MC-ICP-MS仪器简介

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一. MC-ICP-MS发展历史

多接收器等离子体质谱 Multiple Collector ICP-MS

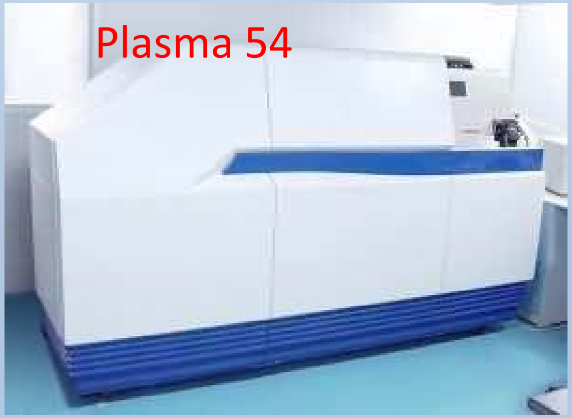
- 1980年 Houk and Gray等发表了关于ICP-MS里程碑式的文章
- 1983年 第一代商业ICP-MS问世
- 1992年第一台商用MC-ICP-MS问世(Walder and Freedman)

MC-ICP-MS侧重于高精度同位素比值；应用于同位素地质学、环境科学、核工业、考古、材料、生命科学等

Name	Manufacturer[a]	Year of introduction	Status	Type of instrument	Geometry
Plasma 54	VG Elemental	1992	discontinued	MC-ICP-SFMS	Nier–Johnson
Nu Plasma	Nu Instruments	1997	discontinued	MC-ICP-SFMS	Nier–Johnson
Axiom MC	VG Elemental	1998	discontinued	MC-ICP-SFMS	Nier–Johnson
Nu Plasma 1700	Nu Instruments	1999	available	MC-ICP-SFMS	Nier–Johnson
Neptune	Thermo Quest	2000	available	MC-ICP-SFMS	Nier–Johnson
IsoProbe-P	GV Instruments	2004	discontinued	MC-ICP-SFMS	magnetic sector + hexapole
SPECTRO MS	Spectro Analytical Instruments	2010	available	MC-ICP-SFMS	Mattauch–Herzog
Nu Plasma II	Nu Instruments	2010	available	MC-ICP-SFMS	Nier–Johnson
Neptune plus	Thermo Scientific	2009	available	MC-ICP-SFMS	Nier–Johnson

Nu plasma 3 Nu instruments 2017
Nu sapphire Nu instruments 2018
Neptune XT ThermoFisher 2019

一.MC-ICP-MS发展历史



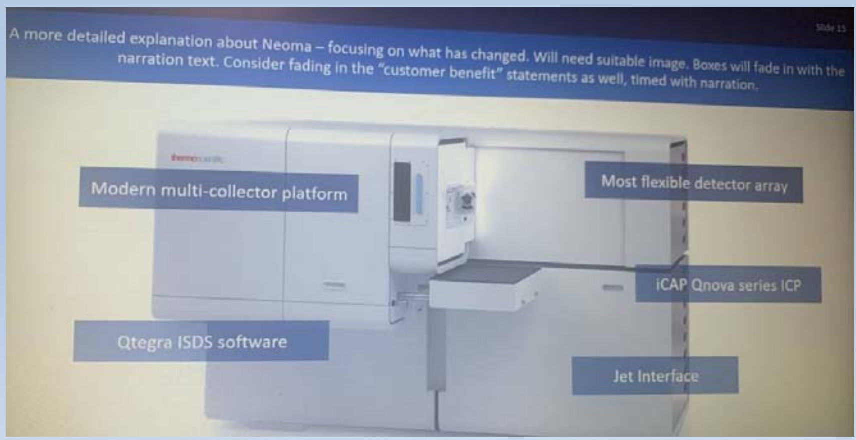
一.MC-ICP-MS发展历史

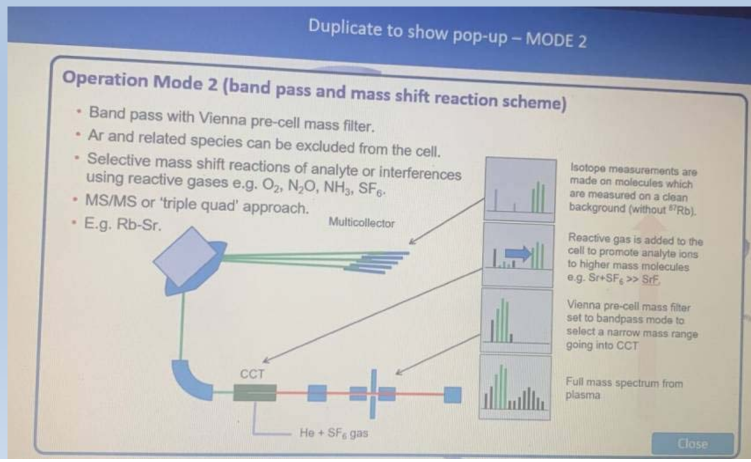
Nu Plasma 3

ThermoFisher

Neptune Plus Neptune XT

ThermoFisher Neoma(概念机)

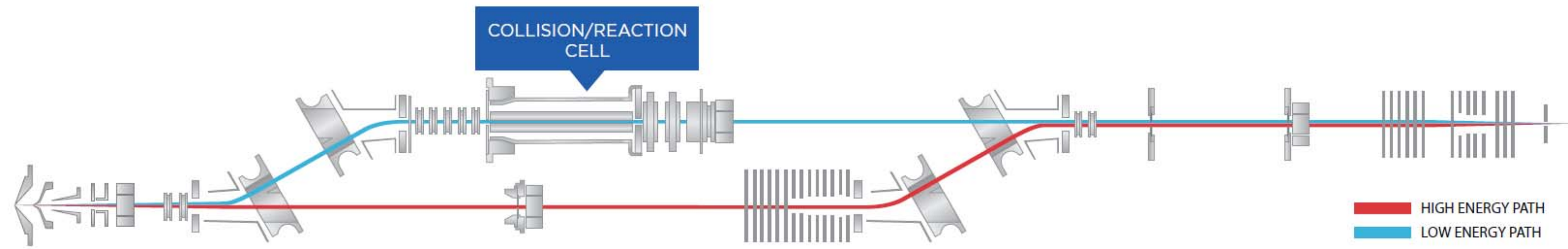




Nu Instrument
独有的两款

Nu Sapphire 2017年发布

全球第一款带碰撞反应池的、双聚焦、高分辨 MC-ICP-MS

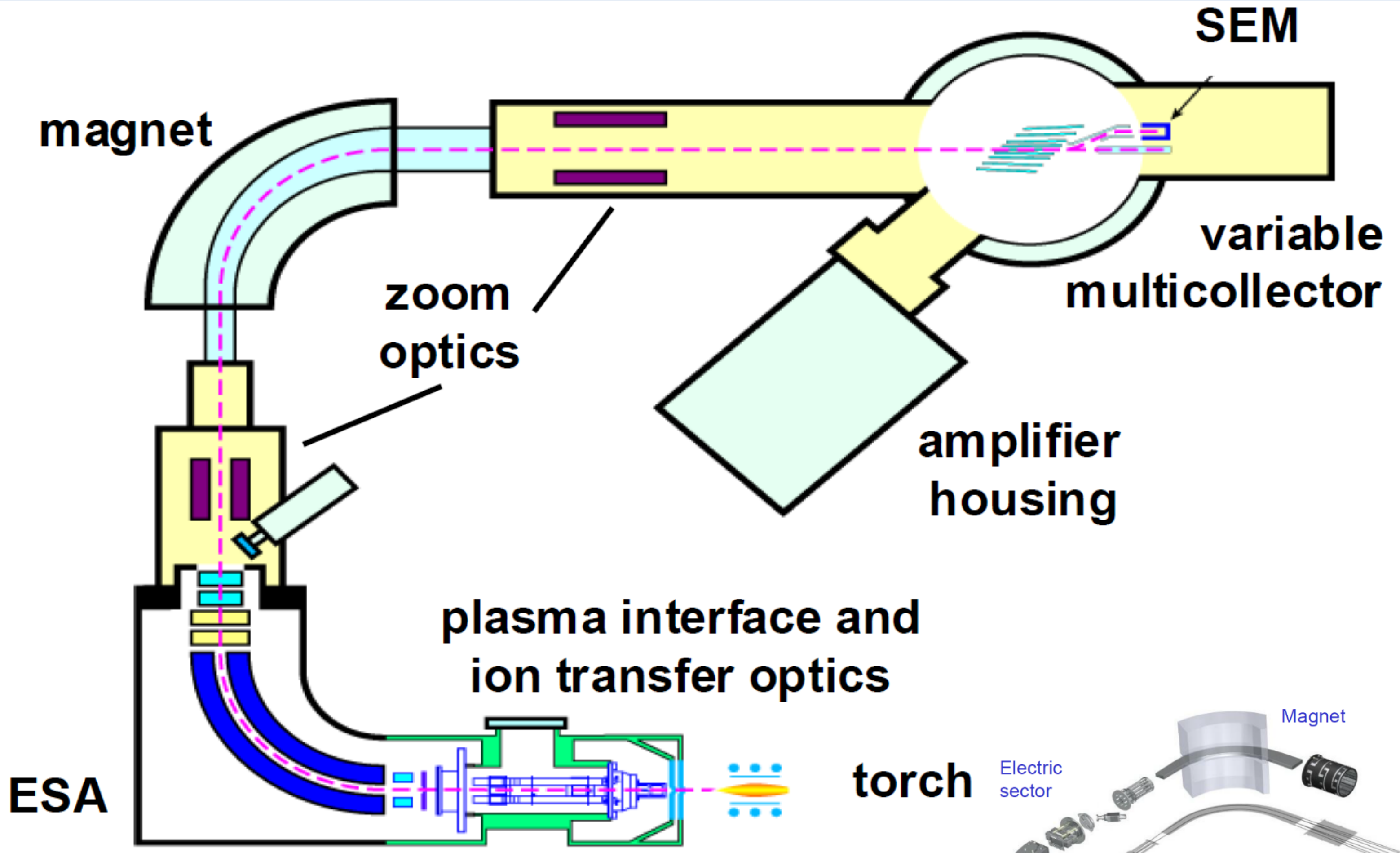


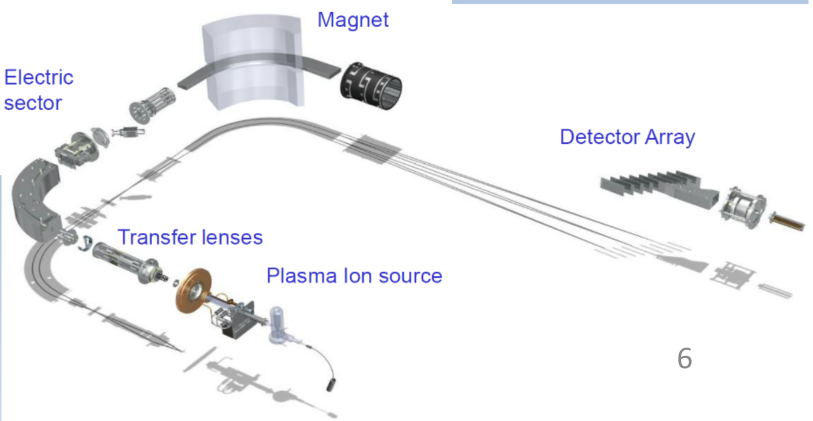
Nu Plasma 1700 1999年发布

1700 属于定制型号，每一台1700都有设计差异；甚至可以有 Nu Sapphire-1700

（南京大学-李伟强教授）

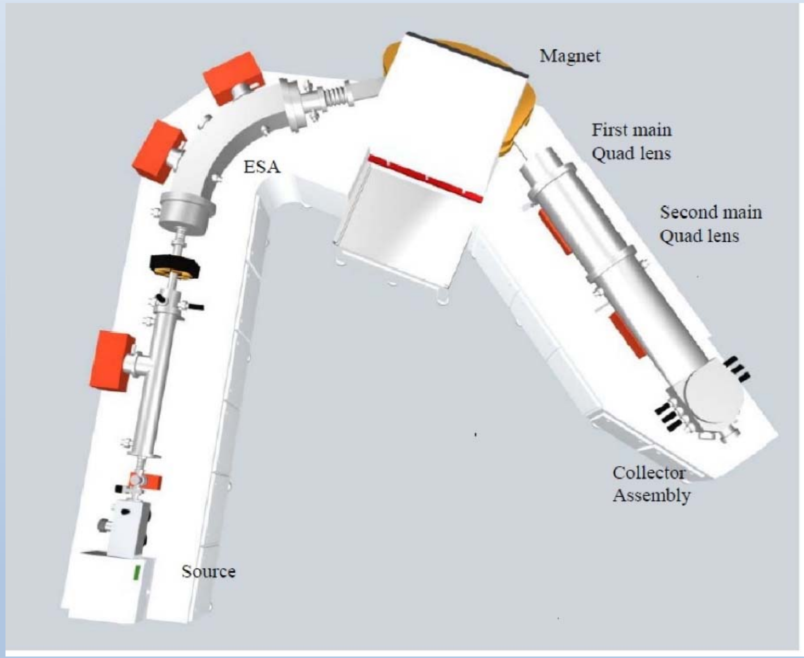
二.MC-ICP-MS结构

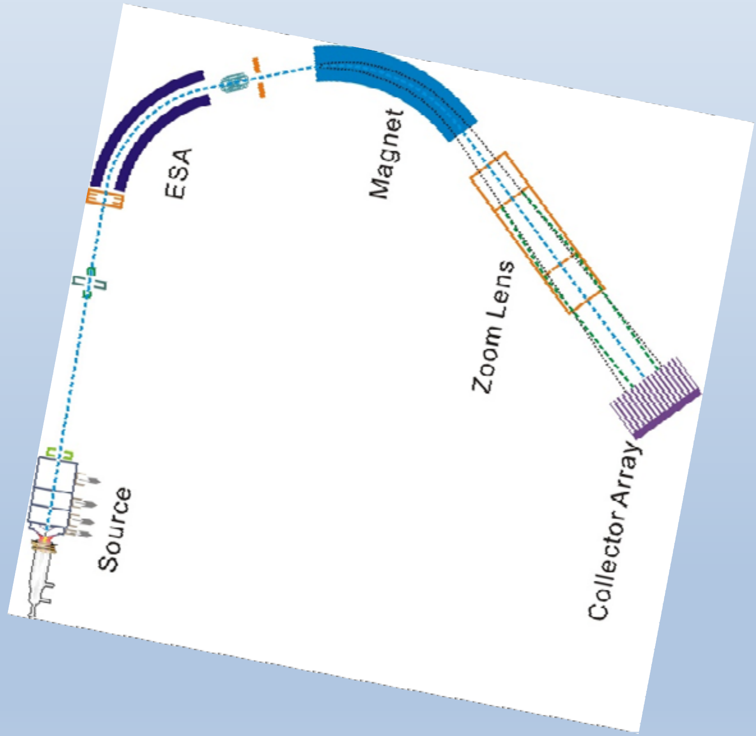




Nier-Johnson型

二.MC-ICP-MS结构

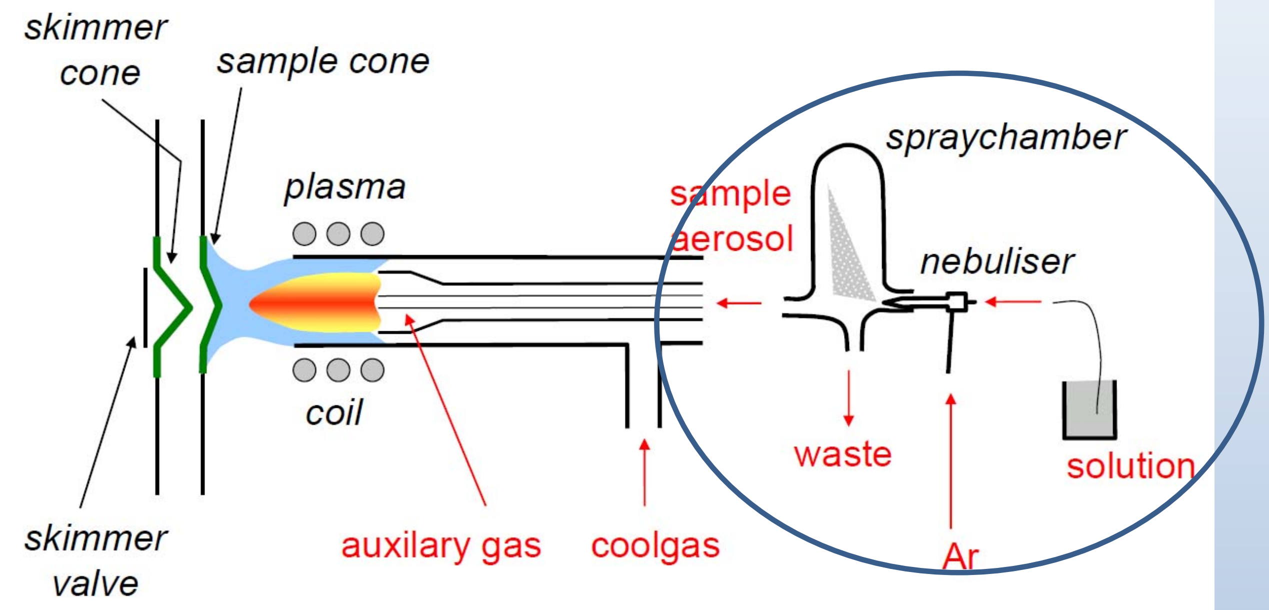

Magnet
ESA
First main
Quad lens
Second main
Quad lens
Collector
Assembly
Source

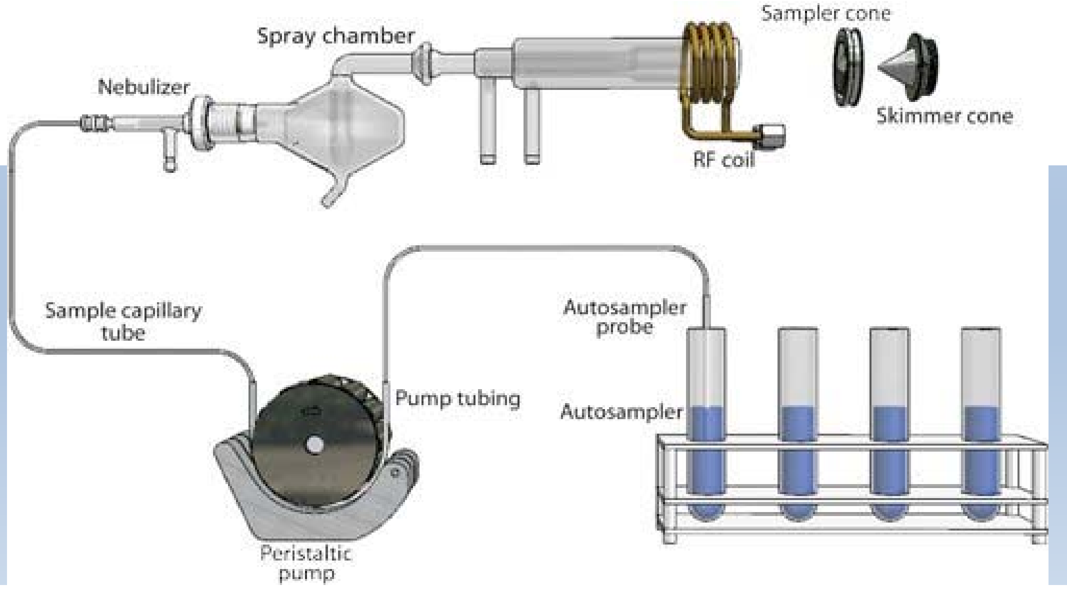

ESA
Magnet
Zoom Lens
Collector Array
Source

二.MC-ICP-MS结构

1. 进样系统
2. ICP系统
3. 接口部分
4. 离子透镜
5. 双聚焦系统：ESA & MSA
6. Zoom透镜
7. 检测器部分
8. 真空系统
9. 其他
10. 一些概念

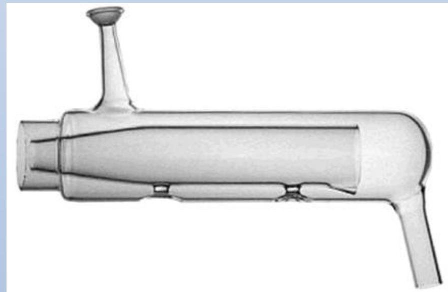
1. 进样系统


skimmer cone
sample cone
plasma
spraychamber
sample aerosol
nebuliser
coil
waste
solution
skimmer valve
auxilary gas
coolgas
Ar


Sampler cone
Spray chamber
Nebulizer
Skimmer cone
RF coil
Sample capillary tube
Autosampler probe
Pump tubing
Autosampler
Peristaltic pump

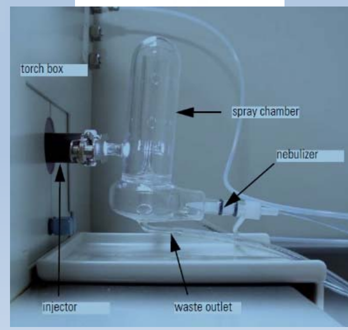
1. 进样系统

雾化器



雾室

湿法



1. 进样系统

膜去溶

干法

激光剥蚀

干法


1. 进样系统

其他

离子色谱IC

液相色谱HPLC

流动注射

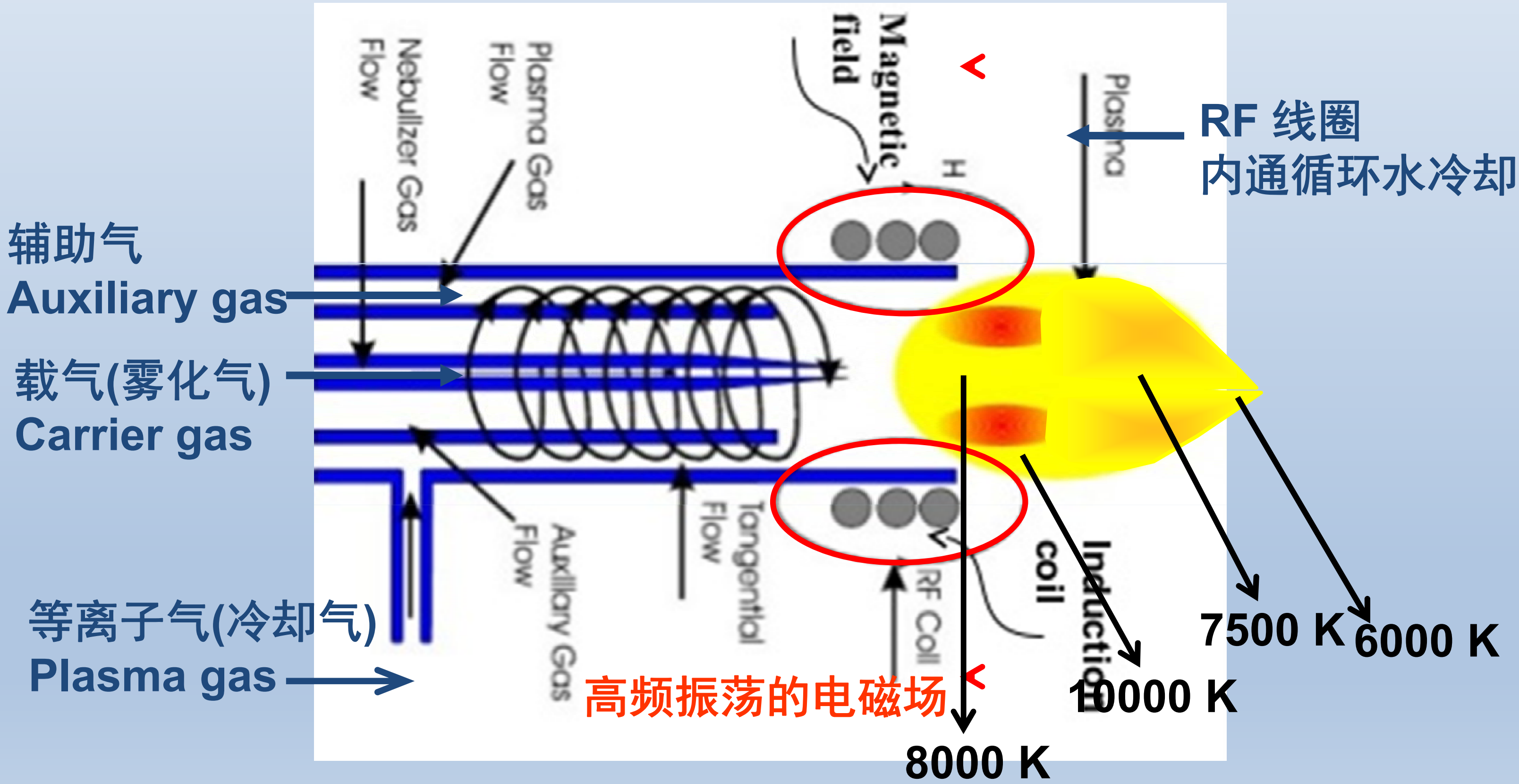
蒸发进样

石墨探针直接进样

……

2. ICP系统

- ICP = Inductively Coupled Plasma 电感耦合等离子体（离子源）
- ICP-Mass Spectrometry 电感耦合等离子体 质谱仪



ICP-MS 不考虑上机溶液元素的价态/价态

去溶与蒸发

Fe^{3+} Fe^{2+} Cl^- As^{3+} As^{5+}

电离成正离子

Fe^+ Cl^+ Se^+ As^+

解离成单原子

Fe Cl Se As

$FeCl_3(H_2O)_m$

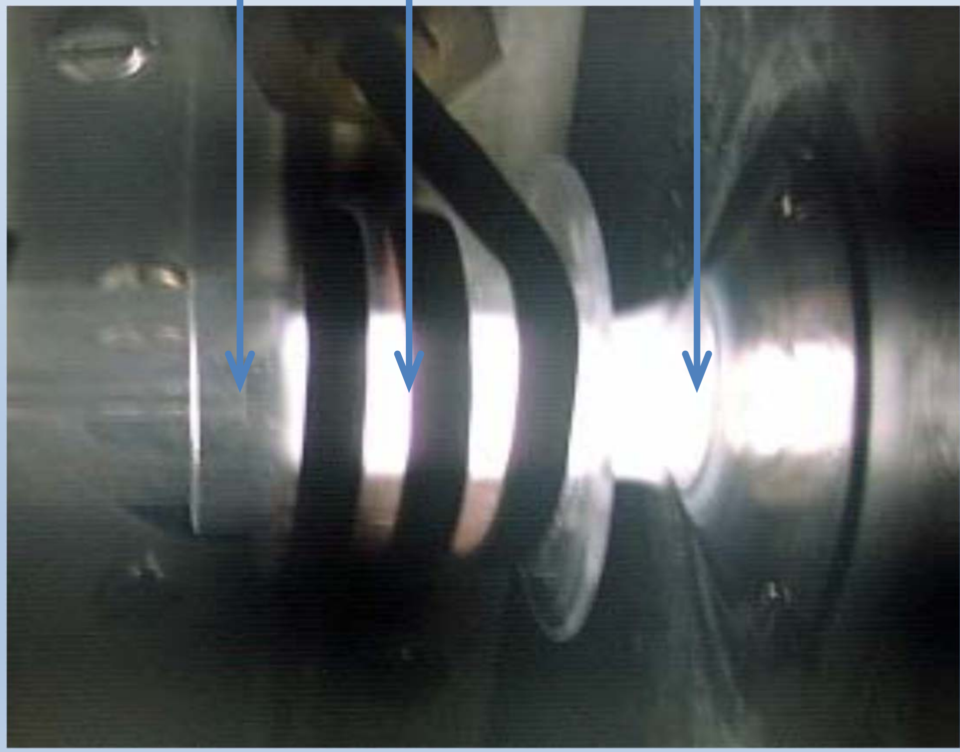
$FeCl_2(H_2O)_n$

$Se^{IV}O_3^{2-}$

$Se^{VI}O_4^{2-}$

As^{3+}

As^{5+}



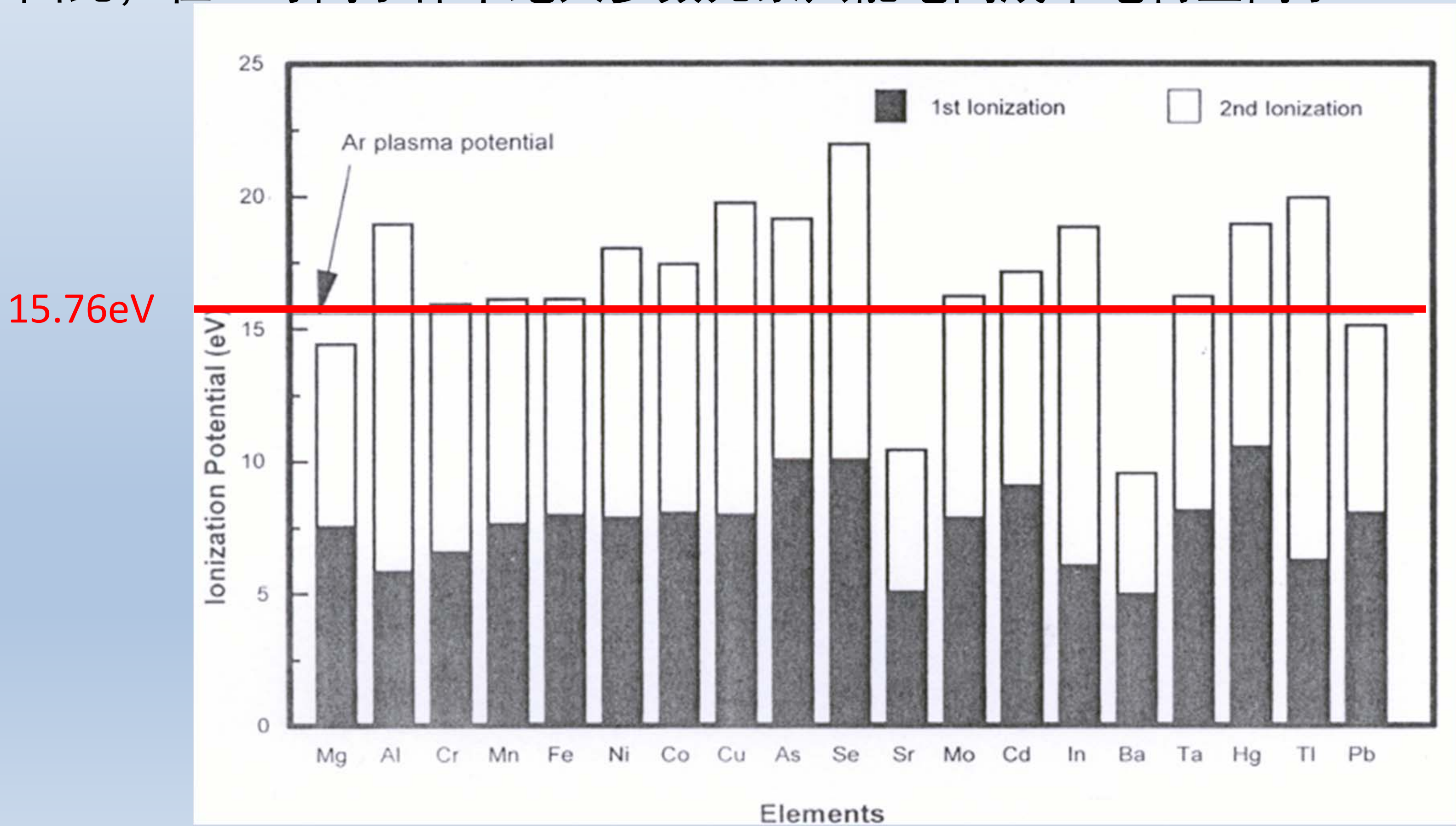
ICP-MS

2. ICP系统

Ar 等离子体的优势

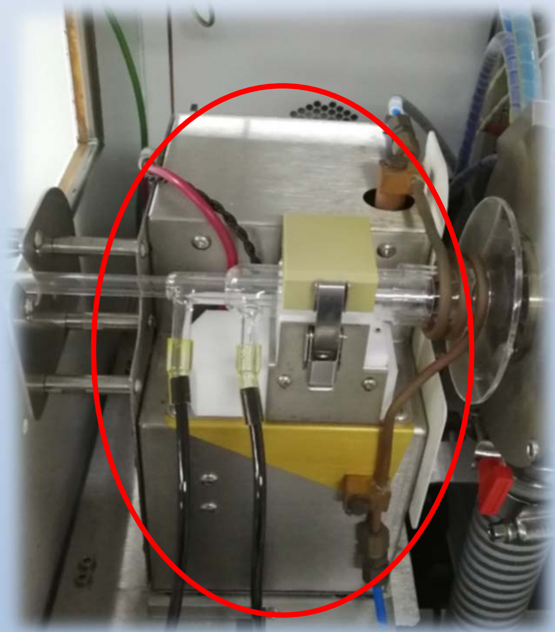
Ar的第一电离能(15.76 eV) 高于绝大多数元素的第一电离能（除He Ne F），且低于大多数元素的第二电离能(除Mg Ca Sr Ba等)

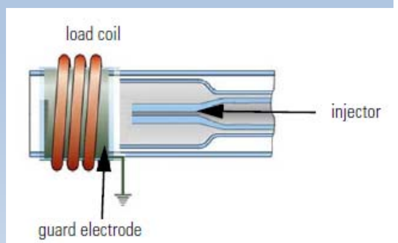
因此，在Ar等离子体中绝大多数元素只能电离成单电荷正离子

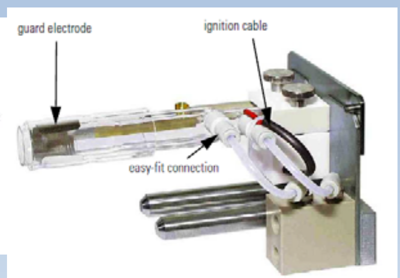


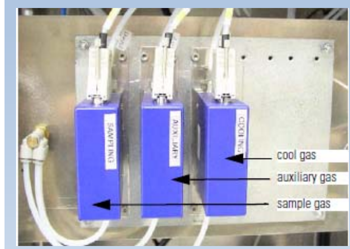
2. ICP系统

ICP离子源系统还包括：炬管、线圈、RF发生器、炬箱（匹配箱）、点火线



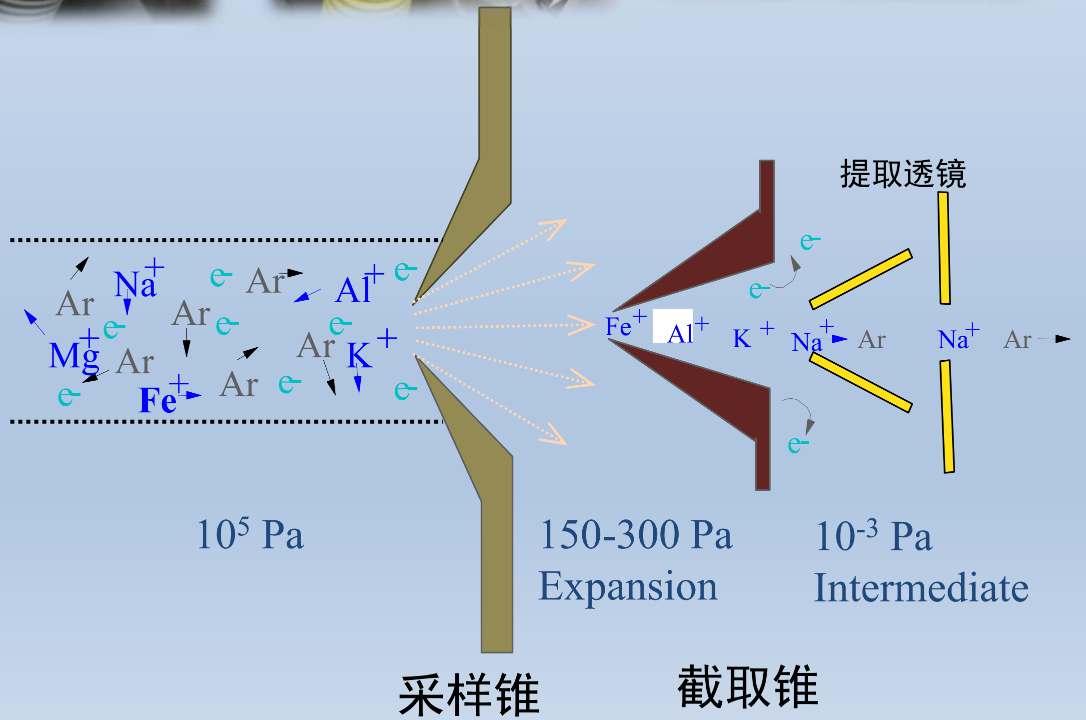






3. 接口部分

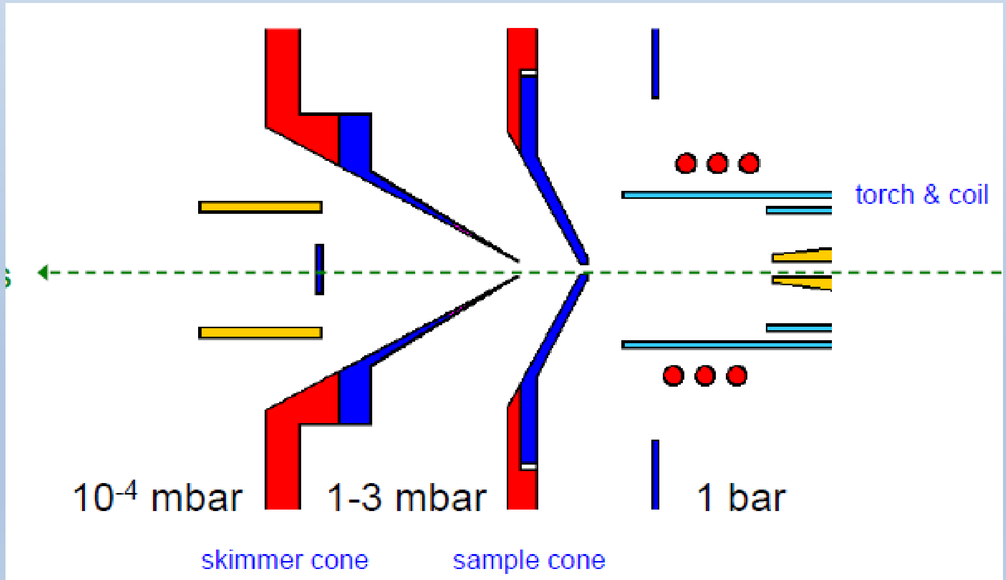
锥界面（一般由2个锥组成）



3. 接口部分

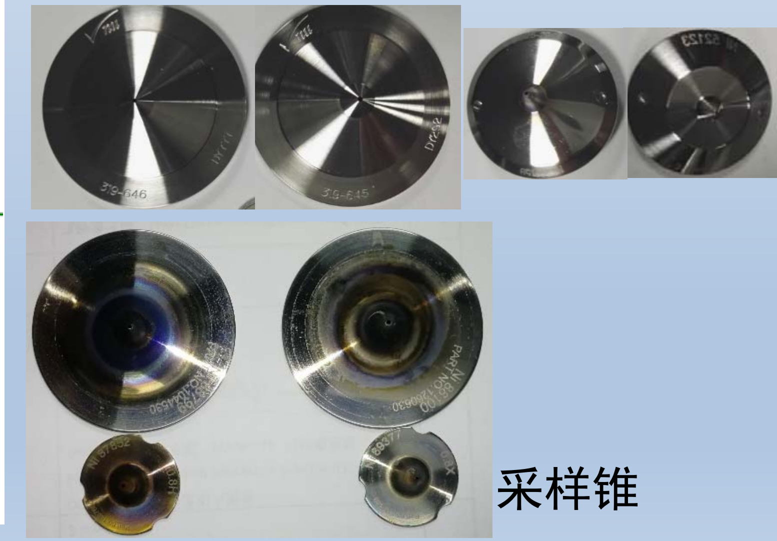
锥界面（一般由2个锥组成）

- 采样锥后是扩散区(150-250 Pa)，离子在穿越锥孔后很短的距离内，等离子热能转化为动能，气体扩散速率(~2500m/s)超过声速。电子温度基本不变(5000-7500 K)，但电子密度在极短时间内骤降，因此电子与正离子是不可能重新结合的。
- 截取锥后是中间区(10^{-3} Pa)，电子沿截取锥内壁呈放射状分布，正离子沿轴向运动。由于大量正电荷在有限的束状空间内相互排斥，即产生空间电荷效应(Space-charge effect)。它与基体抑制、质量歧视有关。



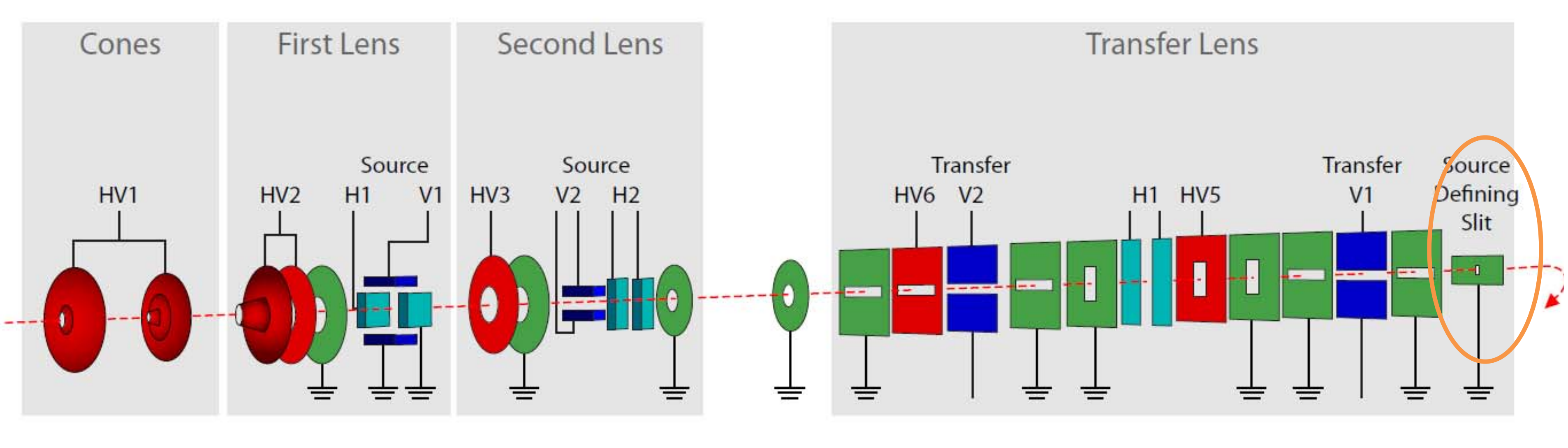
截取锥　　　　采样锥

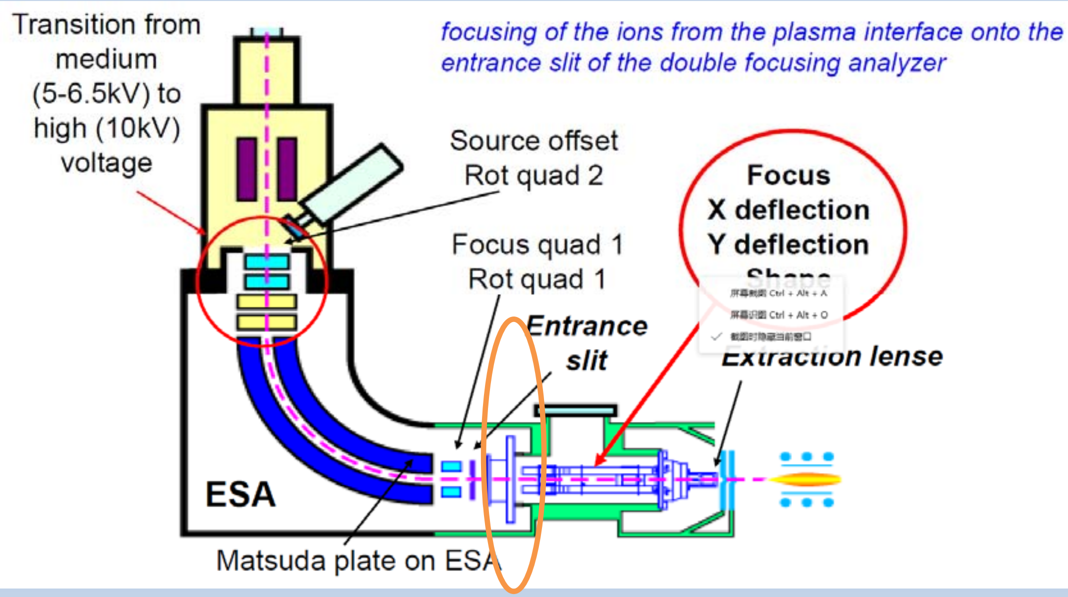
截取锥



采样锥

4. 离子透镜

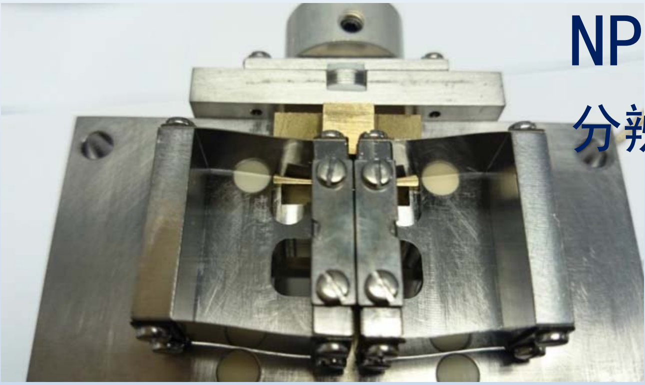




离子提取、加速
源狭缝Source slit

源狭缝Source slit

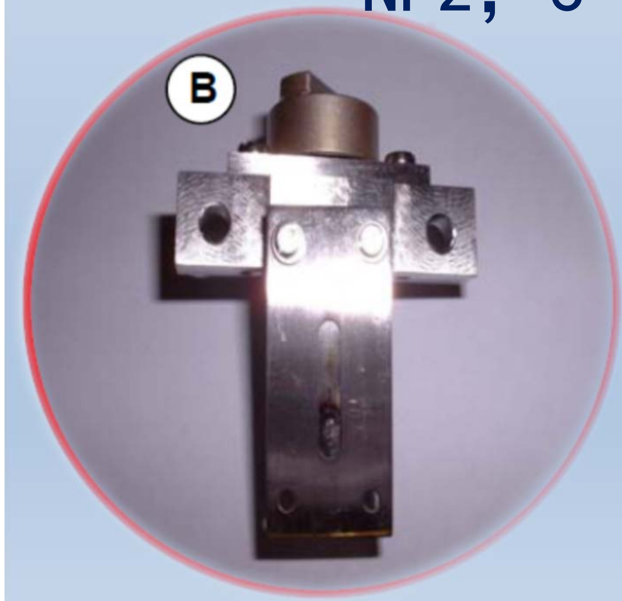
High Resolution: 双聚焦+分辨狭缝

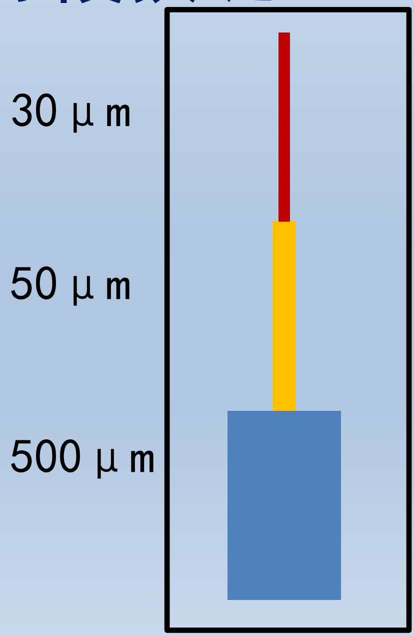


NP1700 连续狭缝

分辨率400-30000连续可调

NP2，3 分段狭缝

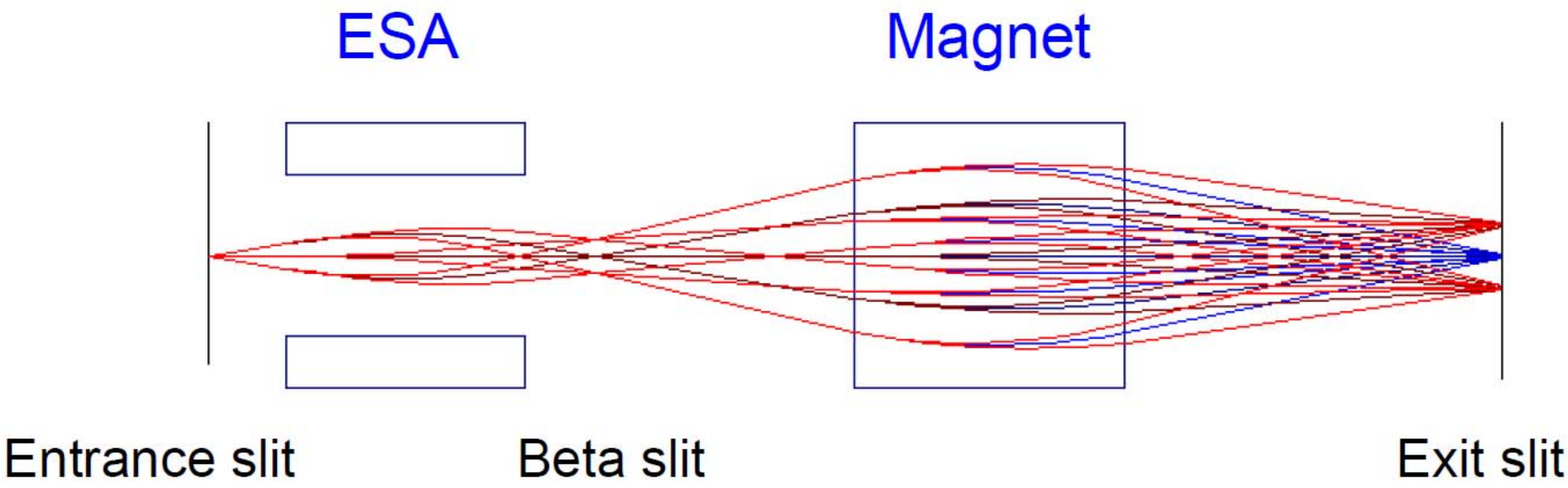




高分辨	低分辨	中分辨
10000	400	4000
16 μ m	250 μ m	30 μ m

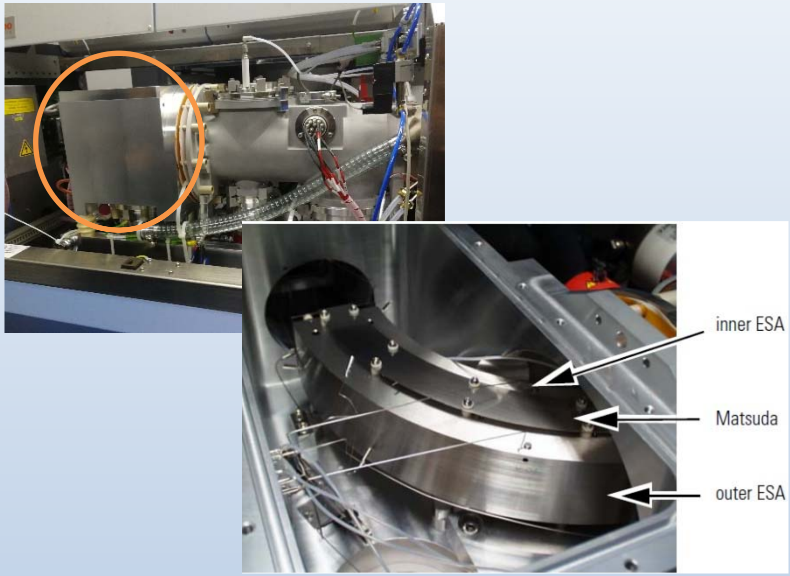
Neptune 舌状狭缝

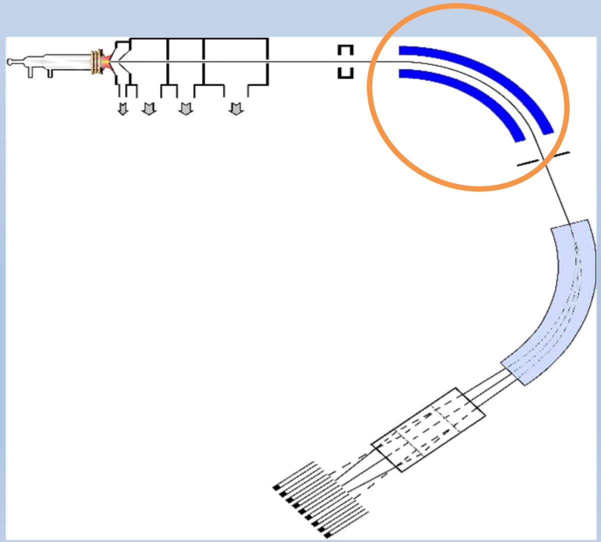
5. 双聚焦-ESA和MSA分析器

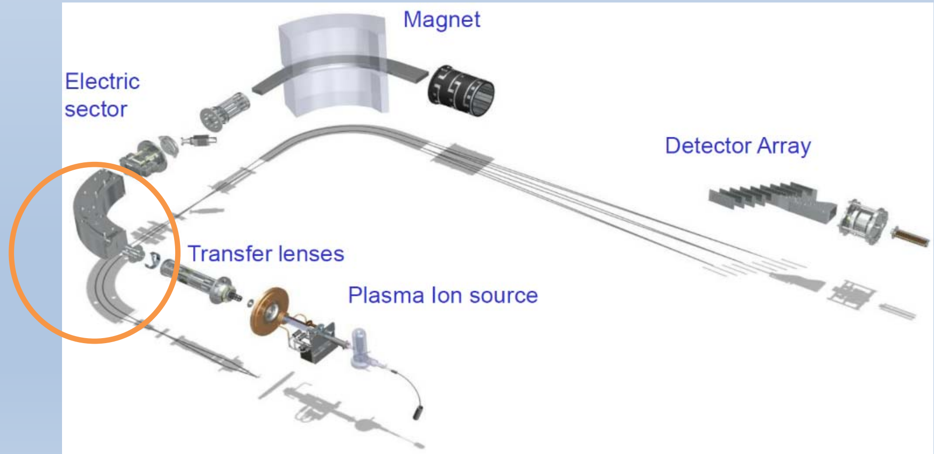


double focusing: ion energies & ion angles

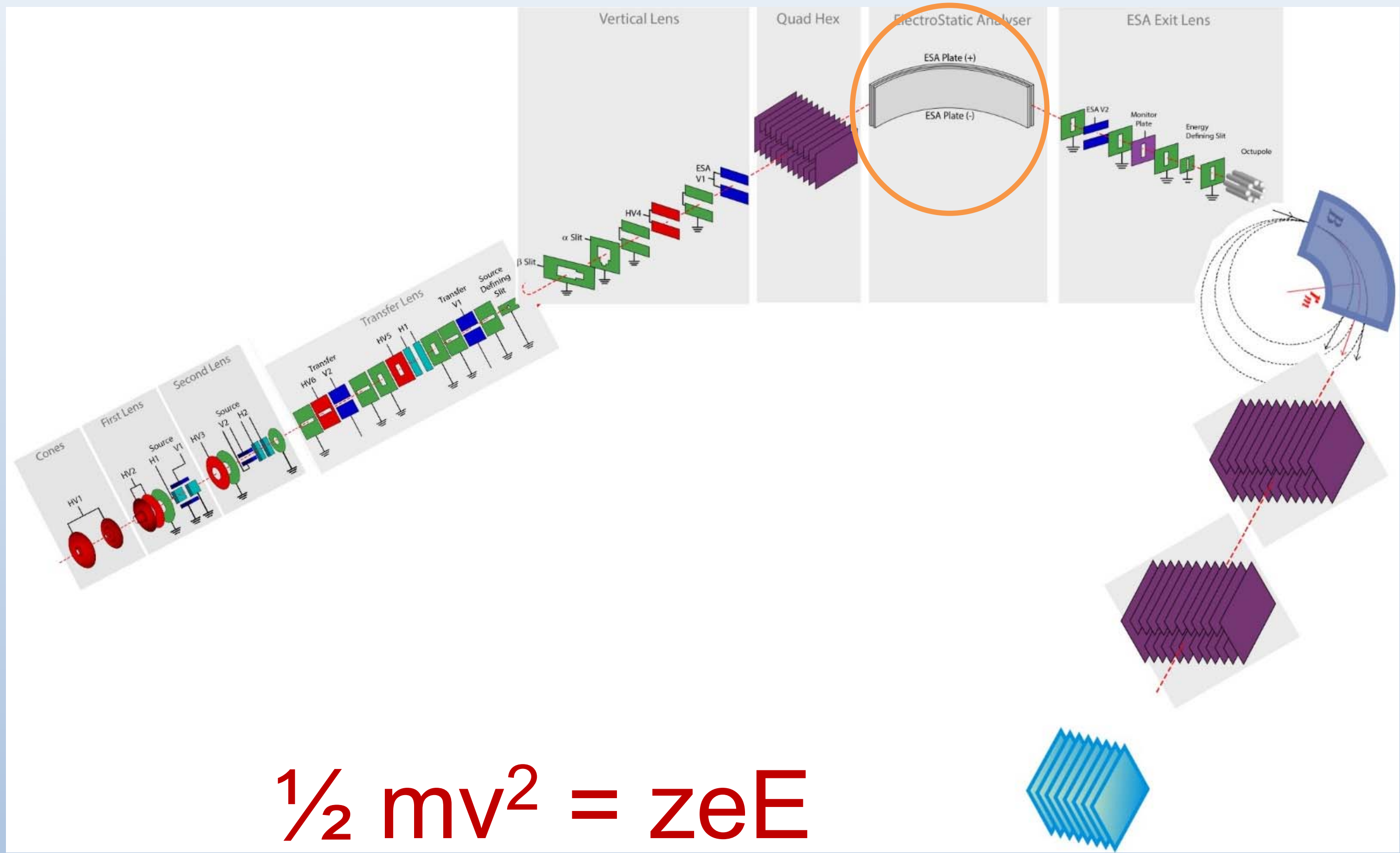
5. 双聚焦-ESA


inner ESA
Matsuda
outer ESA



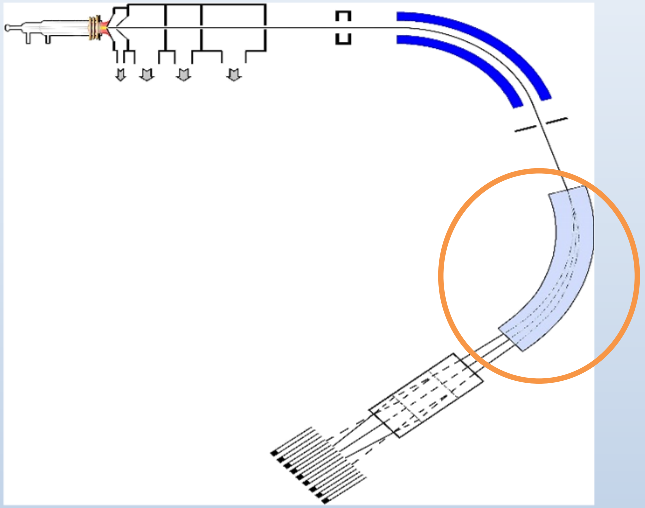

Magnet
Electric sector
Detector Array
Transfer lenses
Plasma Ion source

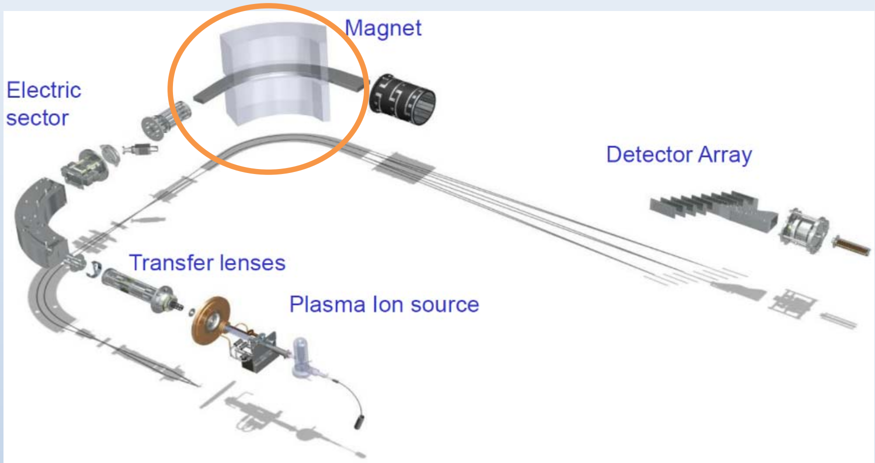
5. 双聚焦-ESA

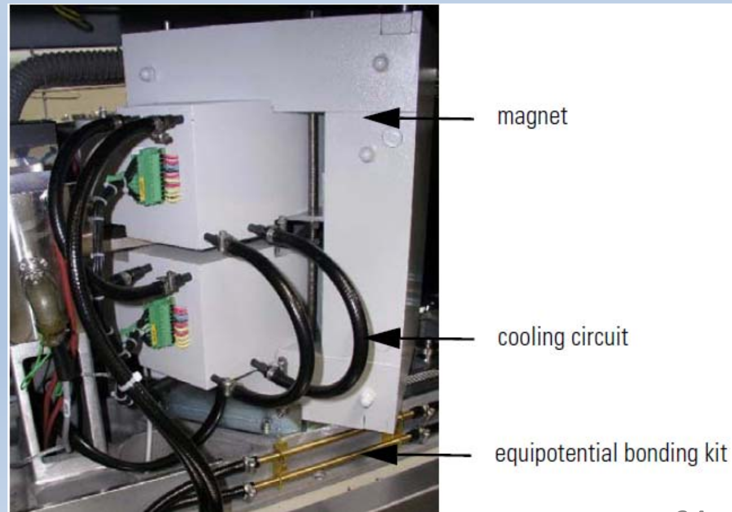


$\frac{1}{2} mv^2 = zeE$

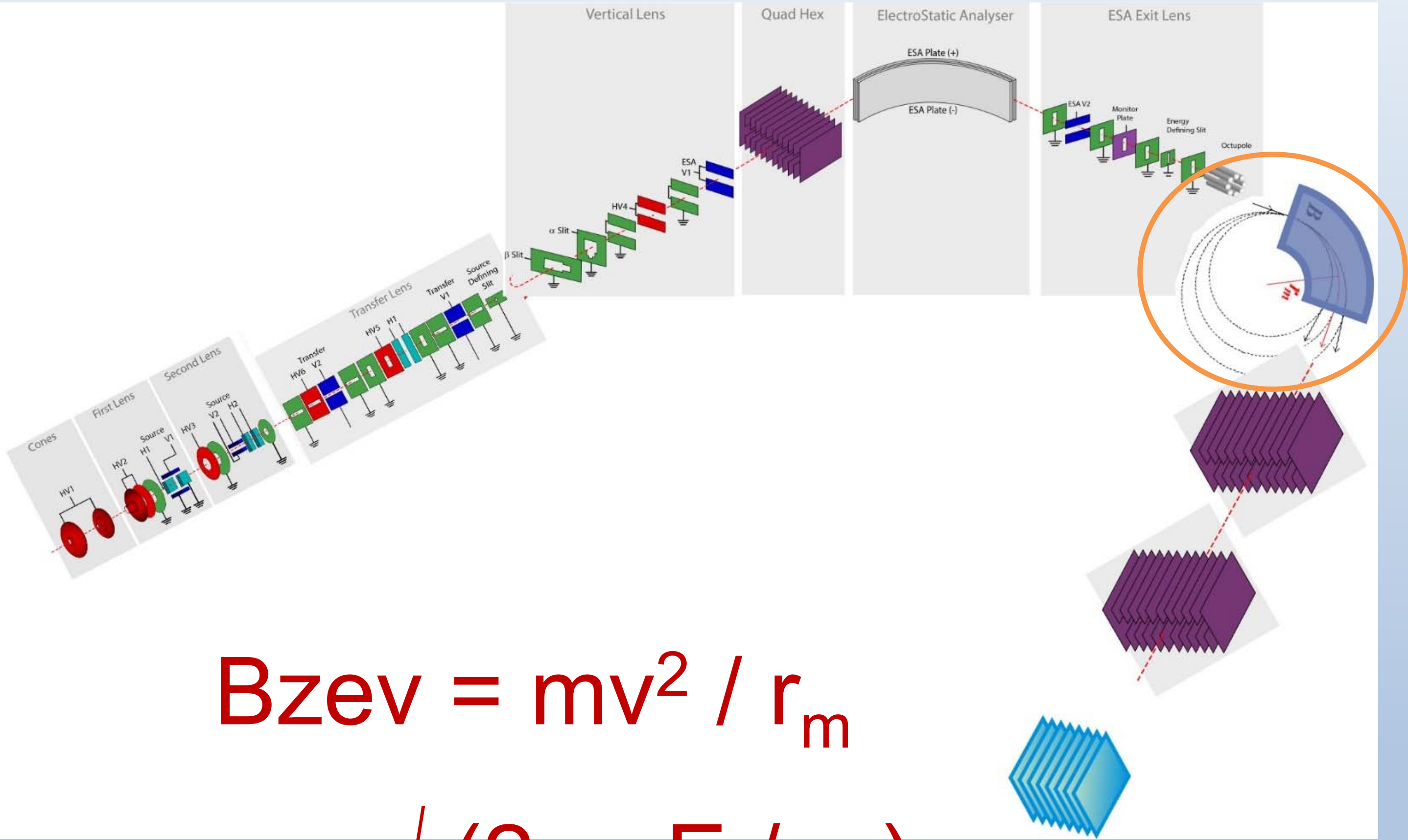
5. 双聚焦-MSA




Magnet
Electric sector
Detector Array
Transfer lenses
Plasma Ion source


magnet
cooling circuit
equipotential bonding kit

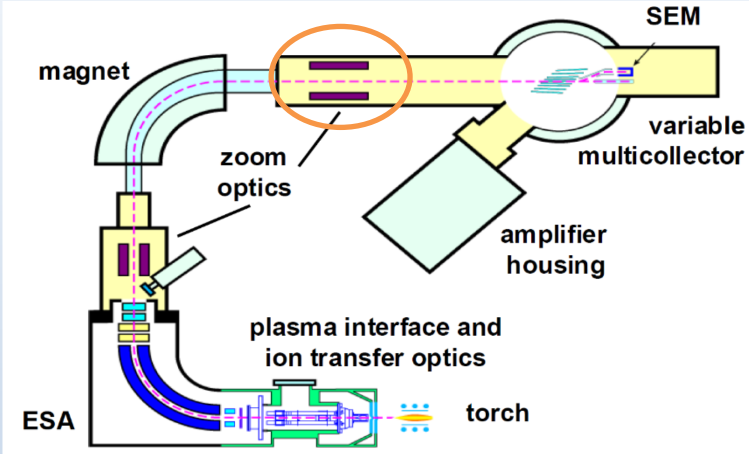
5. 双聚焦-MSA



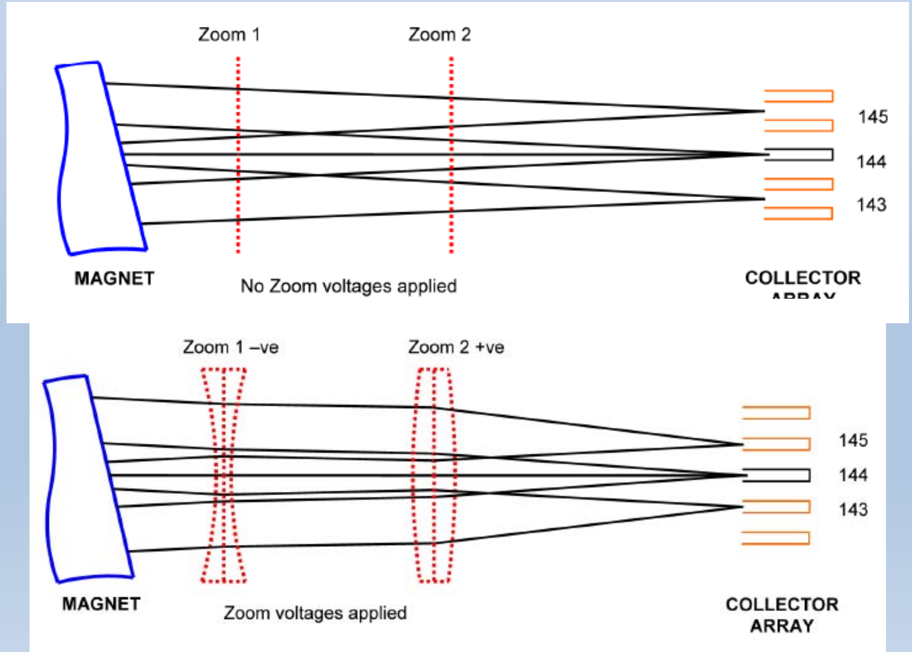
$$Bzev = mv^2 / r_m$$

$$r_m = \frac{\sqrt{(2\, m\, E / ez)}}{B}$$

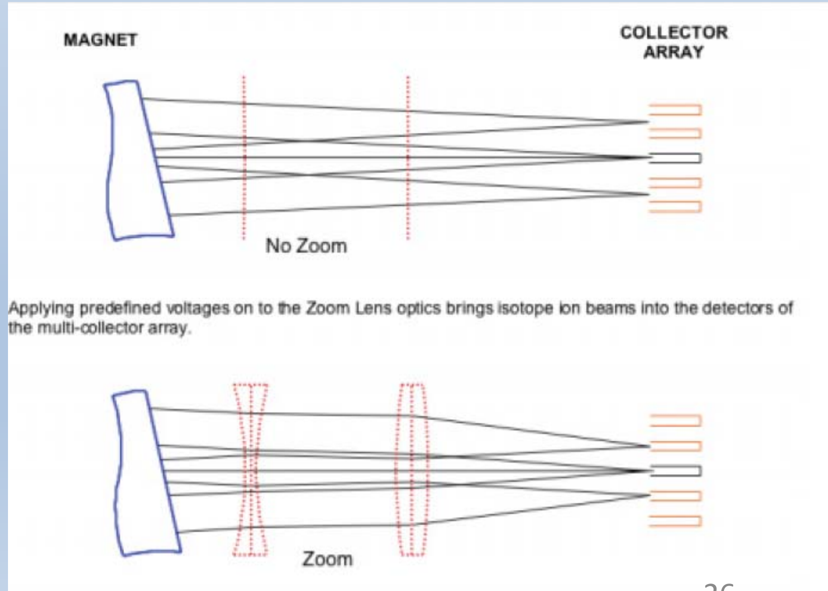
6. Zoom透镜



SEM
magnet
zoom
optics
variable
multicollector
amplifier
housing
plasma interface and
ion transfer optics
ESA
torch



Zoom 1
Zoom 2
145
144
143
MAGNET
No Zoom voltages applied
COLLECTOR
Zoom 1 –ve
Zoom 2 +ve
145
144
143
MAGNET
Zoom voltages applied
COLLECTOR
ARRAY

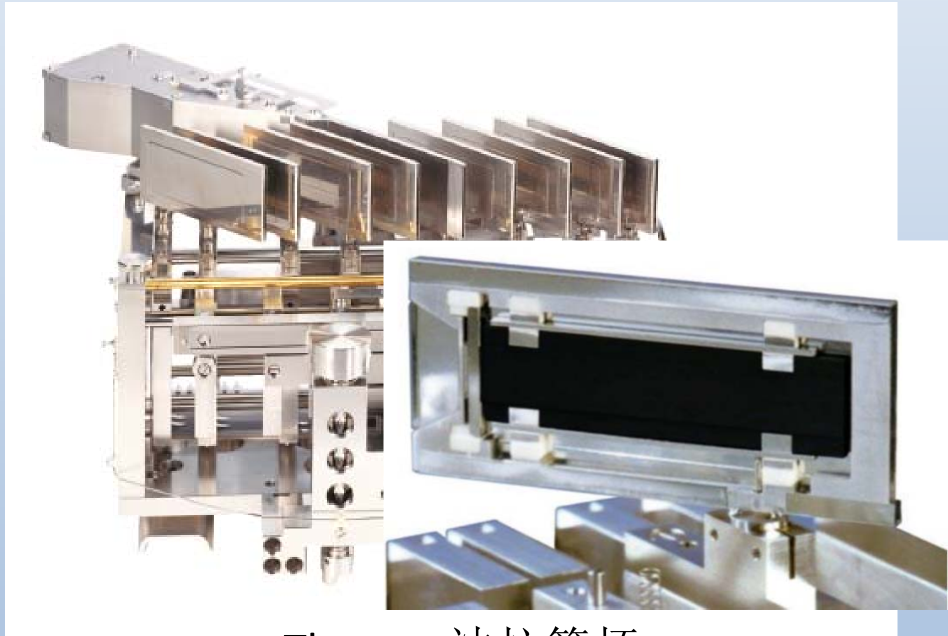


MAGNET
COLLECTOR
ARRAY
No Zoom
Applying predefined voltages on to the Zoom Lens optics brings isotope ion beams into the detectors of the multi-collector array.
Zoom

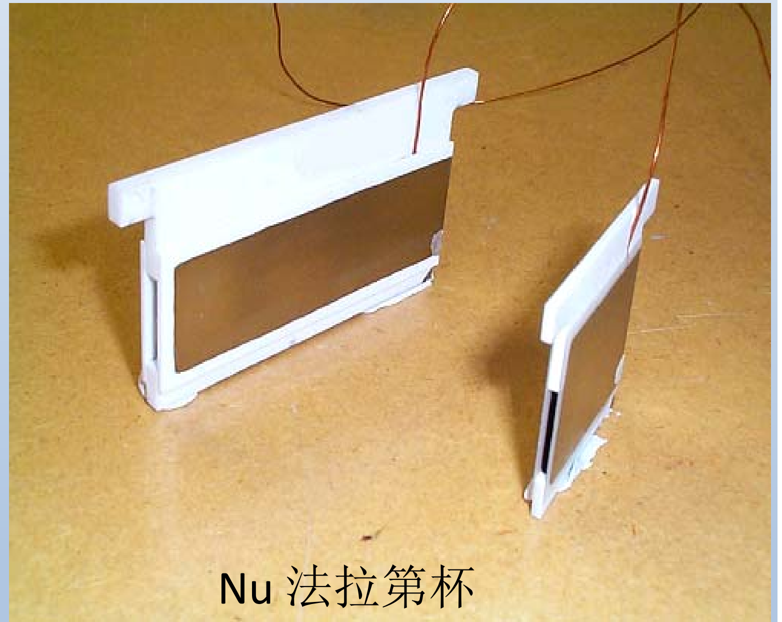
7. 检测器

检测器包括：离子计数器SEM、CDD、Daly和法拉第杯

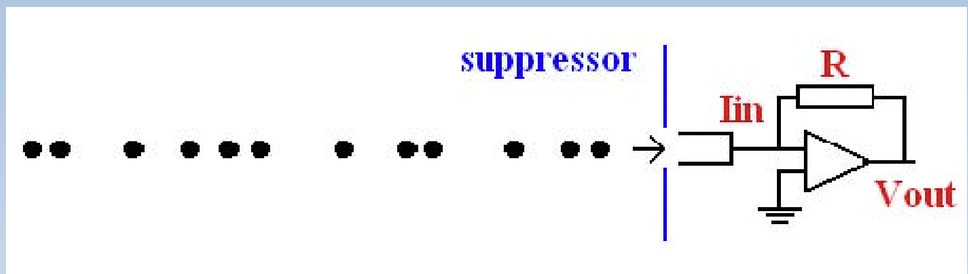
法拉第杯



Thermo 法拉第杯



Nu 法拉第杯

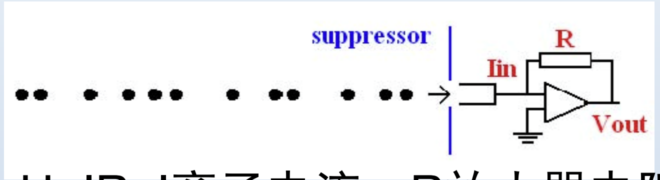


U=IR, I离子电流，R放大器电阻

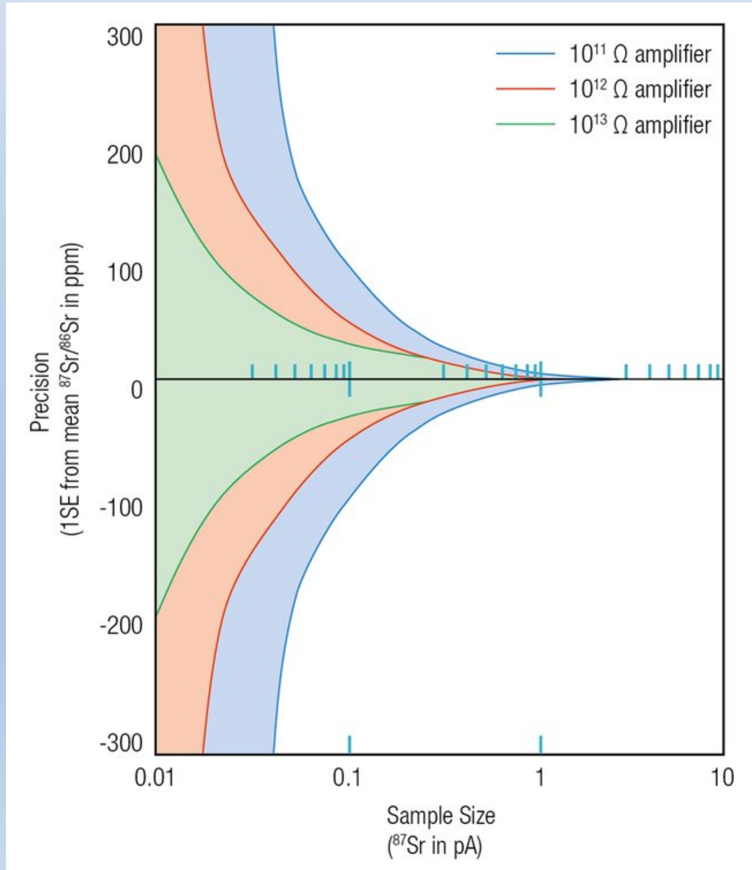
7. 检测器

法拉第杯噪音（Johnson噪音）

$$\sigma(I)=\sqrt{\frac{4kT\Delta f}{R}}$$



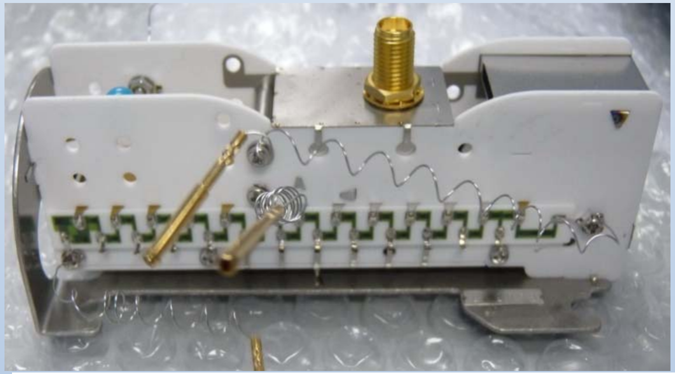
U=IR, I离子电流，R放大器电阻

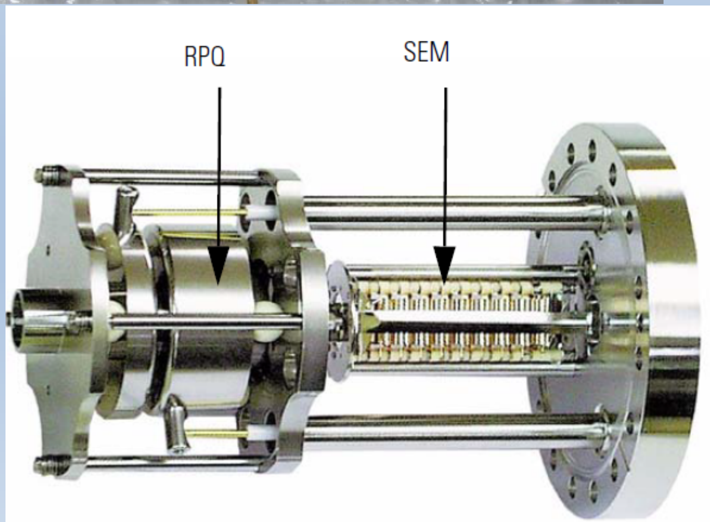


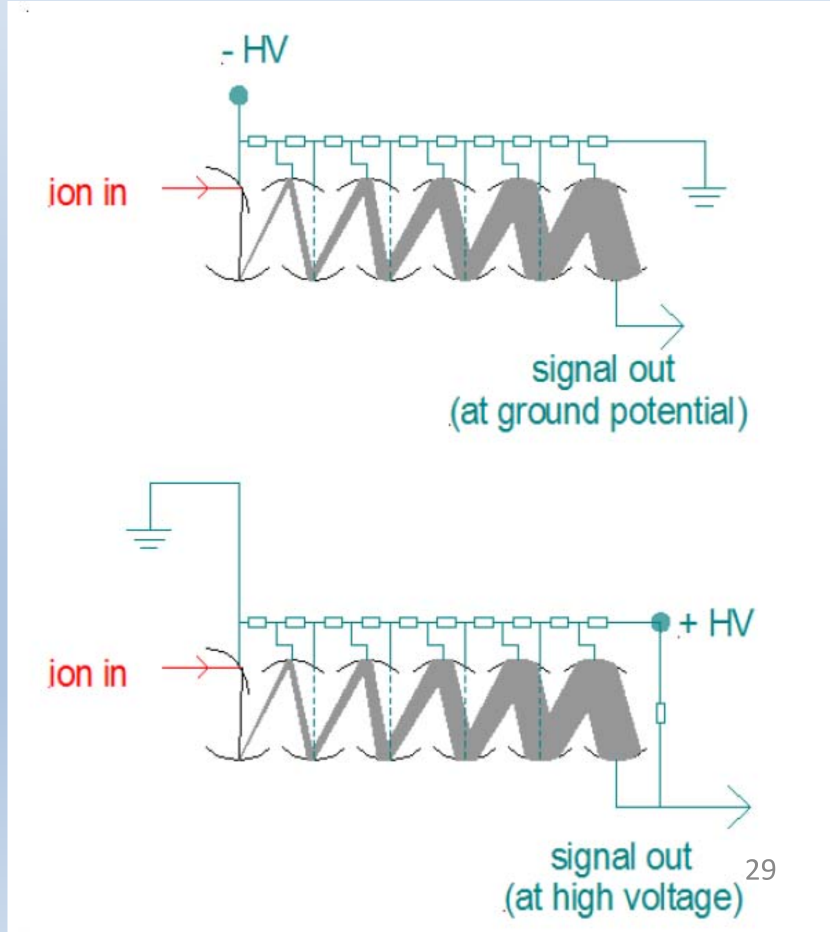
更高的电阻可以获得更大的信噪比
电阻提高10倍，信噪比提高3倍

7. 检测器

- 离散打拿极型二次电子倍增器 Discrete Dynode Secondary Electron Multipliers = SEM
- 通常在入口设负电势，吸引离子撞击转化电极产生电子，然后在剩余打拿极上设正电势，逐级加速倍增电子。

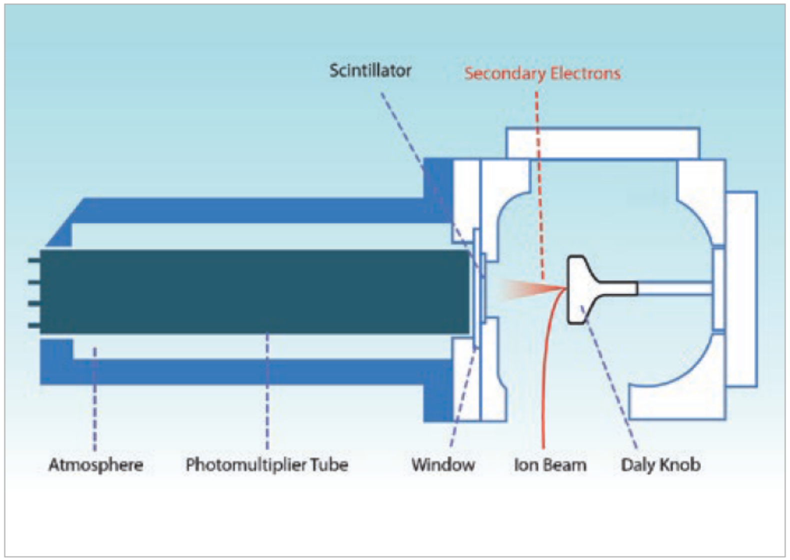






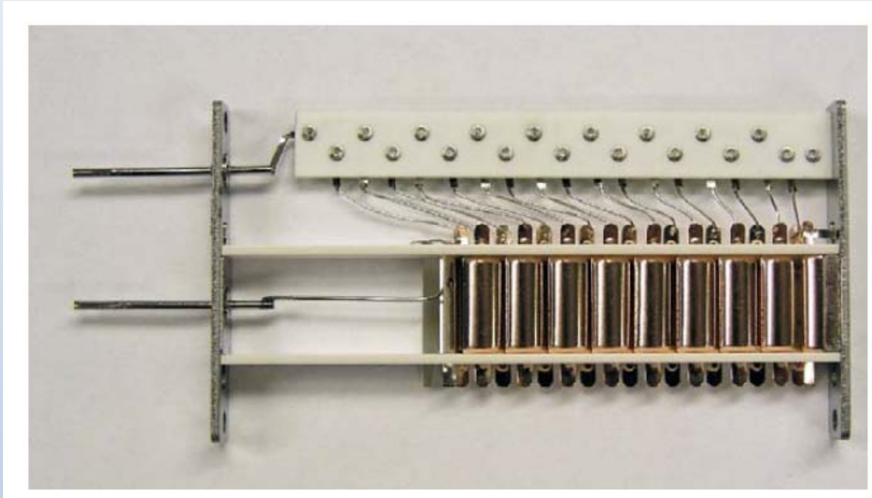
7. 检测器

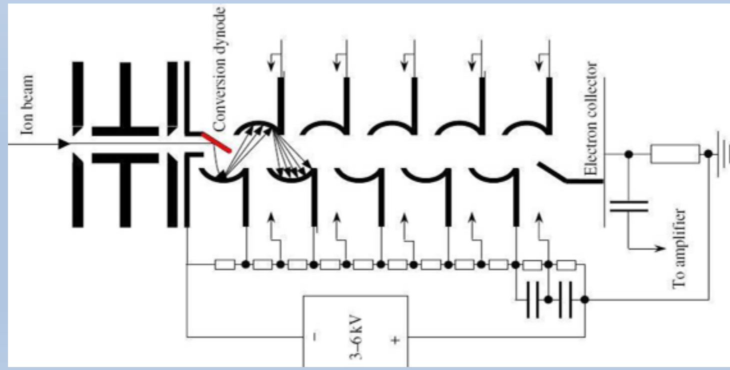
Daly检测器



Schematic of a Daly detector

CDD检测器





7. 检测器

法拉第杯信号（V）和离子计数器信号（cps）换算更具库伦定律计算

1000000cps=16mV

1mV=62500cps

量程：10^{11}欧姆法拉第杯　50V（实际可达56V）

10^{12}欧姆法拉第杯　5V（实际可达4.5V）

10^{13}欧姆法拉第杯　0.5V（实际可达0.4V）

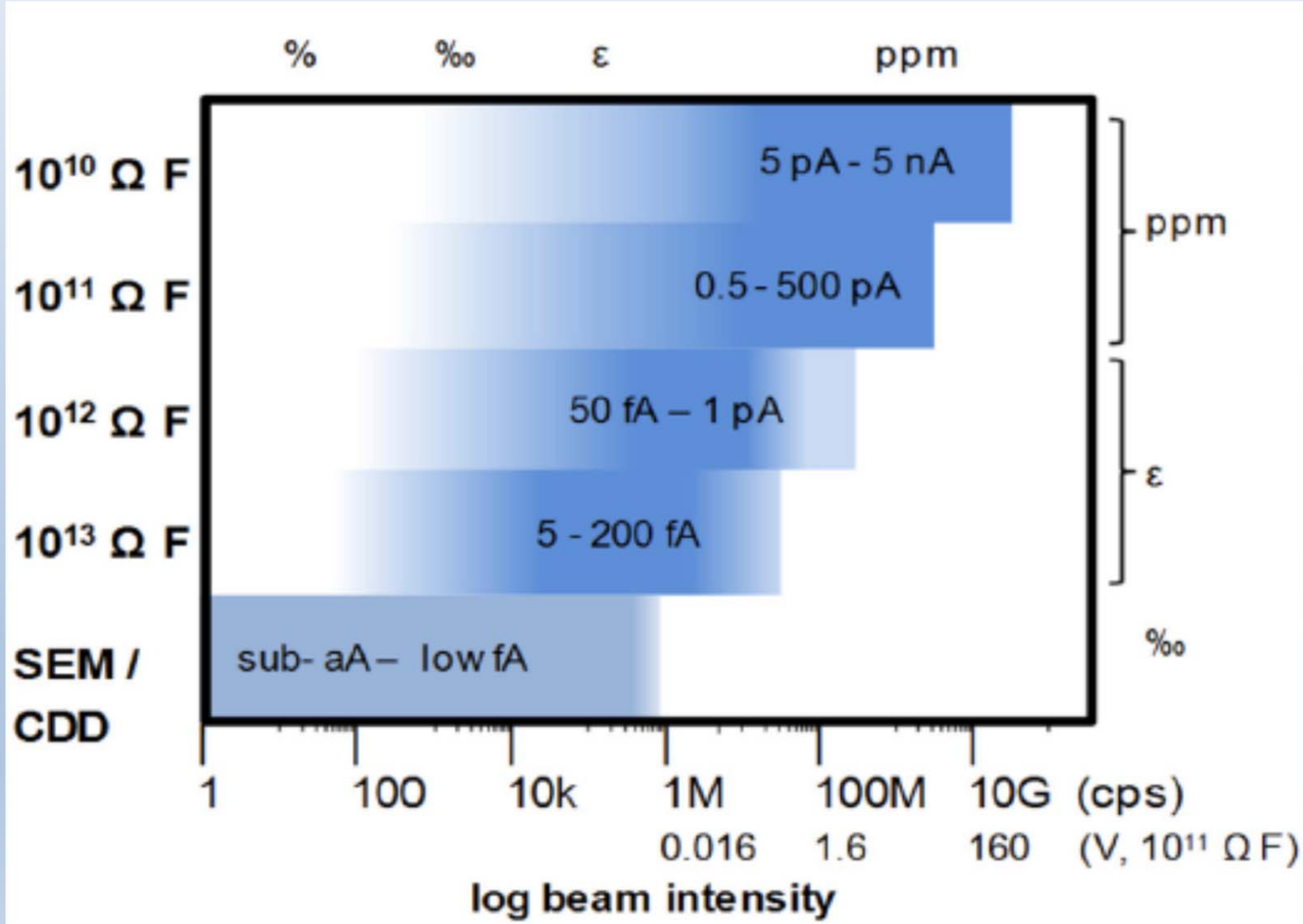
SEM：　2M cps

CDD：　1M cps

Daly：5M cps

7. 检测器

不同检测器的检测范围和分析精度



7. 真空系统

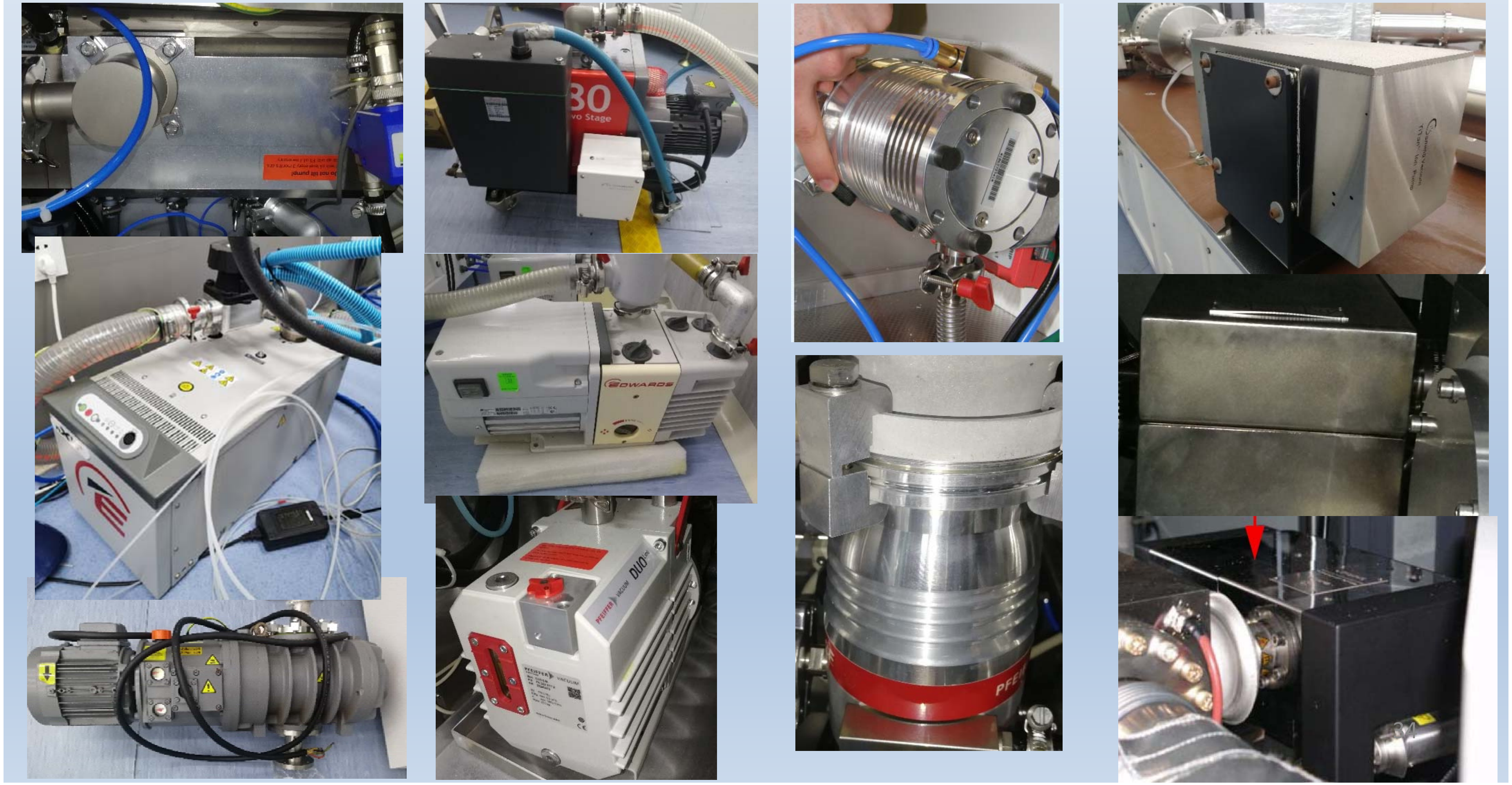
why真空?

离子平均自由程：离子在碰撞到其他粒子前可移动的平均距离

压力/Torr	平均自由程
760（1 atm）	10^{-7}m
0.05	10^{-3}m
10^{-5}	5m
10^{-6}	50m
10^{-7}	500m
10^{-8}	5000m

8. 真空系统

真空泵：罗茨泵（干泵）、机械泵（油泵）、涡轮分子泵、离子泵

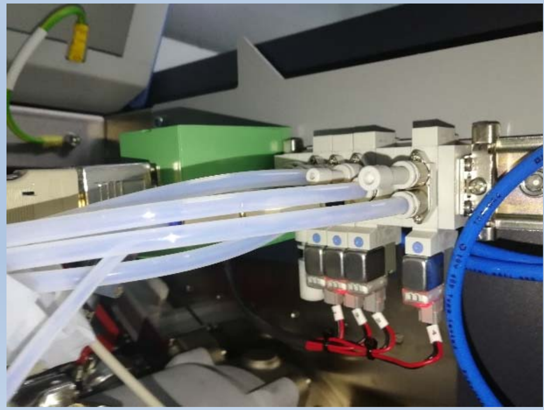
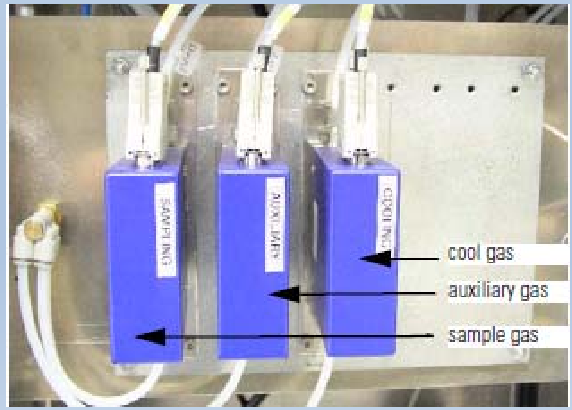


9. 其他

冷却系统：冷却循环水



气路系统：Ar气、N2气、He气、压缩空气等

10. 一些概念

- 灵敏度
- 丰度灵敏度
- 质量分辨率和质量分辨能力
- 质量歧视：离子通透效率、空间电荷效应等
- 基体效应：质谱干扰、浓度、酸度、基体元素等

灵敏度

仪器检测器对样品中元素、同位素到达检测器的离子的信号响应

V / ppm	Nu II Spec	Nu 3 THS	Neptune Plus
Li	300	550	1000
Mg	430	760	1200
Sr	500	1280	1500
Nd	550	1360	1500
Hf	600	1160	1500
Pb	1000	2250	2200
U	800	1610	2000

信号放大器：10^{11} 欧姆

Cetac Aridus 2 膜去溶进样，100ul/min 提升量

灵敏度

离子通透率Ion transmission efficiency

ITE=measured ion/number of atom in sample

- 溶液湿法：~0.05-0.06%
- 溶液干法：～0.6-0.8%
- 激光法：～1-2.5%

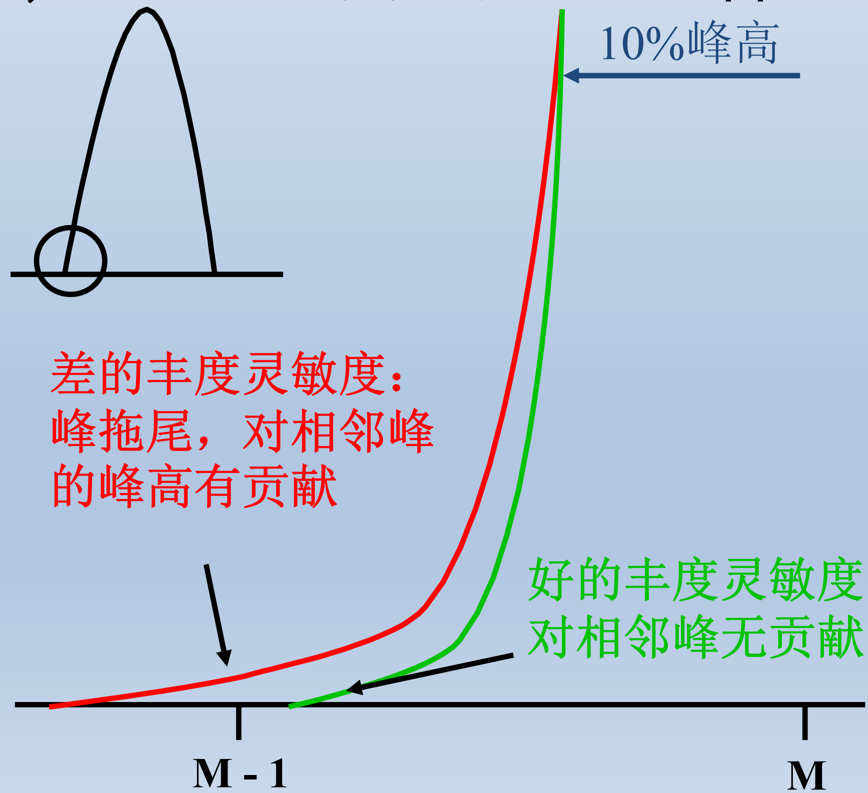
丰度灵敏度

某个质量数的离子对相邻质量数的干扰强度

如M对M-1和M+1处的质量数的拖尾干扰

以238U为例，其在237和239出的拖尾可以测量：237/238

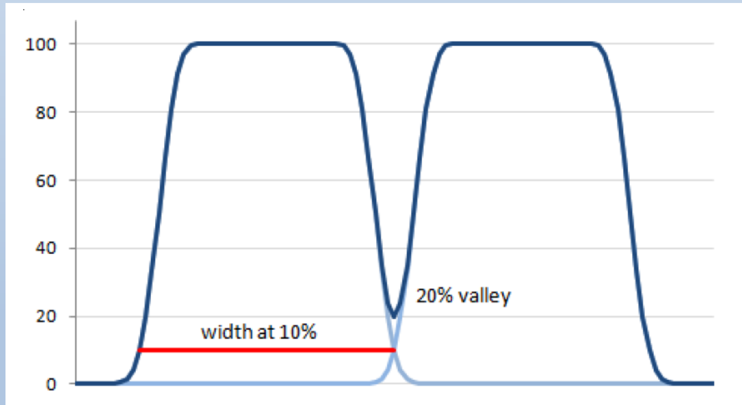
一般2.5-5ppm，通过RPQ可以到0.2-0.5ppm

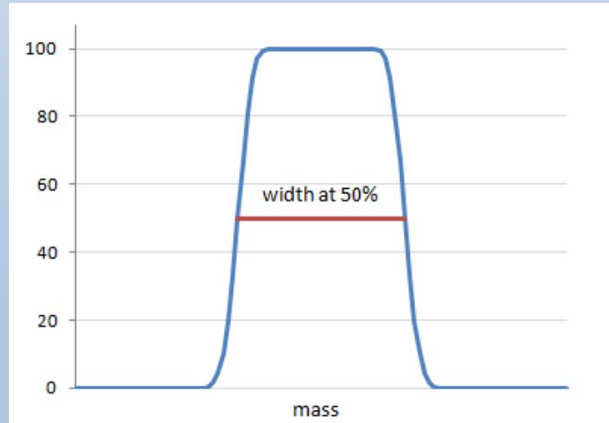


质量分辨率和分辨能力

Mass resolution and mass resolving power

$$\text{Mass Resolution} = \frac{M}{dM}$$

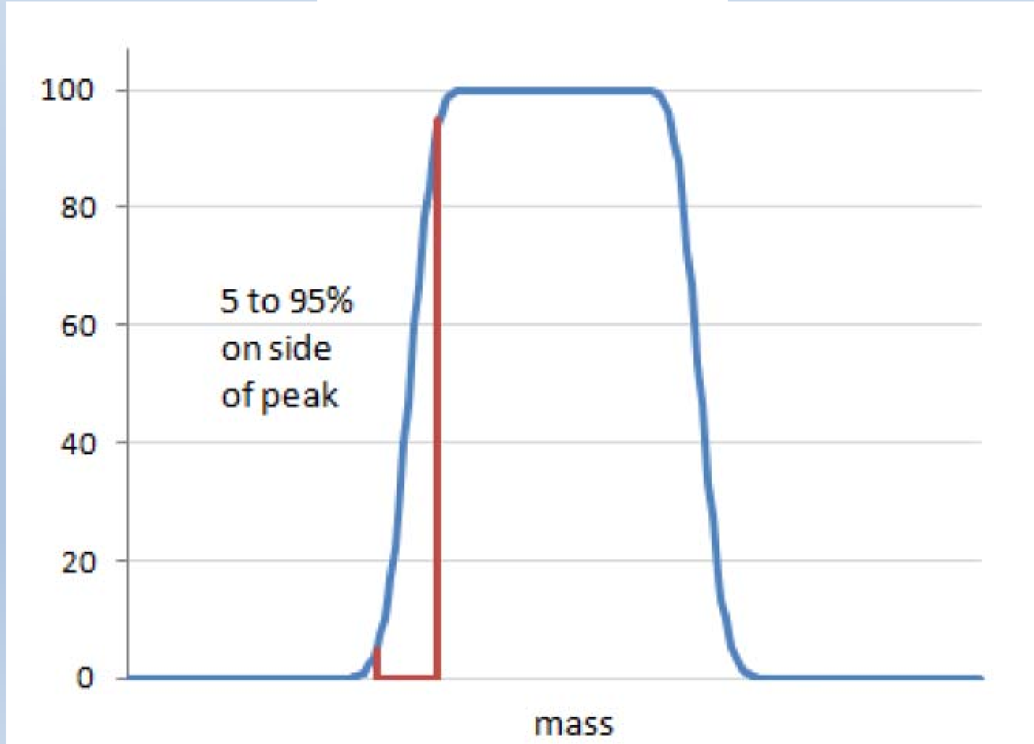




质量分辨率和分辨能力

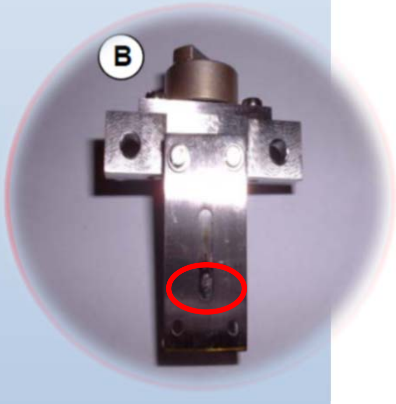
Mass resolution and mass resolving power

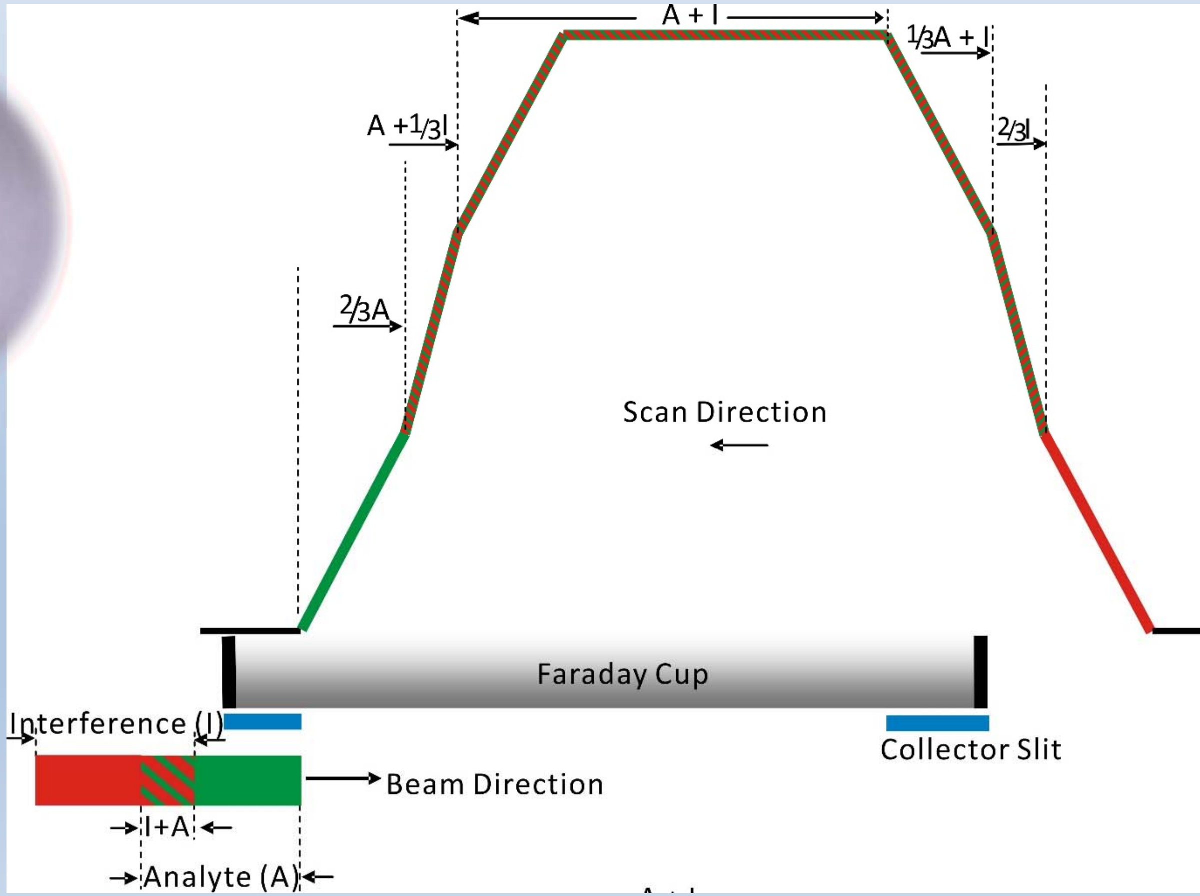
$$MRP = \frac{M}{dM_{5-95}}$$

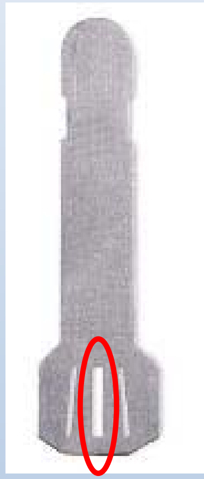


质量分辨率和分辨能力

LR

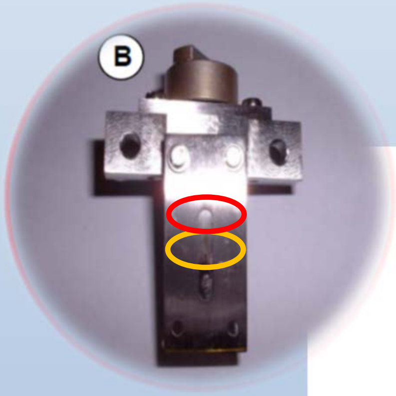


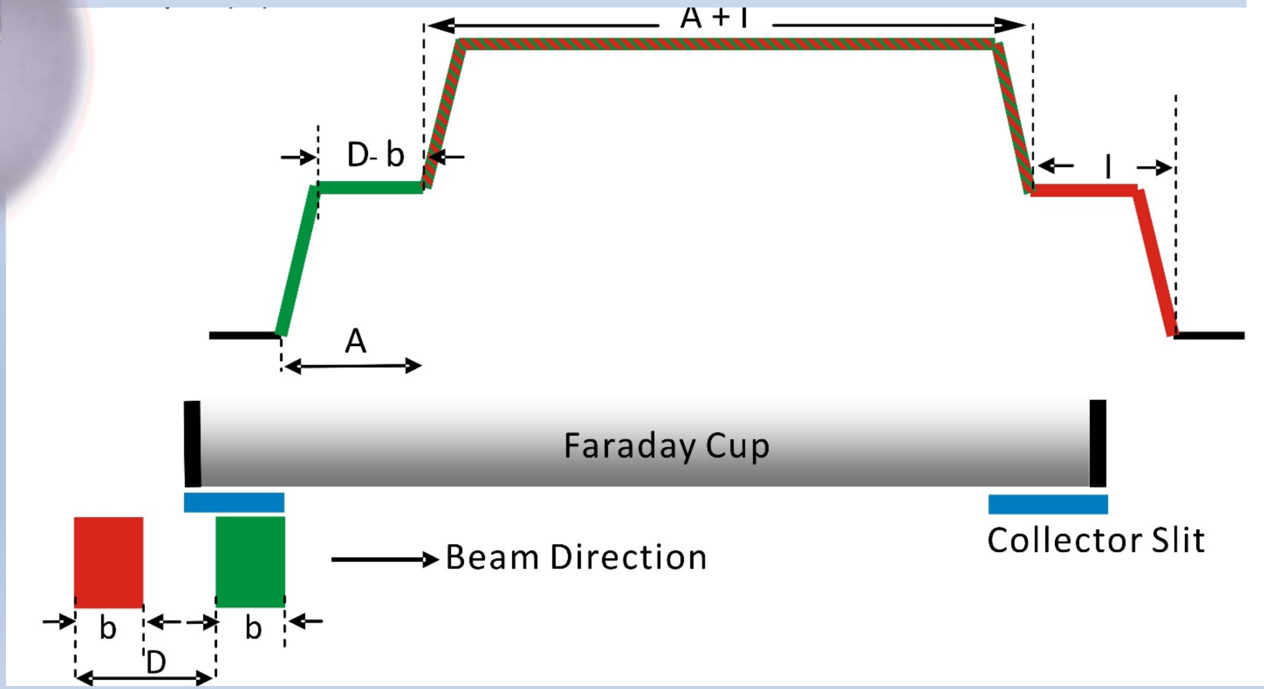




质量分辨率和分辨能力

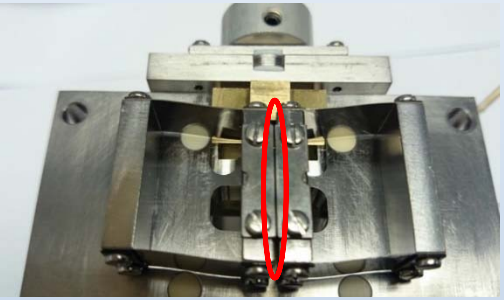
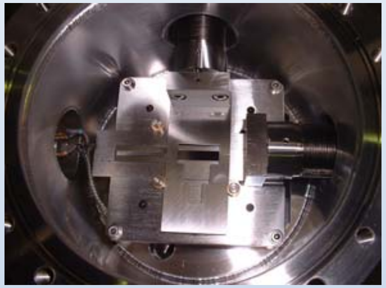
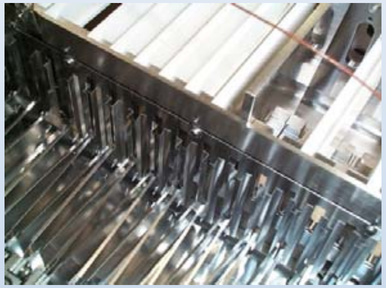
MR

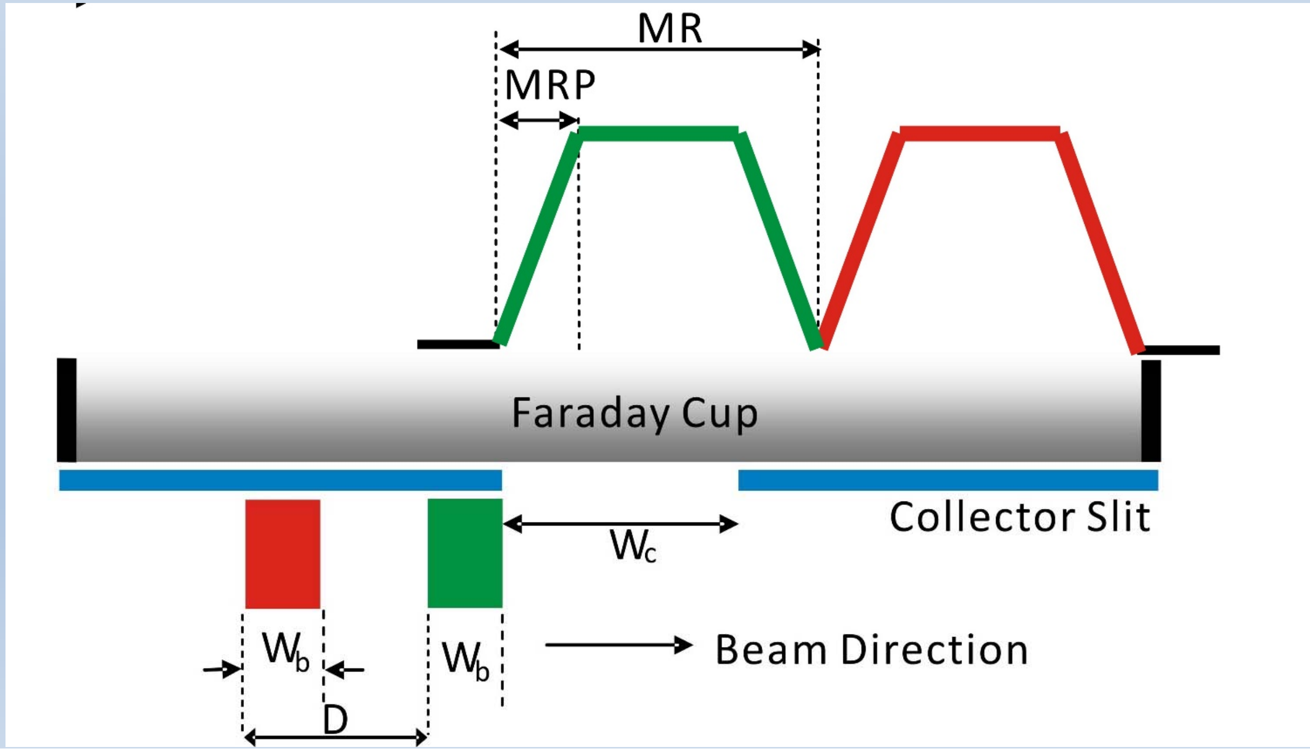




质量分辨率和分辨能力

HR

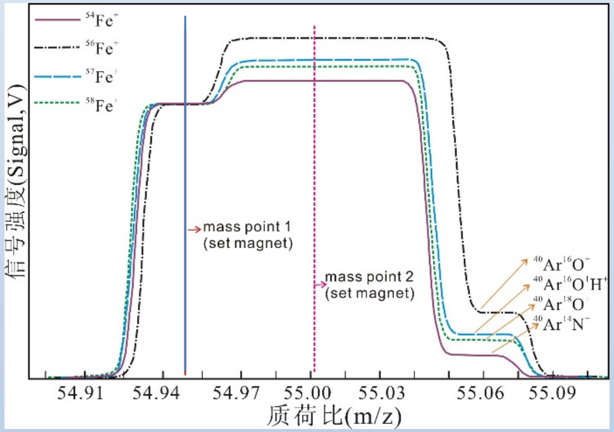






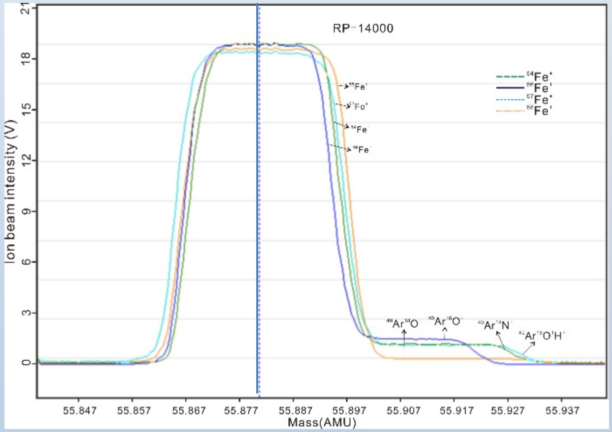
质量分辨率和分辨能力

Mass resolution and mass resolving power

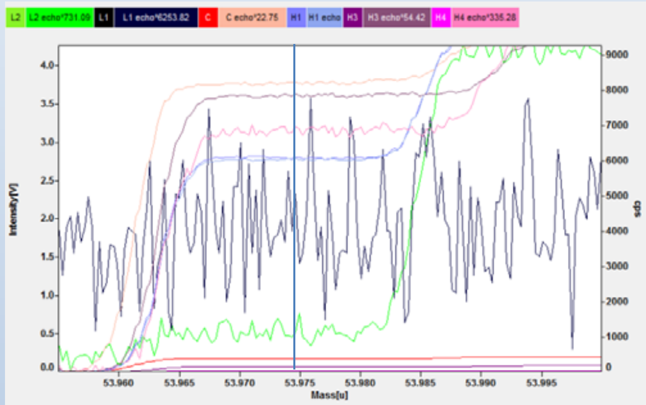
RP=8000-10000



RP=20000



RP=8000-10000



三.MC-ICP-Ms的未来

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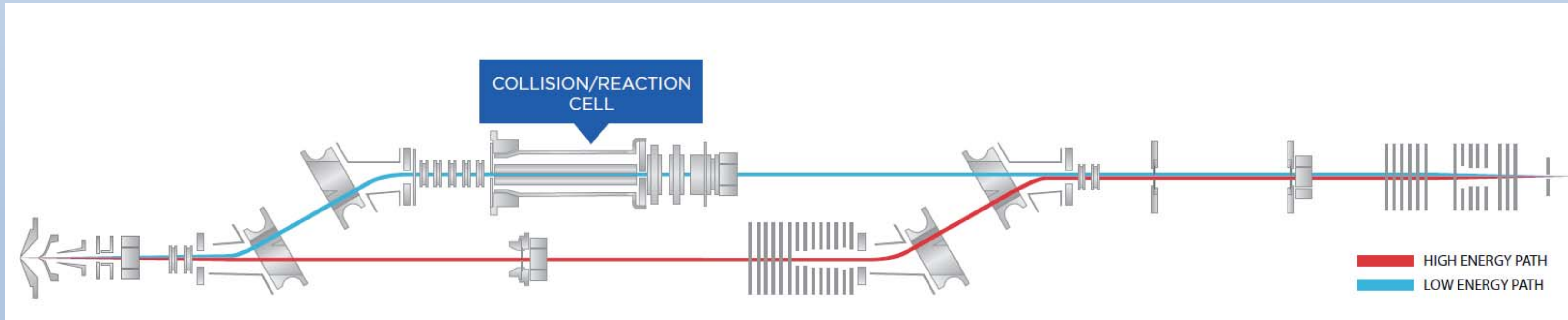
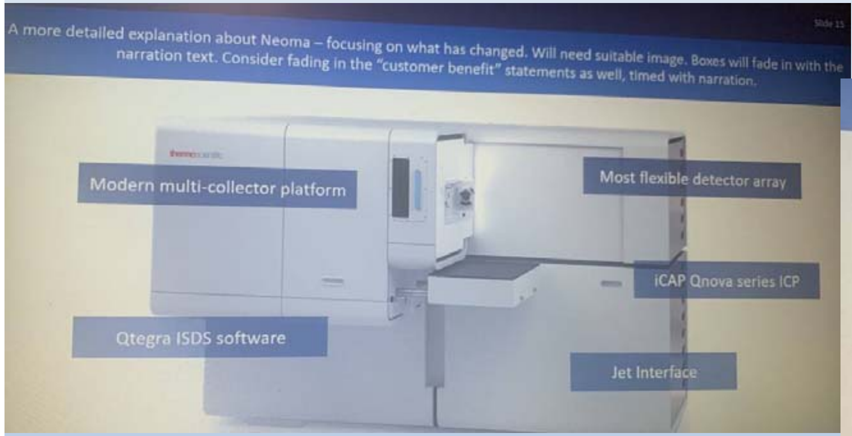
1. 碰撞反应池的应用

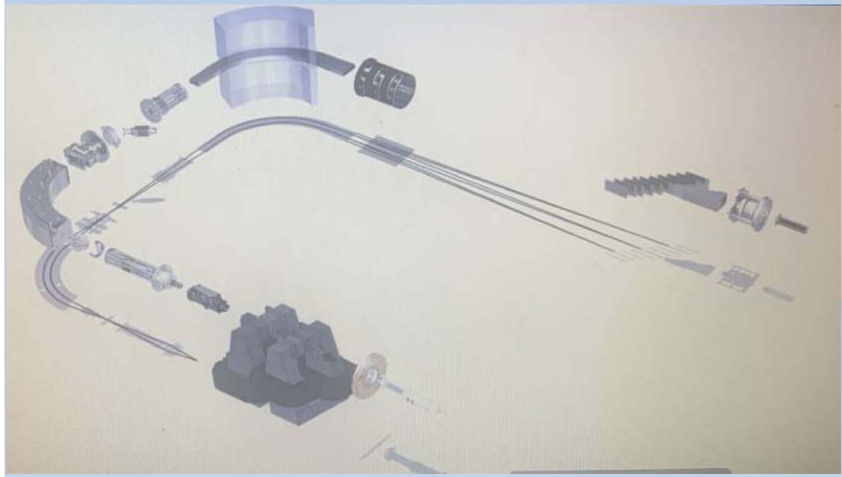


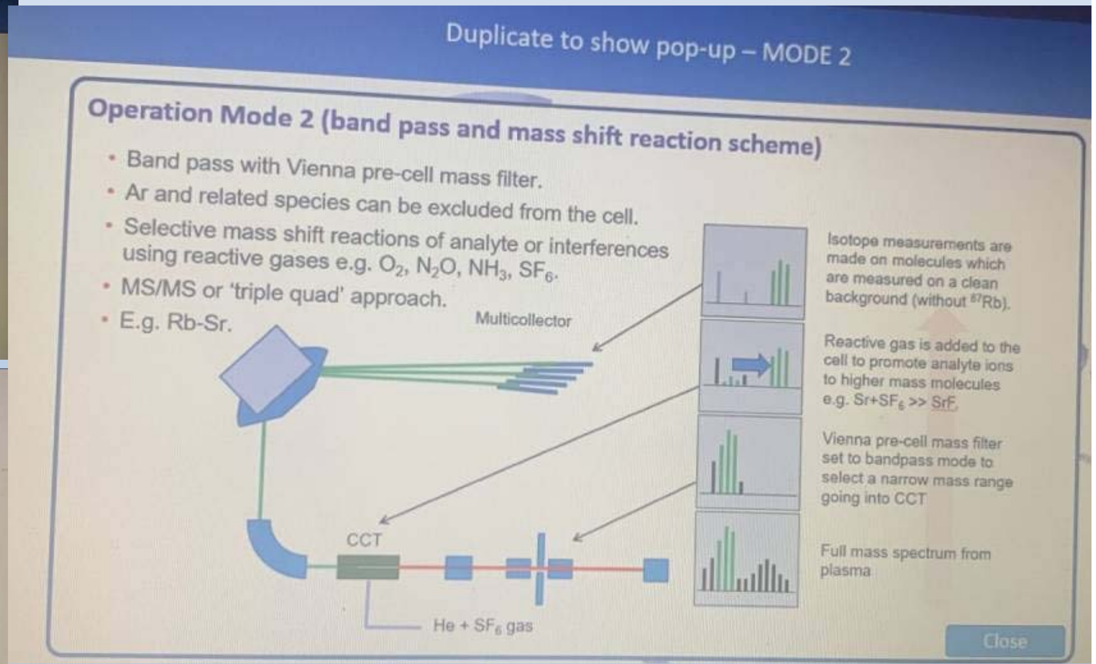
三.MC-ICP-Ms的未来

1. 碰撞反应池的应用

MC-ICPMS + ICP-MS/MS

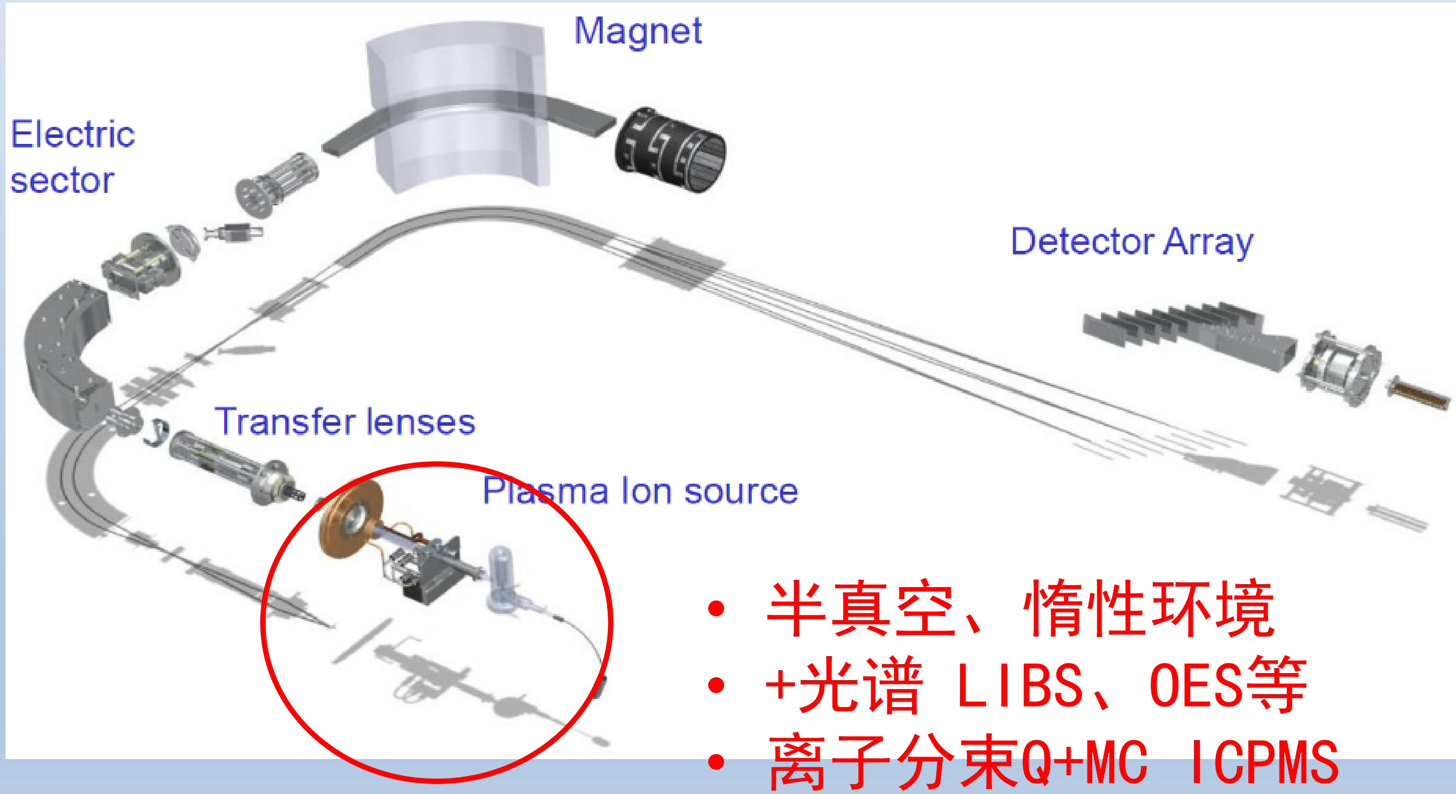






三.MC-ICP-Ms的未来

2. 进样系统和离子源的改进和革新



- 半真空、惰性环境
- +光谱 LIBS、OES等
- 离子分束Q+MC ICPMS
- ……