mV step)

— : Calculated PHD

$^{28}\text{Si}$  ions

(Np 7.4, Ne 2.7)

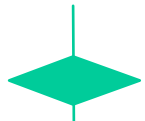


# Detection Quantum Efficiency DQE

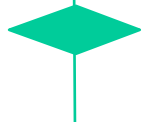
$$\text{DQE} = (\text{nb of pulses} > \text{Th}) / (\text{nb of incoming ions})$$

DQE(Th) depends upon:

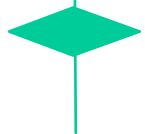
- $\langle N_p \rangle$



Isotope mass



Impact position on conversion dynode



Conversion dynode wearing out

- Global gain (decreasing with dose)

# Modeling PHDs

Fitting experimental PHDs with a semi empirical algorithm based upon Poisson statistics

Parameters:  $\langle N_p \rangle$  and  $\langle N_e \rangle$  (electron /electron yield)

## EM isotopic fractionation

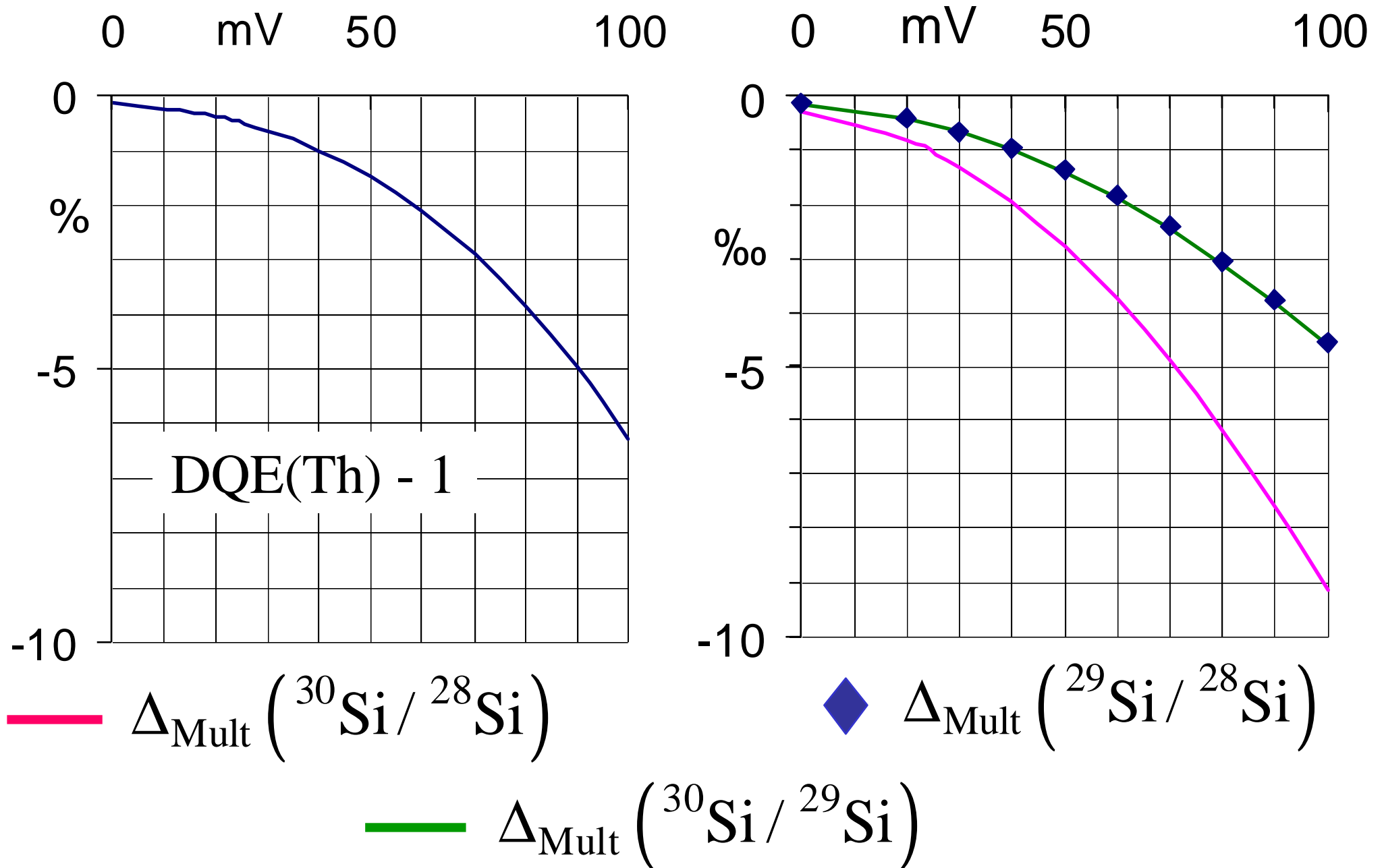
$$N_{p1} > N_{p2} > N_{p3}$$

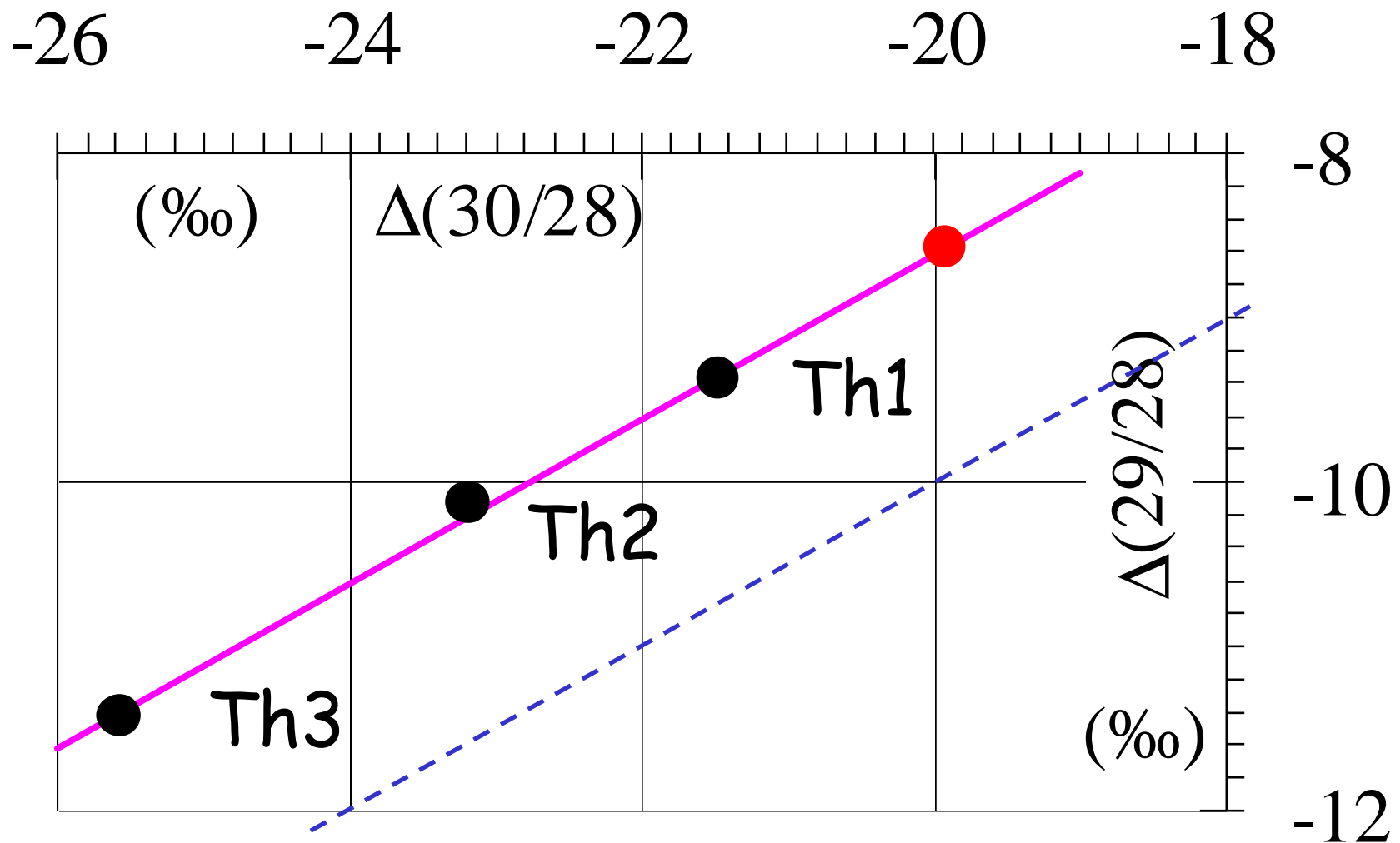
For isotopes of a given element

$$\frac{\Delta N_p}{N_p} = \alpha \frac{\Delta M}{M}$$

$$\Delta_{\text{Mult}}(2/1) = \left( \frac{\text{DQE}(\text{Th}, {}^2\text{A})}{\text{DQE}(\text{Th}, {}^1\text{A})} - 1 \right) \times 1000, \dots$$

# Linear mass fractionation





Th1 44mV, Th2 68mV, Th3 94mV and Max 240mV

This algorithm can be used to "reconstruct" lost information in conversion and amplification ( ● )

# Sources of "non linear" discriminations

- ➔ Dead time
- ➔ Quasi Simultaneous Arrivals, **QSA**
- ➔ Different impact areas for different isotopes on the conversion dynode
- ➔ Conversion Dynode Heterogeneity
- ➔ Not yet identified,...

# Quasi Simultaneous Arrivals QSA

Ions created in 1ps and in a narrow energy band will, on average, arrive within time intervals on the order of the pulse width.

Events will be recorded as single ion arrivals

Relation between the number  $N_S$  of secondary ions arriving in the detector and the number  $N_E$  of counted events, assuming a Poisson statistics

$$N_S = \frac{K}{1 - e^{-K}} N_E$$

K	1	0.1	0.01	
$N_S/N_E$	1.5820	1.0508	1.0050	$1+K/2$

# Limitations of EM detection

Maximum count rates  $10^6$  counts/s

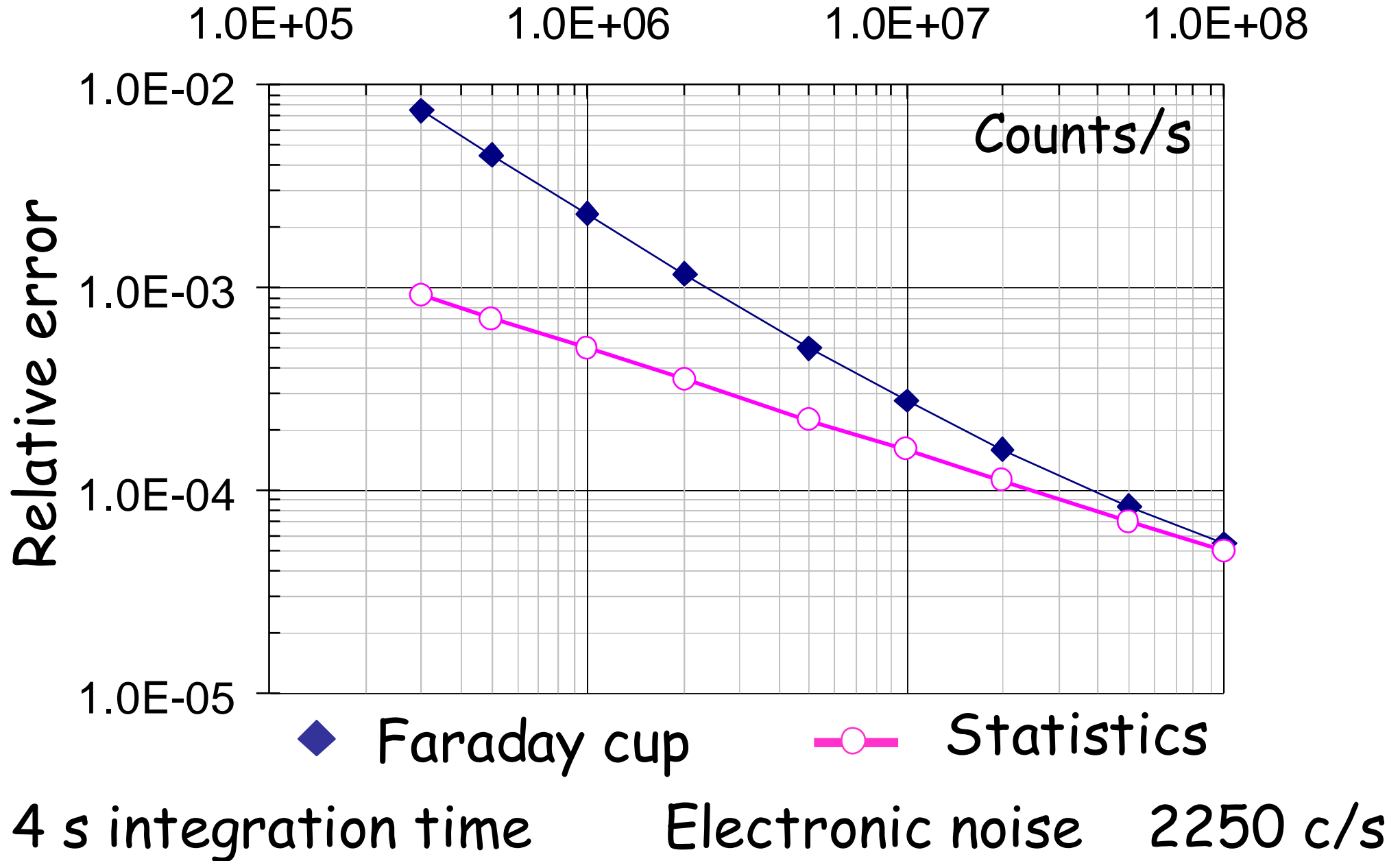
	$^{16}\text{O}$	$^{17}\text{O}$	$^{18}\text{O}$
Counts/s	$10^6$	400	2000
Counts/s	$10^8$	$4 \times 10^4$	$2 \times 10^5$

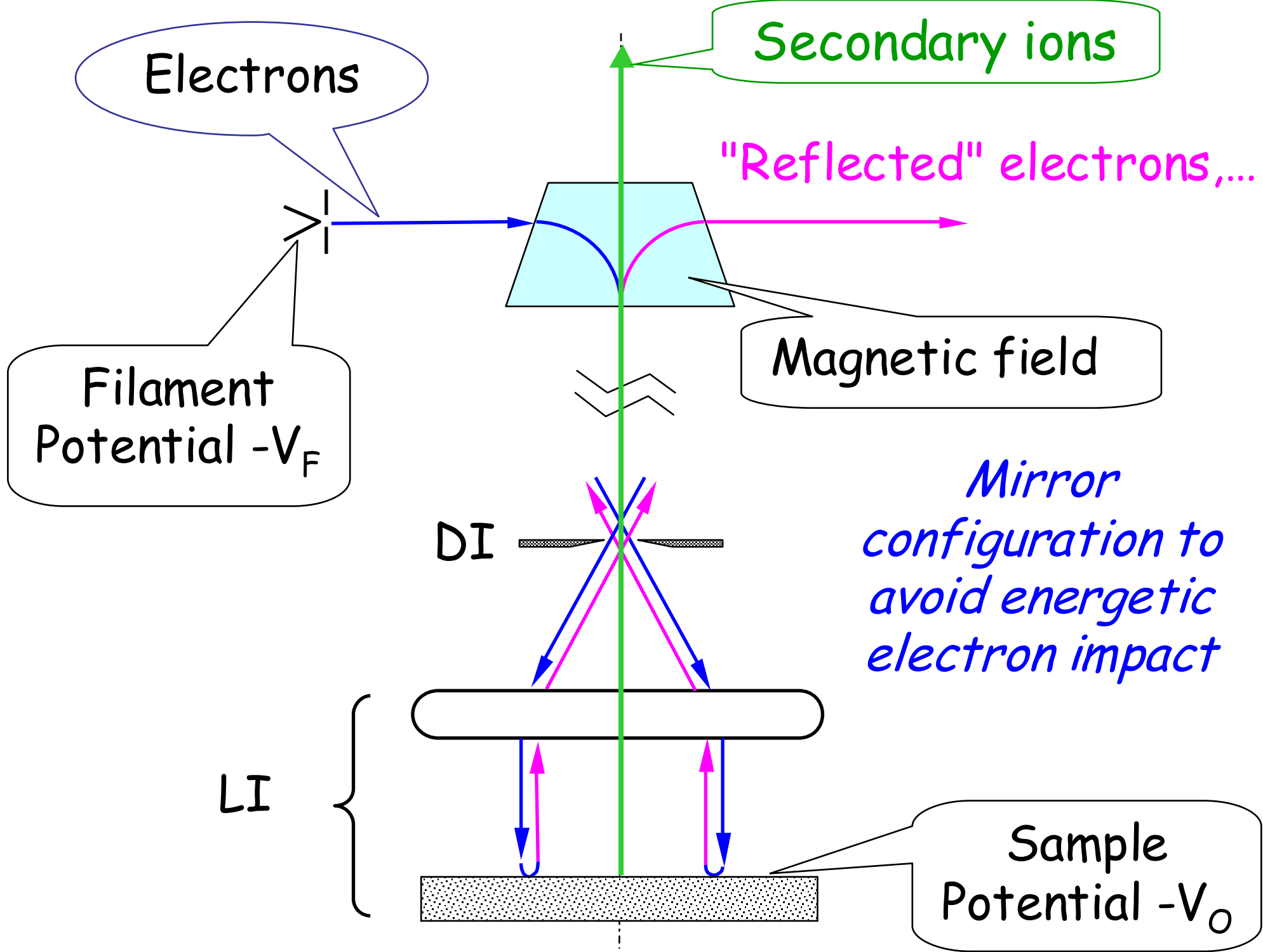
➔ Measurements with Faraday cups

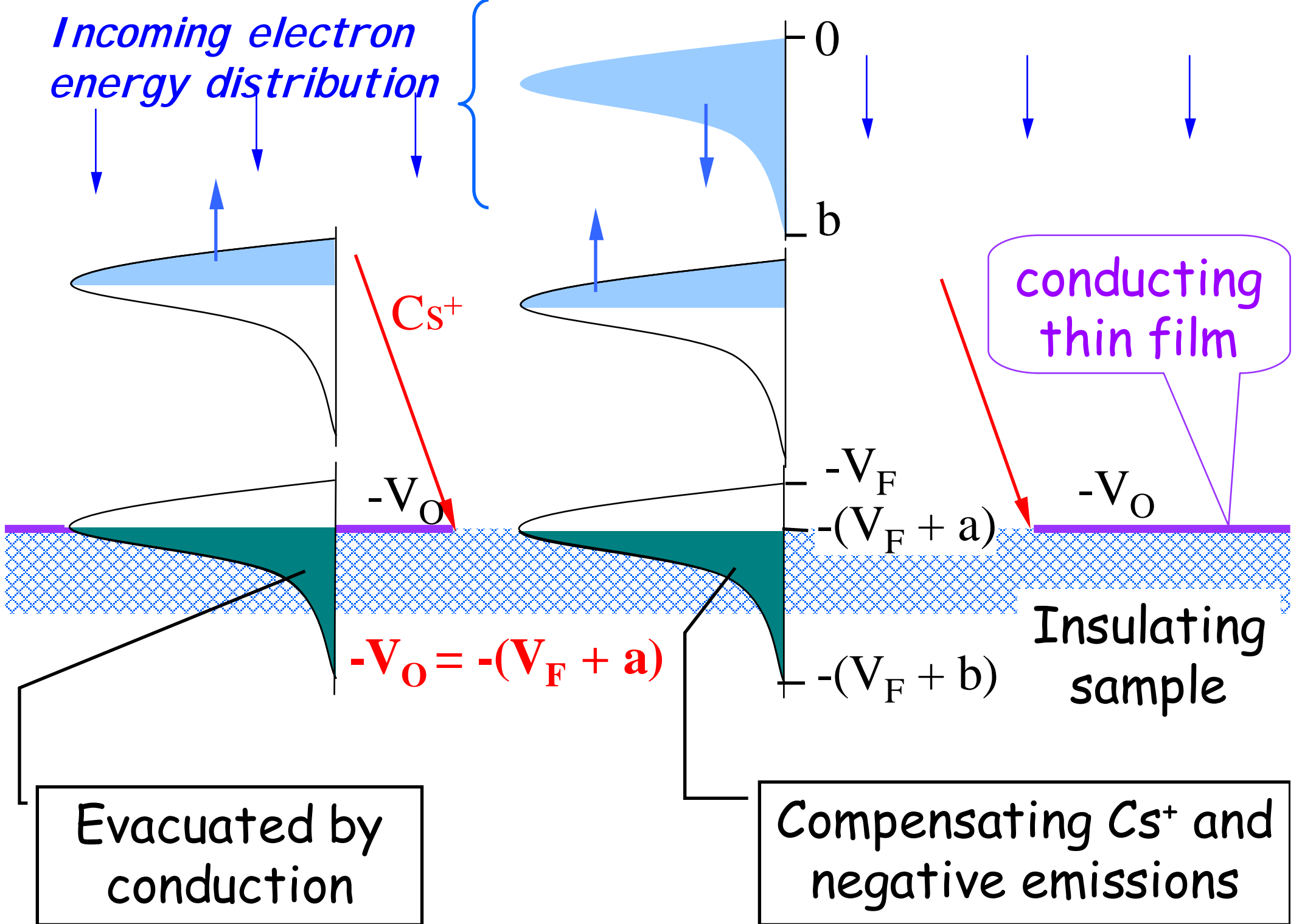
➔ Increase of Primary beam density

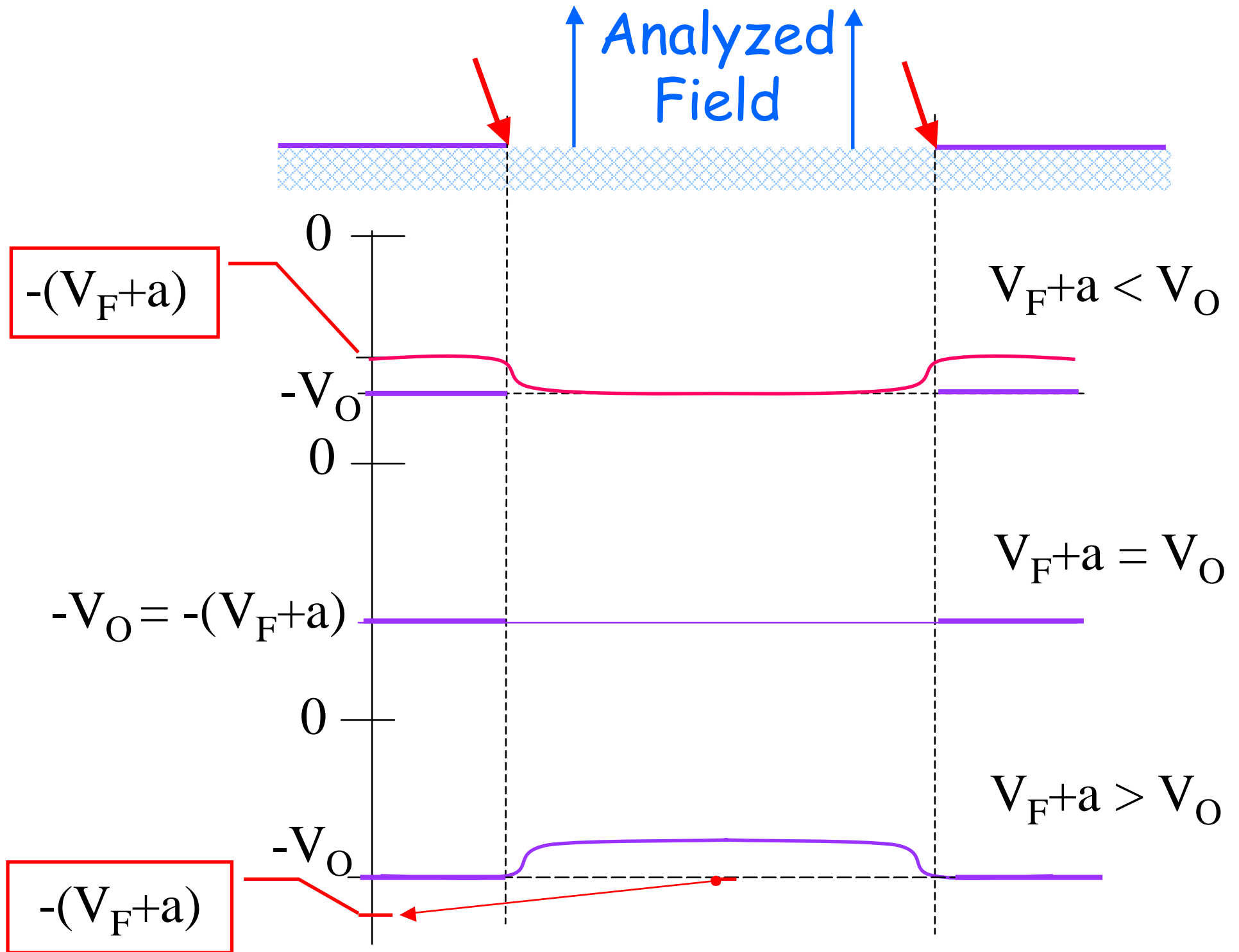
- ◆ Space charge effects on secondary ion trajectories in the sample surface vicinity ?
- ◆ Surface potential stabilisation on insulating samples ?

# "Faraday cup" versus "EM"

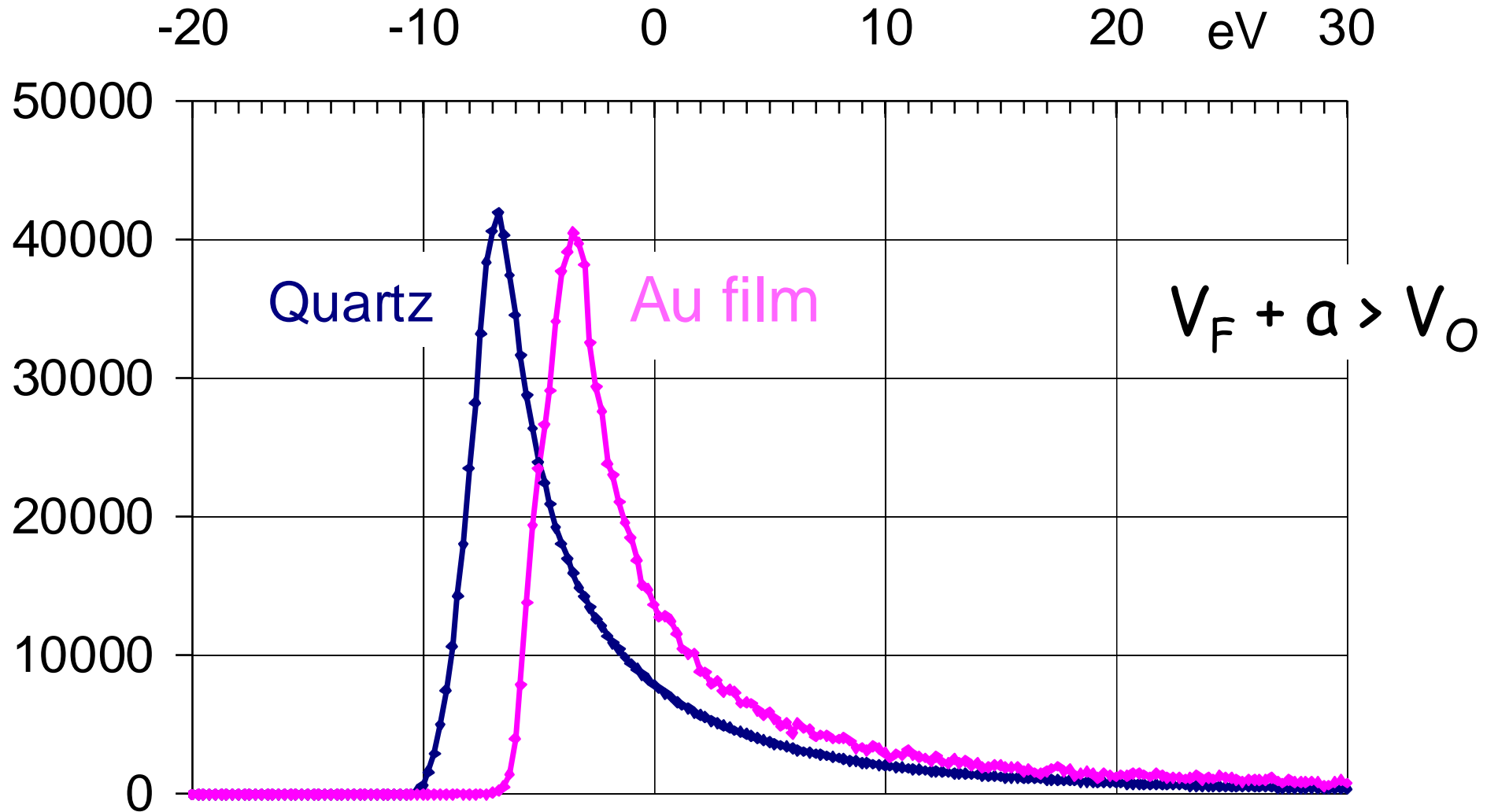








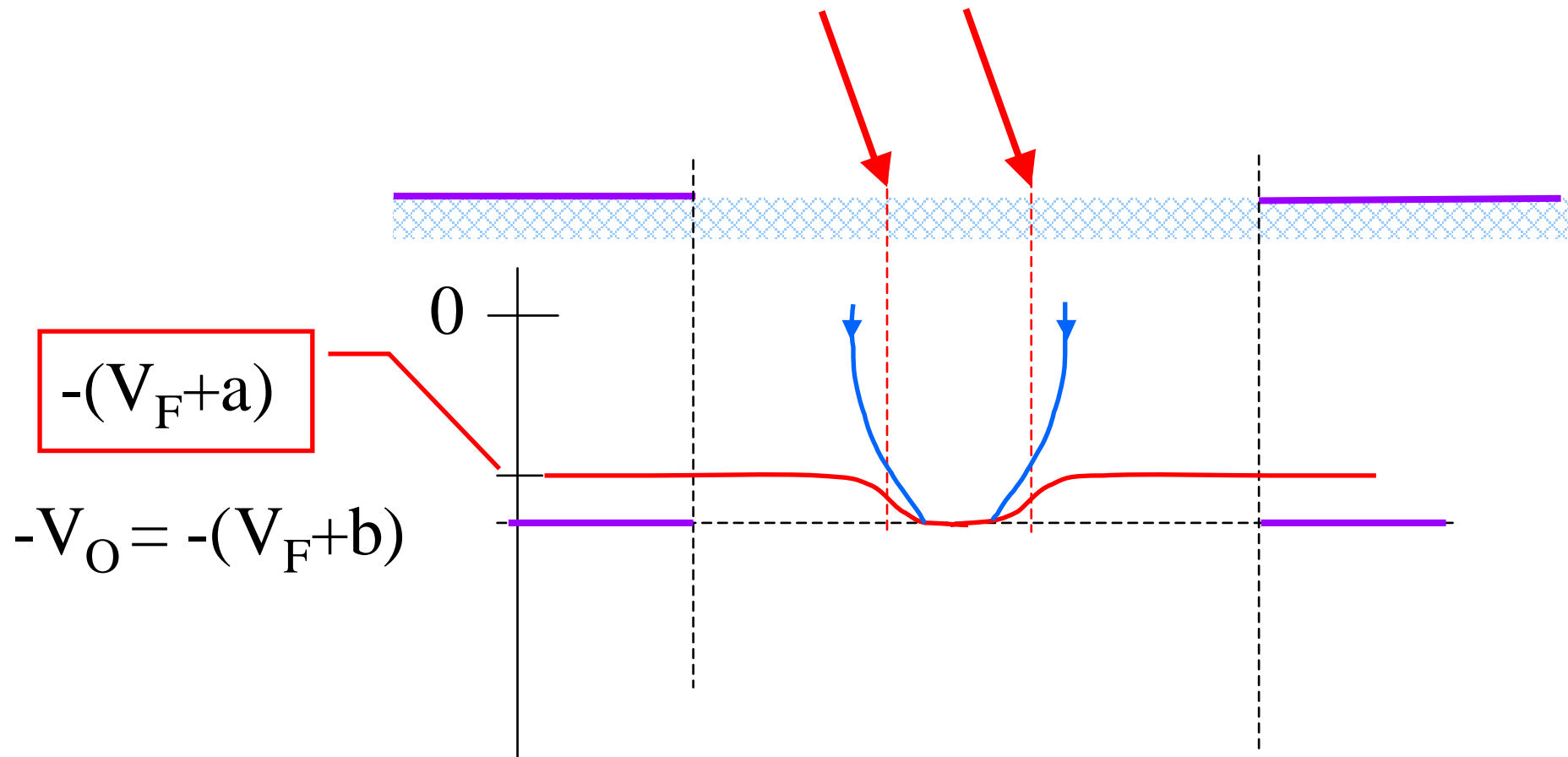
# Energy distribution of $^{16}\text{O}$



Area distributions normalized at  $10^6$  cps

Static Formed Probe:  $35\mu\text{m}$

Incoming electron beam density lower than primary beam density plus induced secondary emission density



(one case among others,...)

## Concluding remarks

There is a constant strive for higher precision, better repeatability and reduced acquisition times on small sample areas. Progress can be made

### 1) Ion Detection with EM

- Fundamentals on ion induced electron emission
- New materials for conversion dynode
- New designs (or revisiting older ones)

### 2) Measurements with Faraday cups

- Overlap with EM    QSA, Dead time
- New electronic designs (?)

### 3) Instrumental improvements

- compensation of deleterious magnetic fields
- refined adjustment protocols
- ...(?)

### 4) Strong incentive for more "fundamental studies"

- ionization and sputtering
- fractionation amplitudes depending upon changes in beam definition (angles, energies...)? Space charge effects ?
- Matrix effects
- Implantation, roughening, migration, relief, ...
- Insulators in positive mode, heterogeneous samples, small grains,

5) Optimize the use of present instruments by more exchange of knowledge and skills via Summer Schools and Workshops.

*Thank you for your attention*