

Spectroscopy  **Thermo**
SCIENTIFIC

Introduction to and Instrumentation for Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

LIVE WEBCAST: Tuesday, February 14, 2012 at 11:00 am EST

WEBCAST NOTES

- Interact with speaker by typing your questions in the “Submit Question” box located below the video window.
- You can enlarge the slide window at anytime by clicking on the “Enlarge Slides” button, located below the presentation window. The slides will advance automatically throughout the event.
- If you are experiencing technical problems with viewing or hearing this webcast, please click on the “Help” button below the video window.

INTRO TO ICP-MS

R. S. HOUK

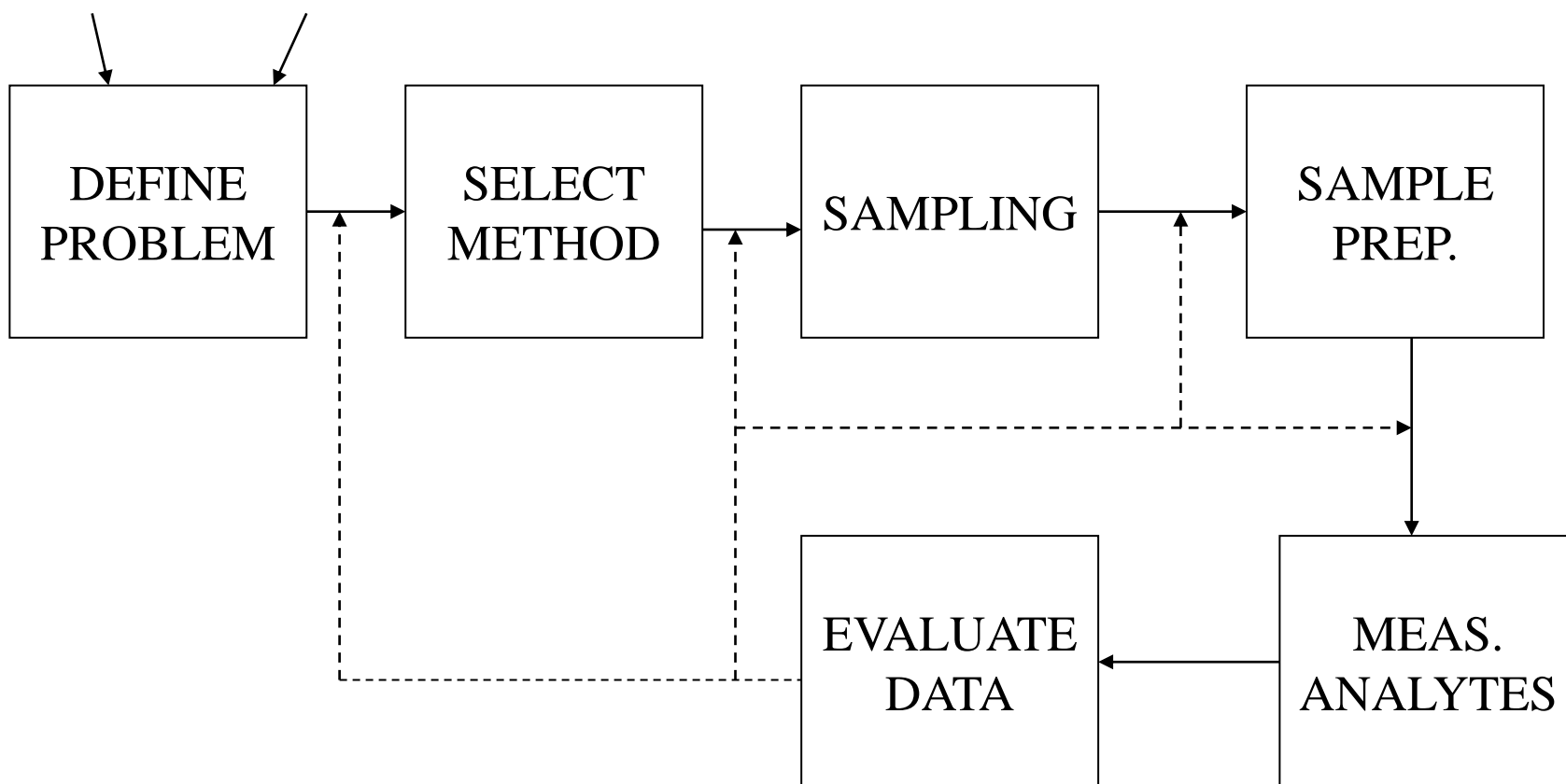
AMES LABORATORY - USDOE, IOWA STATE UNIV.

TOPICS:

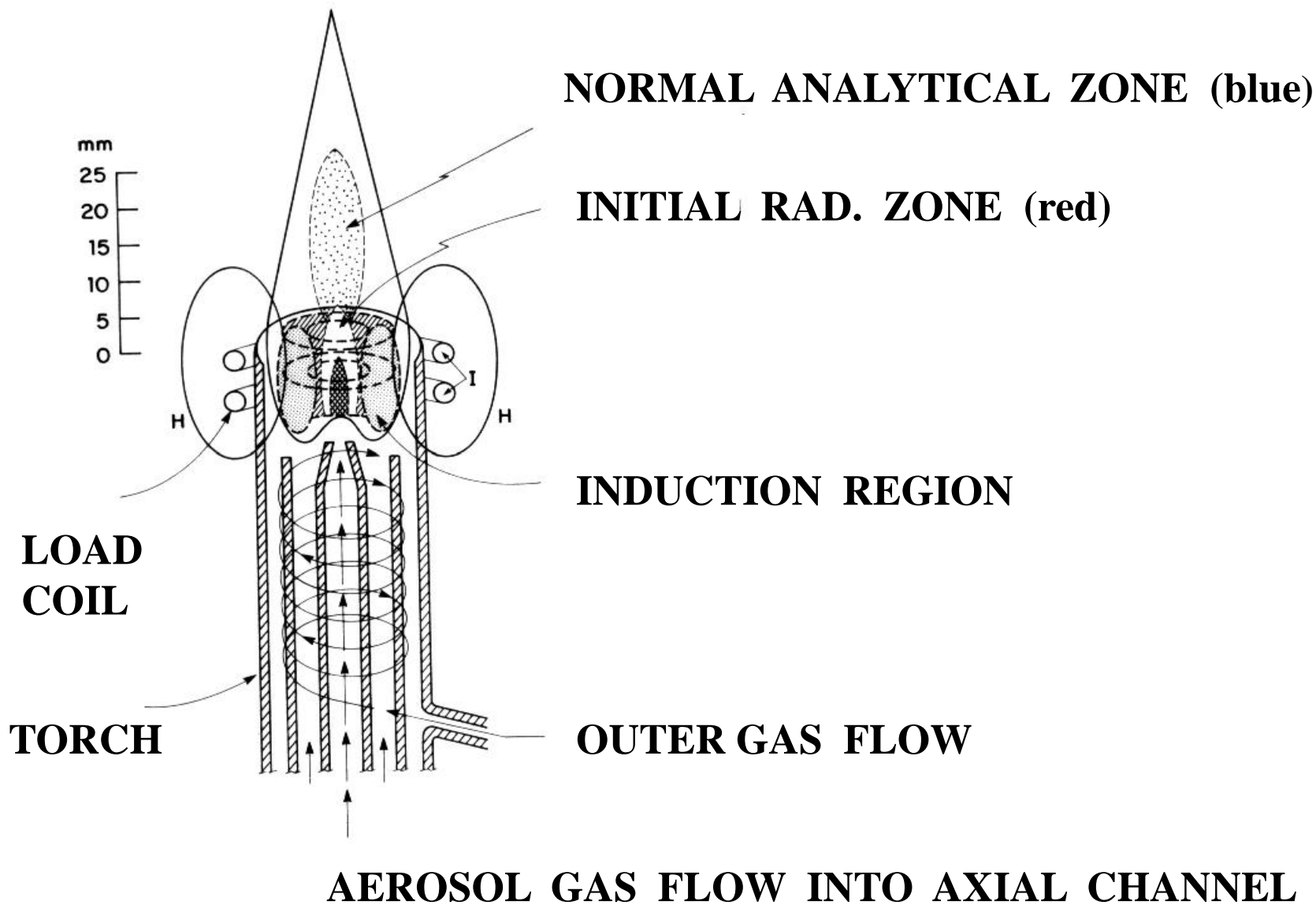
- 1. GENERAL ANALYTICAL CAPABILITIES**
- 2. ICP AS ION SOURCE**
- 3. SAMPLE INTRODUCTION**
- 4. ION EXTRACTION**
- 5. MASS ANALYSIS – QUADRUPOLE, MAG. SECTOR**
- 6. ION DETECTION**
- 7. MATRIX EFFECTS**
- 8. APPLICATIONS SURVEY**
- 9. SOLVENT REMOVAL & COLLISION CELLS**

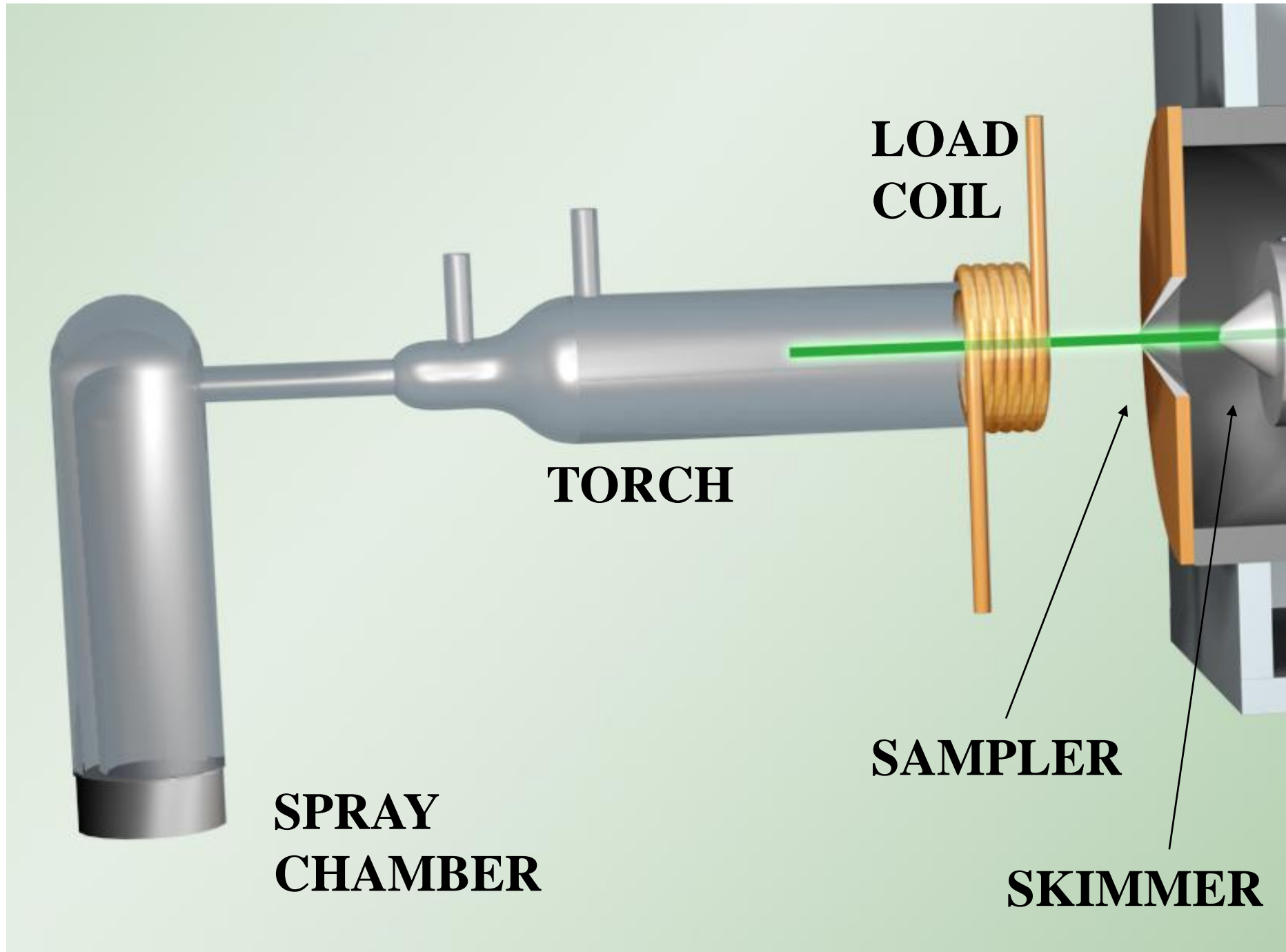
OVERALL ANALYTICAL PROCESS

Analyst Client

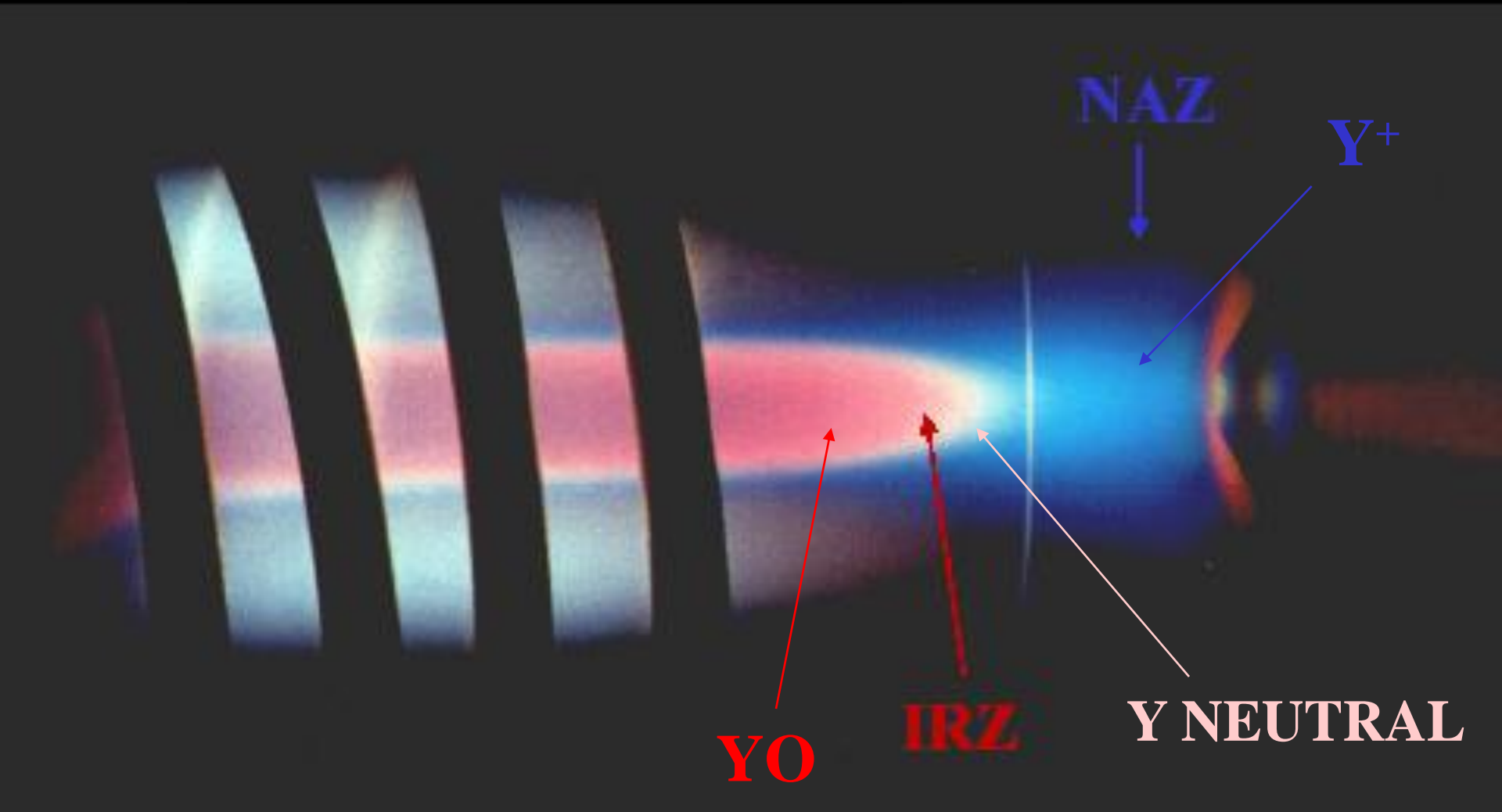


ICP AS ION SOURCE

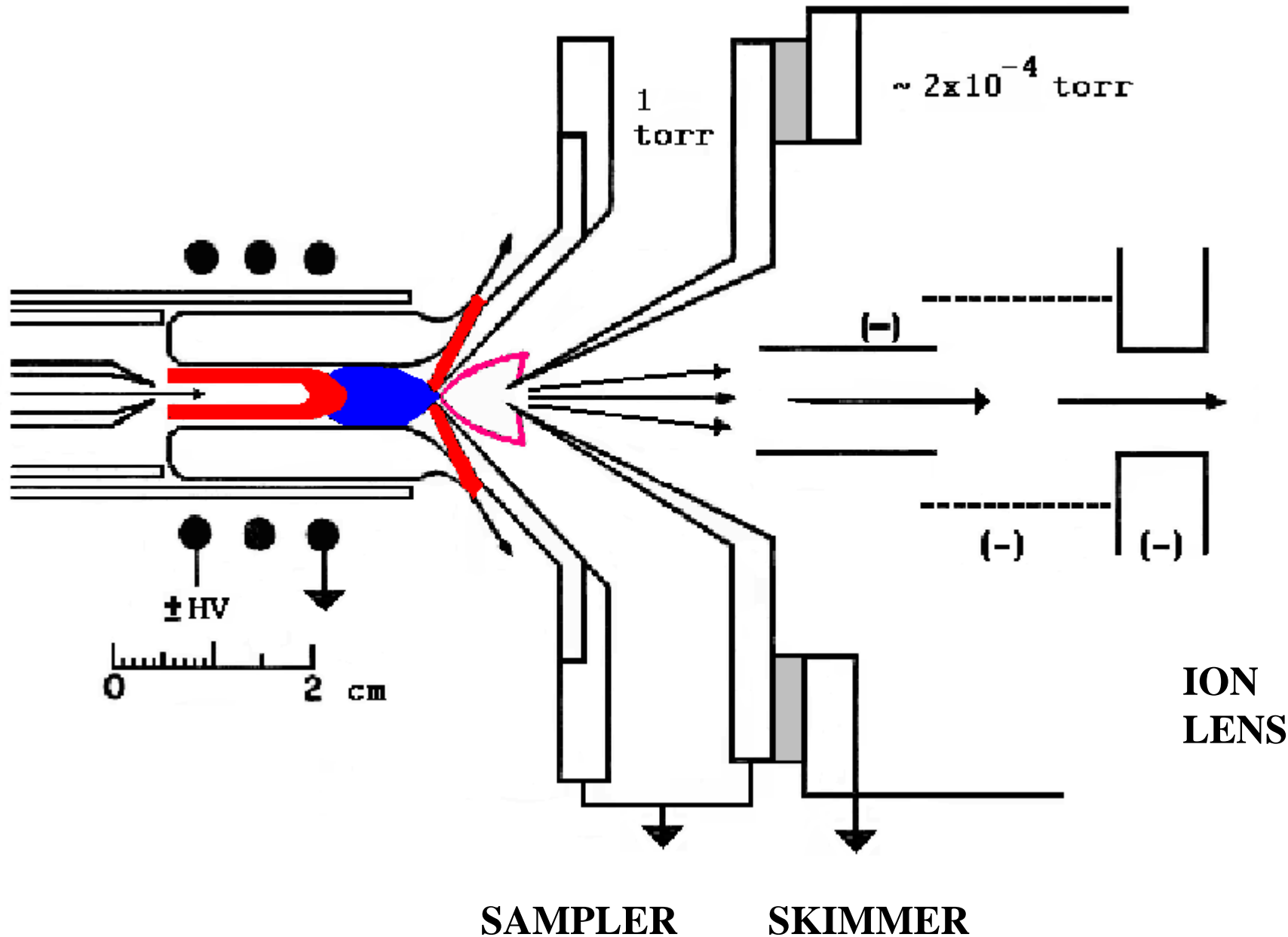




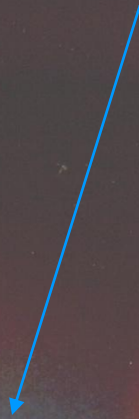
YO, Y(I), Y(II) EMISSION ZONES



ION SAMPLING INTERFACE



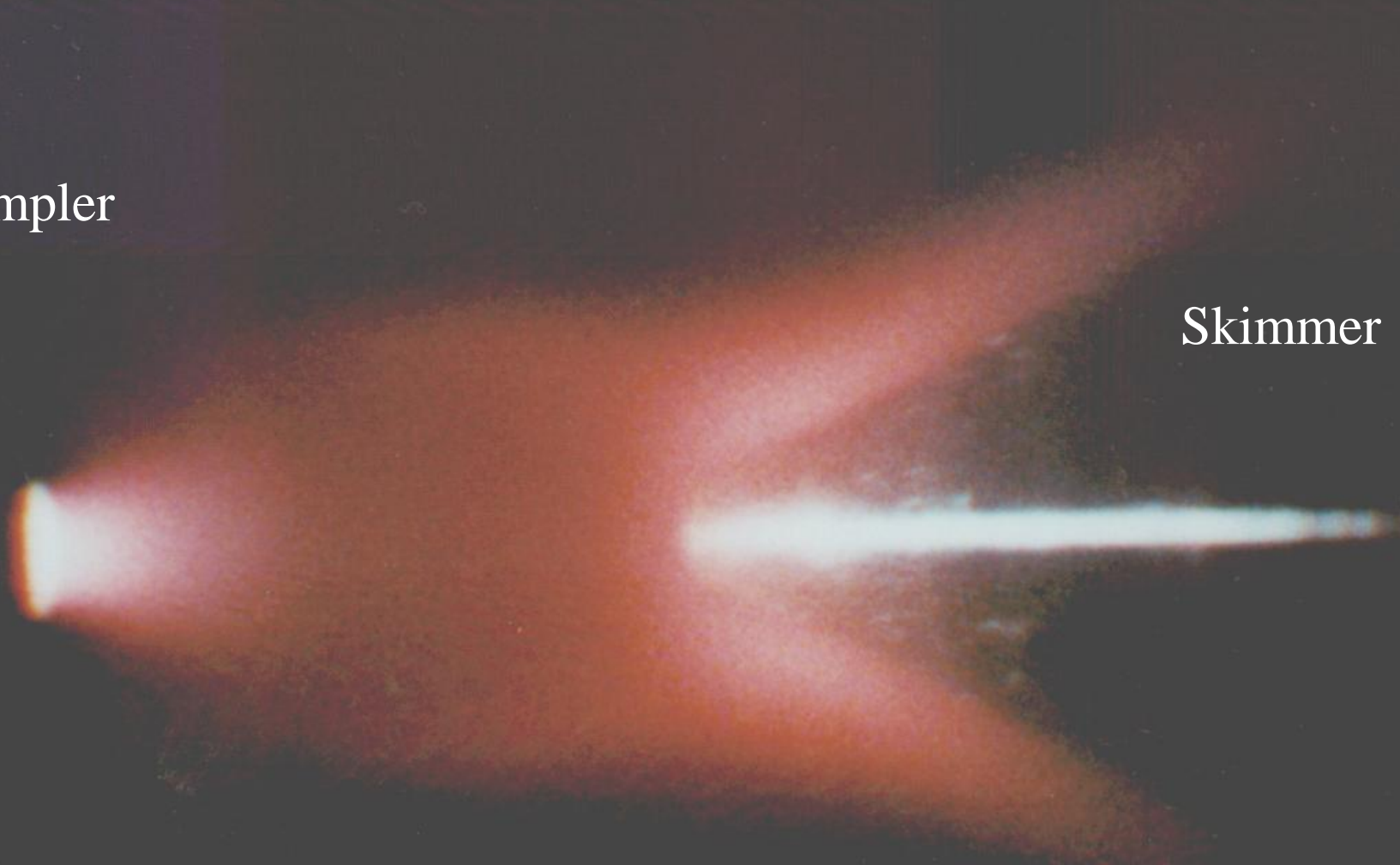
**Y⁺ IONS
INTO SAMPLER**



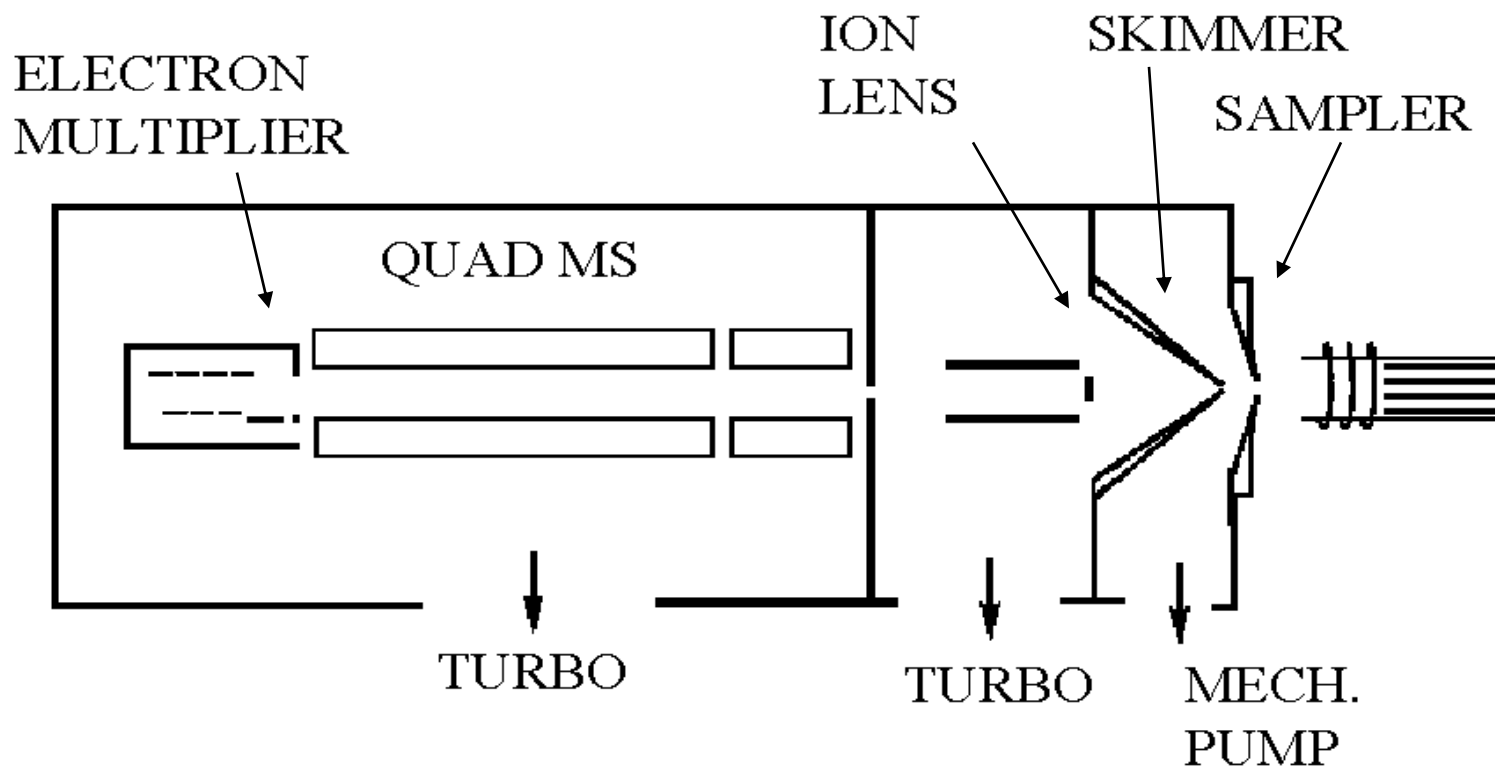
Sampler

Skimmer

Photo by A. L. Gray

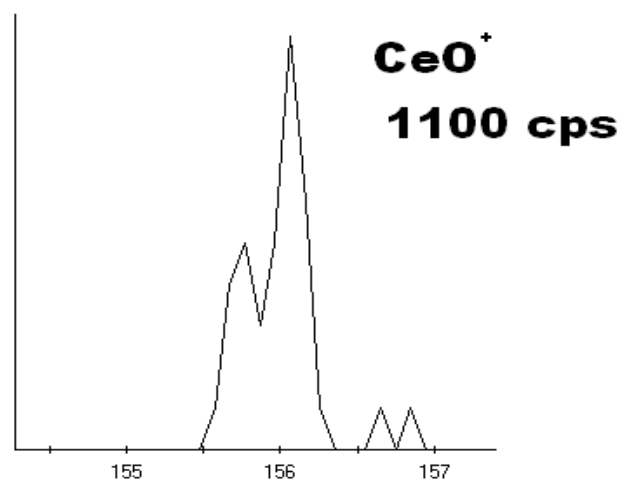
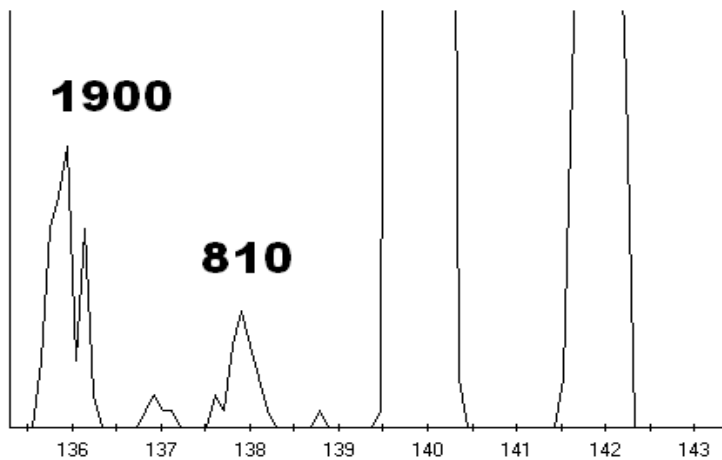
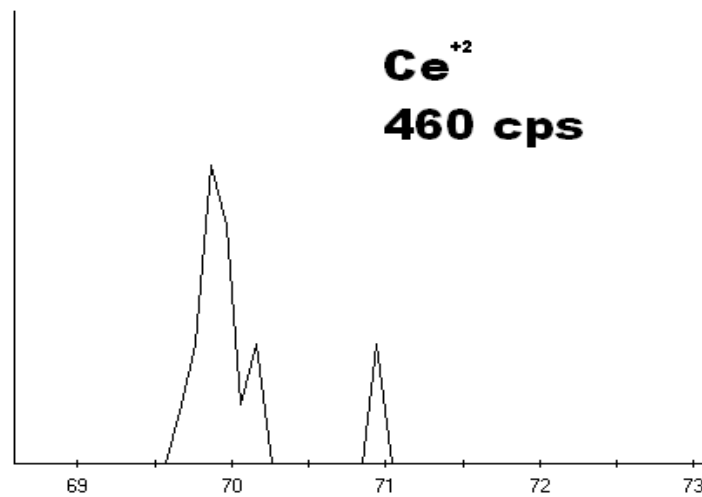
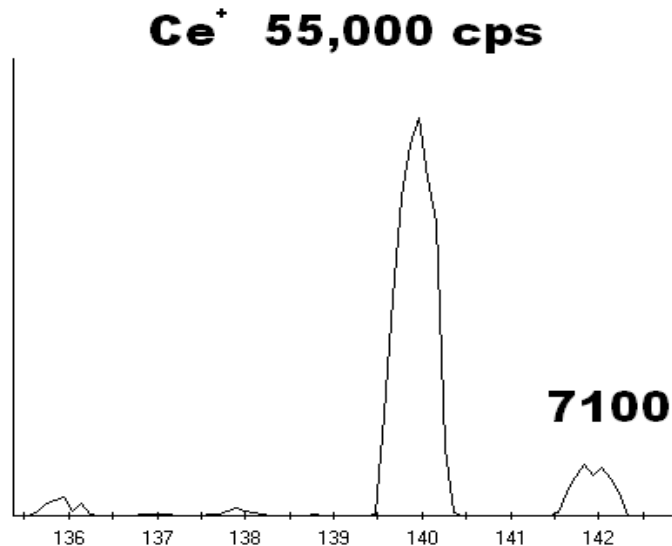


ICP-MS DEVICE



1 ppb Ce

ION COUNT RATE



m/z RATIO

ICP-MS CAPABILITIES

DETECTION LIMITS

0.1 - 10 ppt routine

10 ppq SOME INSTS.

USUALLY BLANK-LIMITED

TOTAL SOLUTES

0.1% USUALLY OK

1% USUALLY PROBLEMS

UNLESS USE FLOW INJECTION

PRECISION

3% RSD ROUTINE

1% GOOD

1% ROUTINE W. INT. STDS.

ACCURACY COMPARABLE TO PRECISION IF
COMPENSATE FOR INTERFERENCES

INTERFERENCES (REL. TO ICP-AES)

**SPECTRAL
OVERLAP** **LESS FREQUENT THAN AES
LESS SEVERE
MORE PREDICTABLE
EASIER TO CORRECT**

**MATRIX
INTS.** **WORSE IN
ICP-MS**

- PLUGGING**
- CHANGE OF SIGNAL
(usually loss)**

APPLICATION AREAS

1. ENVIRONMENTAL ANALYSIS

2. GEOCHEMISTRY

3. SEMICONDUCTORS

4. NUCLEAR INDUSTRY

5. BIOMEDICAL

6. FORENSICS

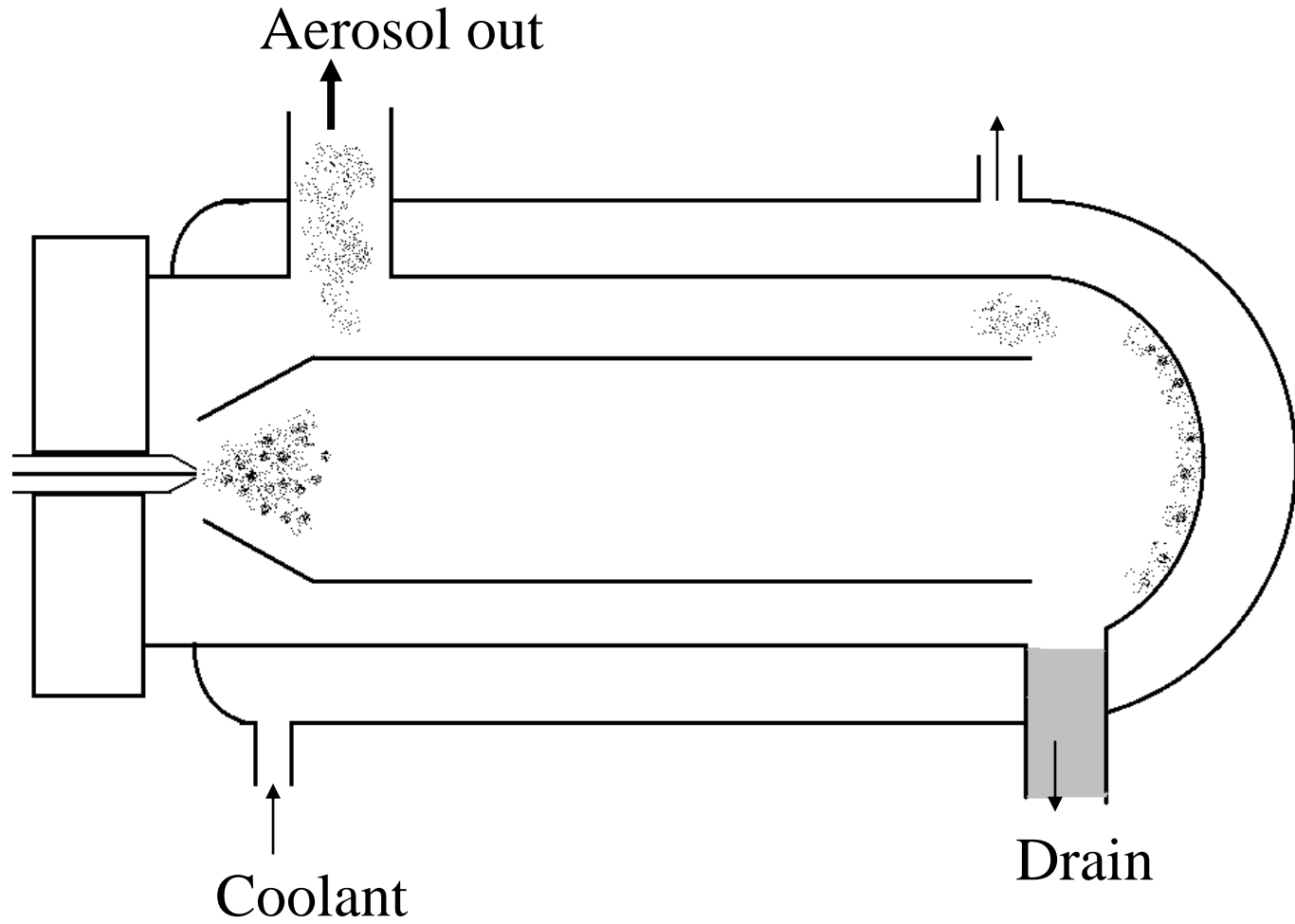
Solution Samples

Concentric Pneumatic Nebulizer

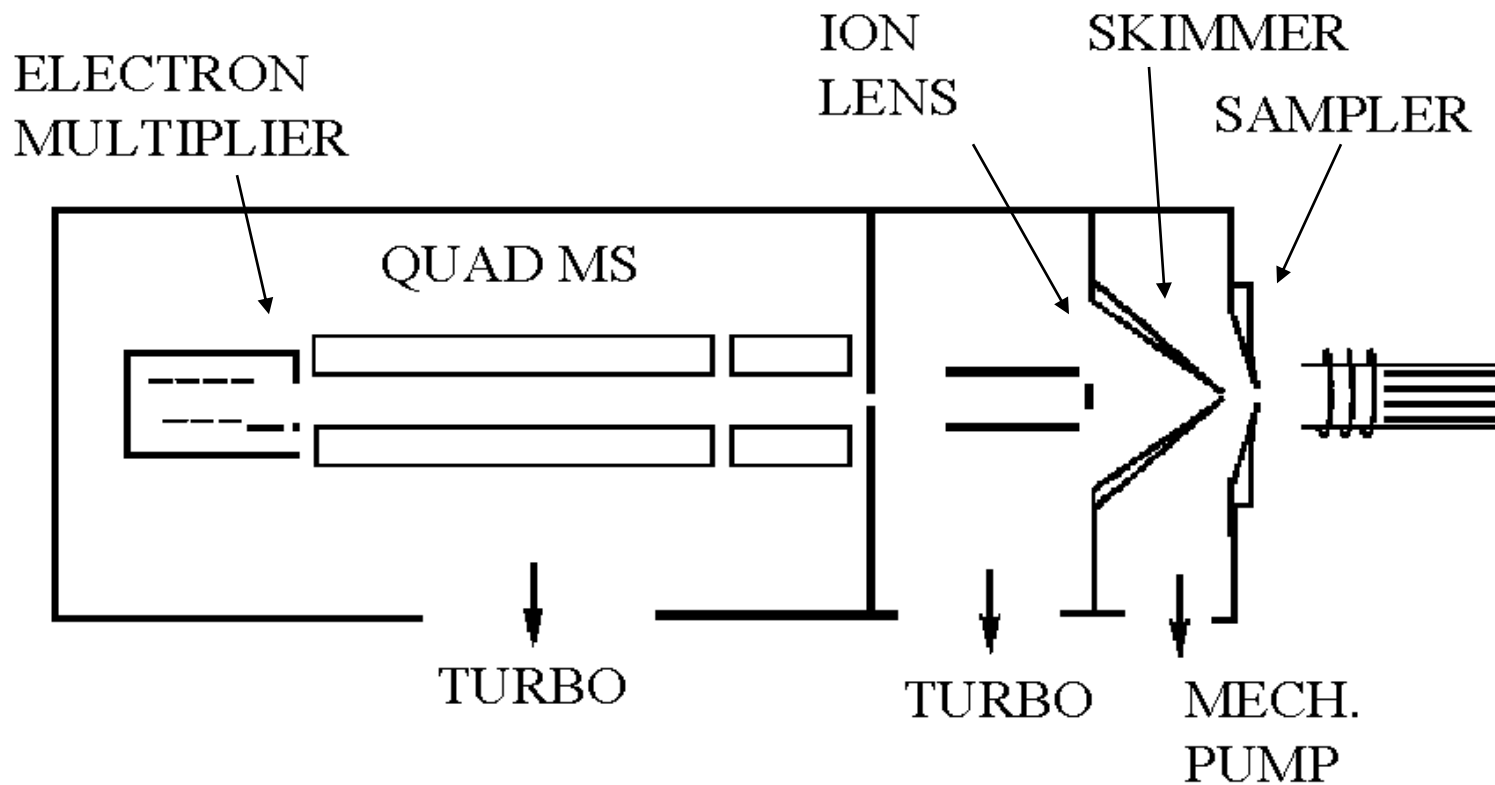
- 100% Teflon
- Self-aspiration:
 - 20 $\mu\text{L}/\text{min}$
 - 50 $\mu\text{L}/\text{min}$
 - 100 $\mu\text{L}/\text{min}$
 - 400 $\mu\text{L}/\text{min}$



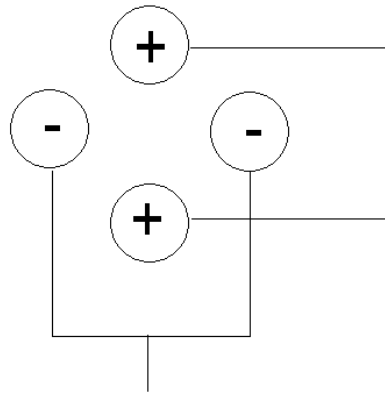
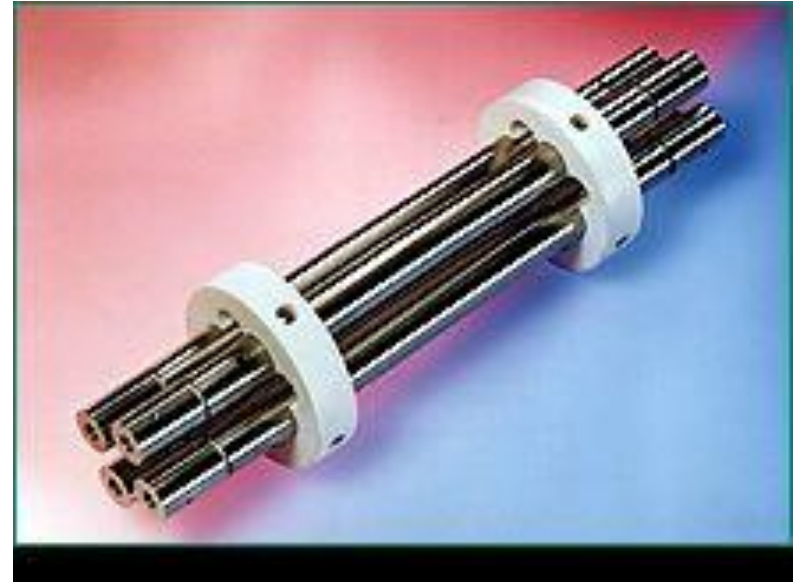
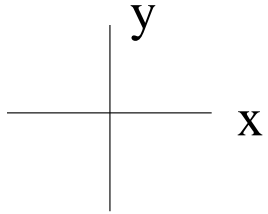
SPRAY CHAMBER & SOLVENT REMOVAL



ICP-MS DEVICE

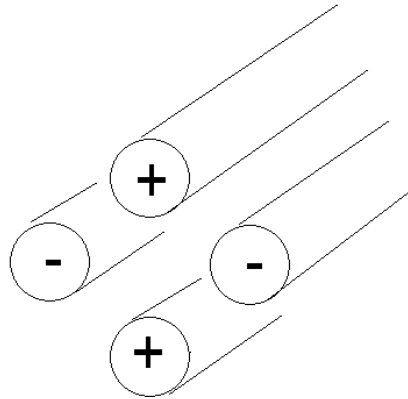


QUADRUPOLE MASS ANALYZER

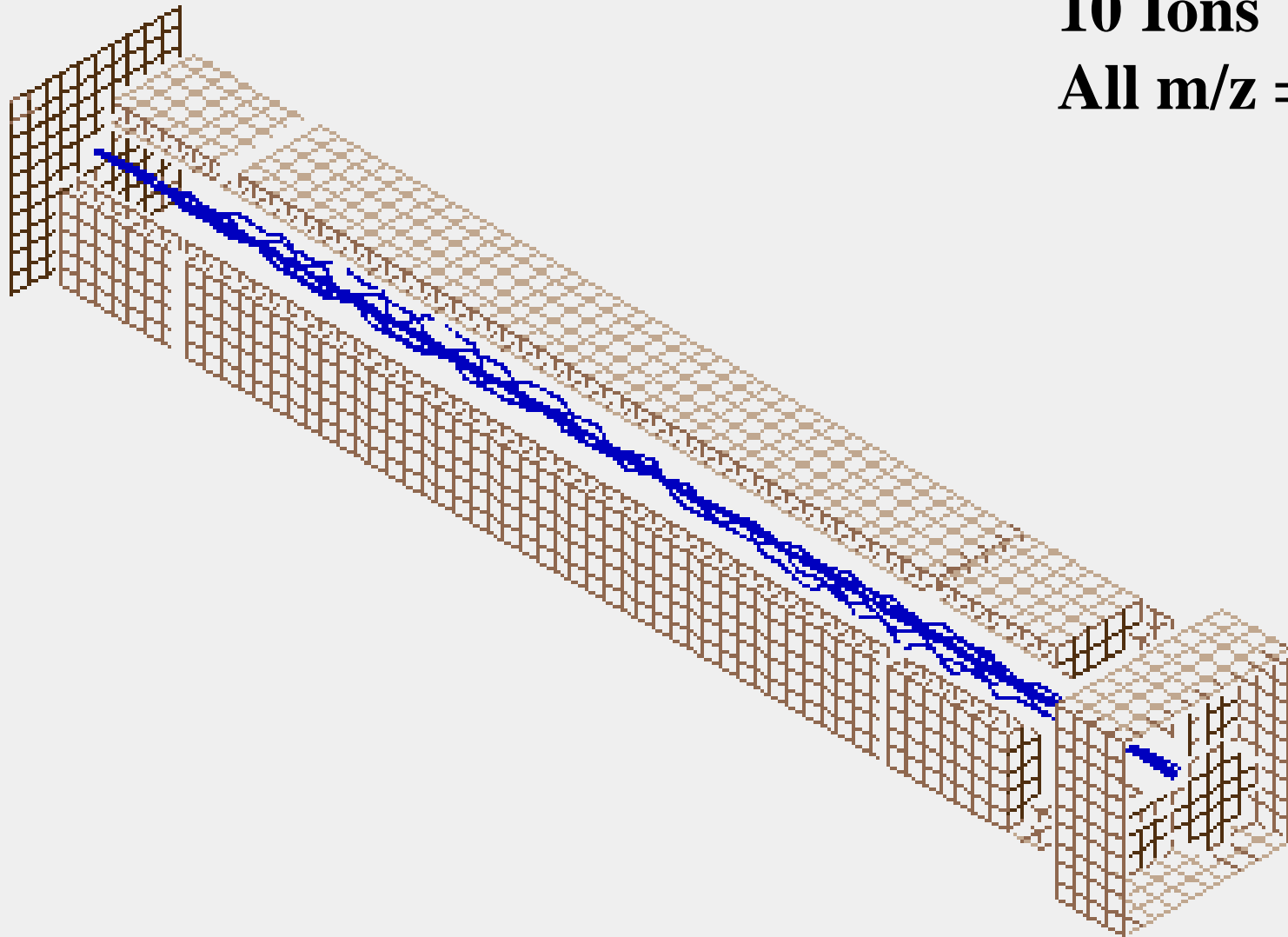


$$U + V \cos \omega t$$

$$-(U + V \cos \omega t)$$



SIMION - QUADRUPOLE



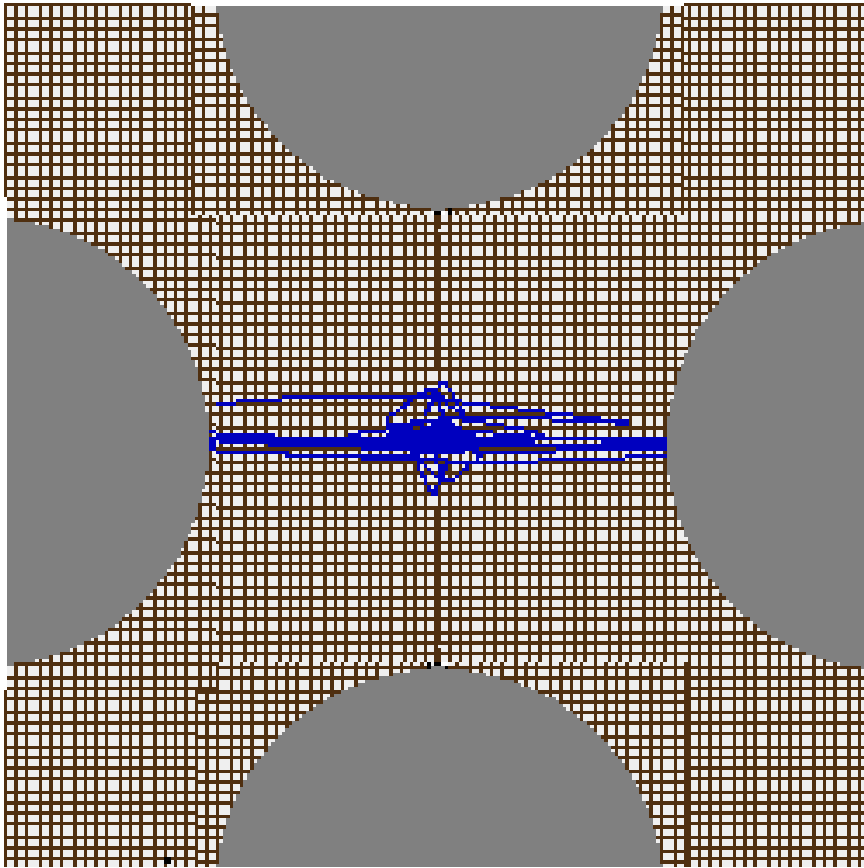
10 Ions

All $m/z = 100$

$m/z = 100$ STABLE

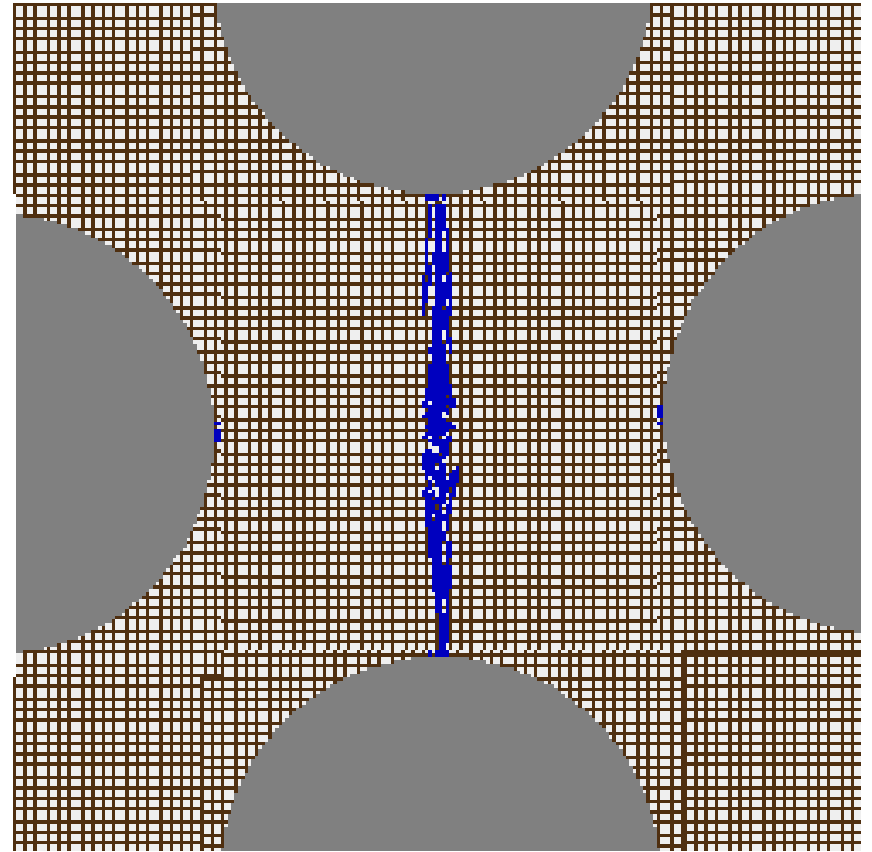
10 Ions

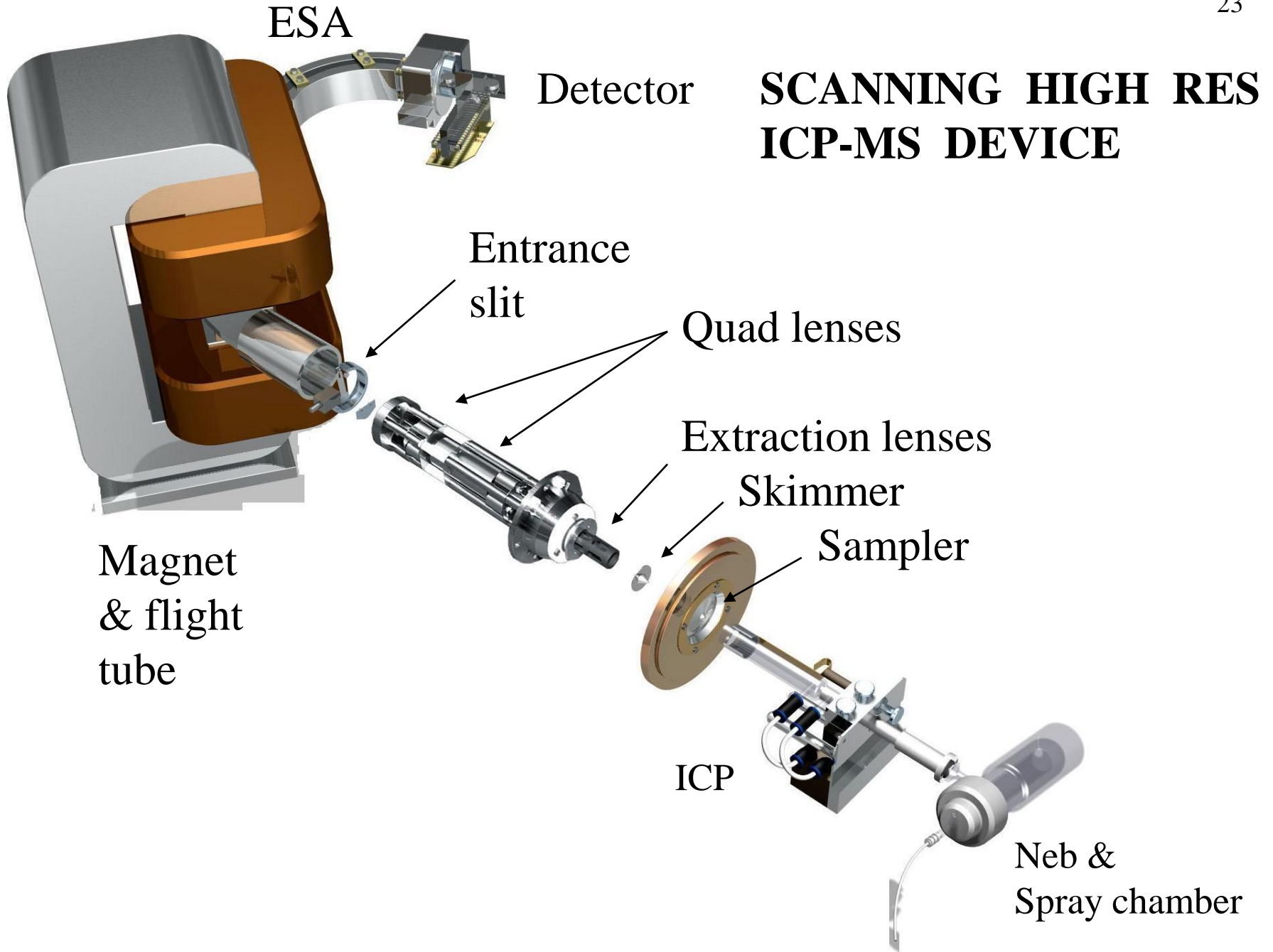
All $m/z = 90$

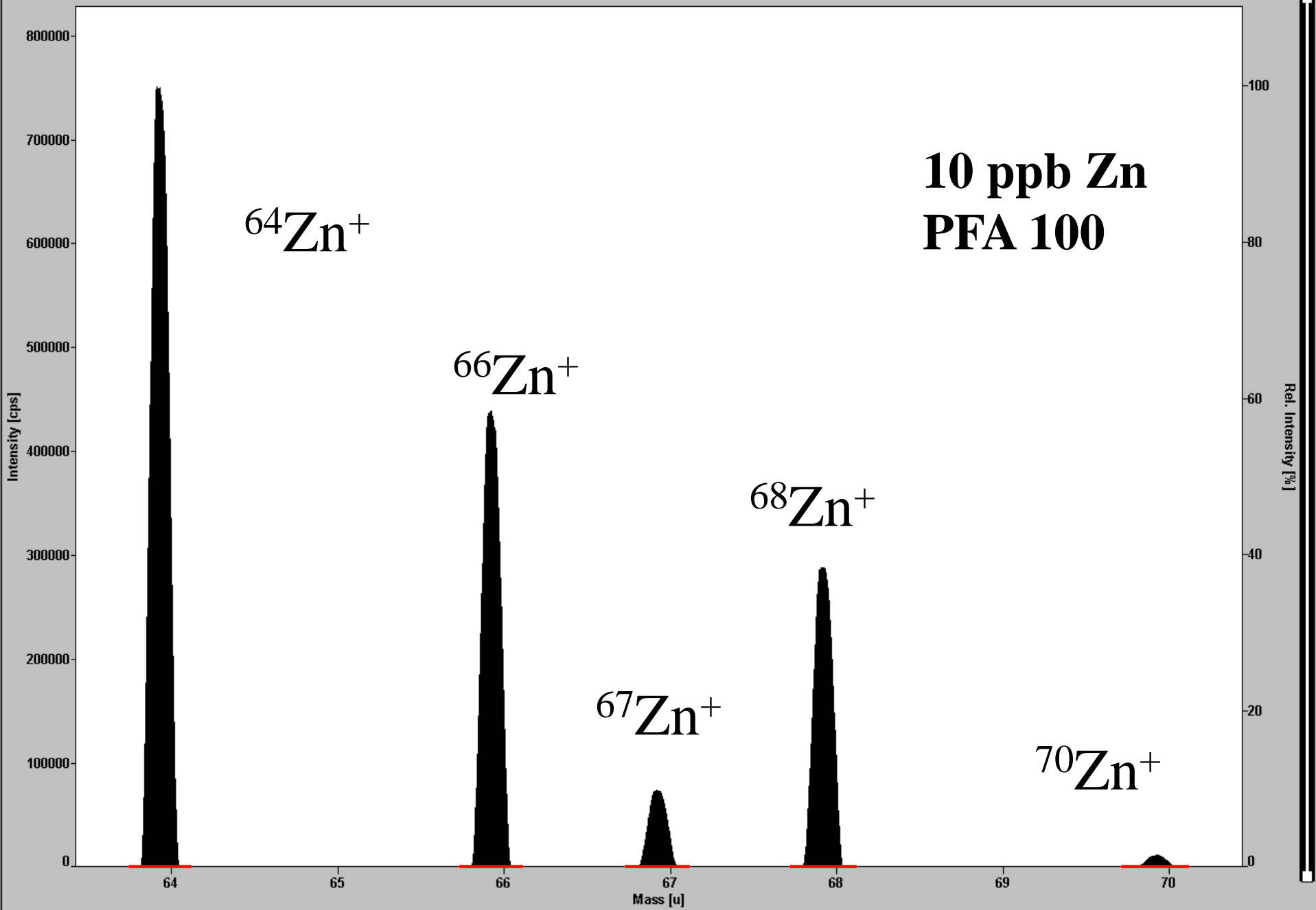


10 Ions

All $m/z = 110$



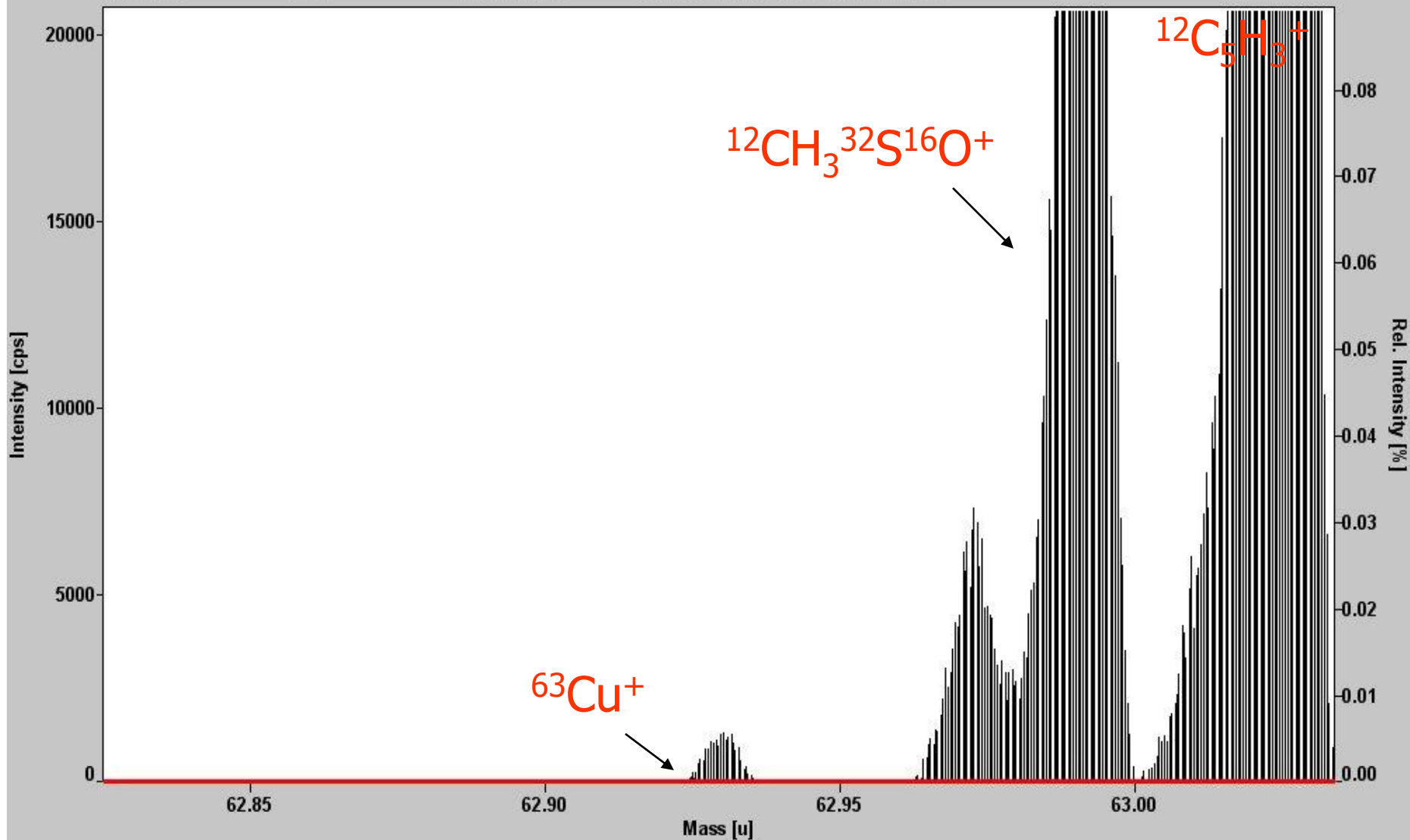




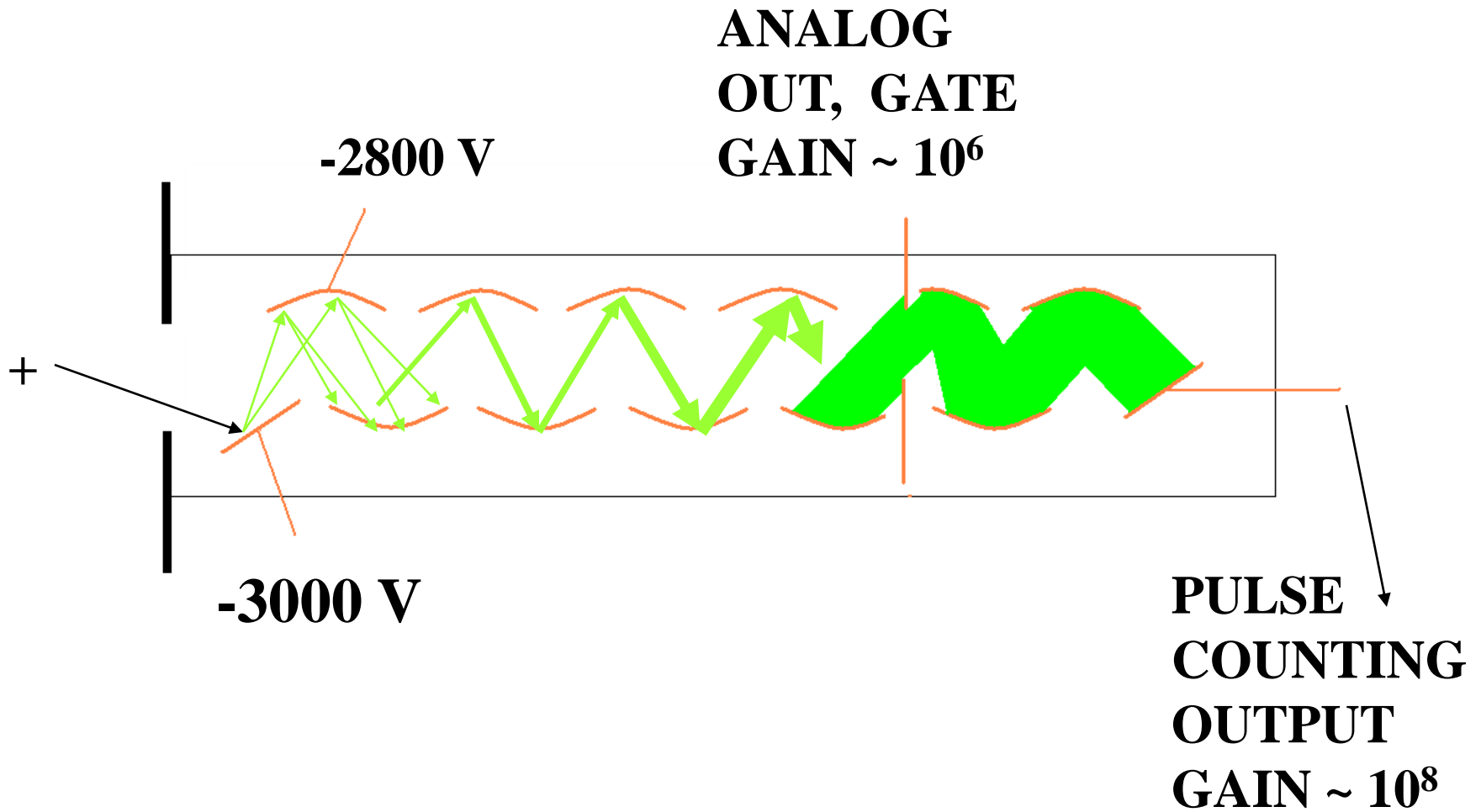
10 ppb Zn
PFA 100

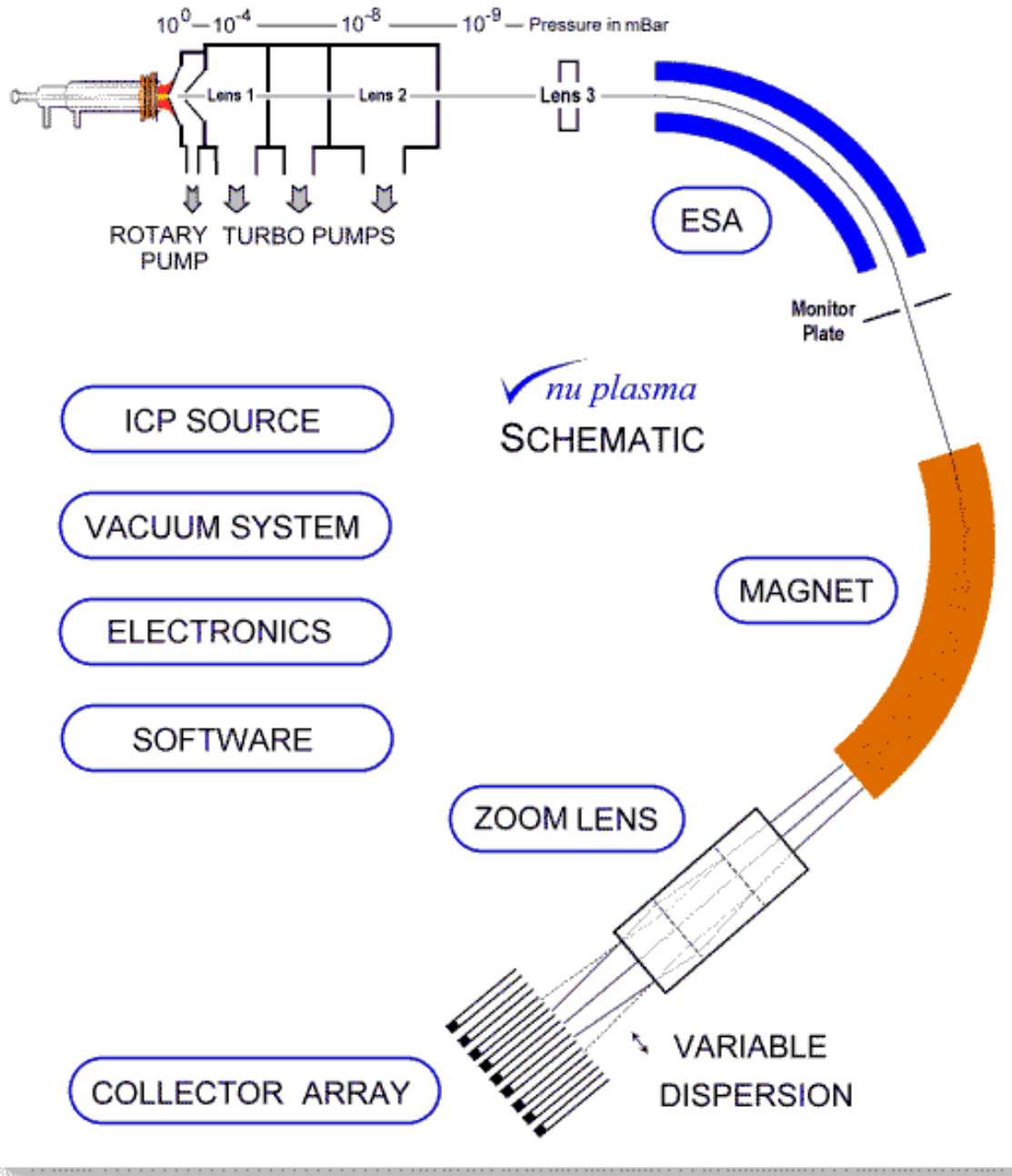
Photoresist Interferences on Cu

Date: 19-Oct-1998 Analysis: C:\TEMP\SHOW_TMP.DAT
Time: 15:47:19 Method:
Resolution: Medium Mass Range: 7.016 - 238.086
Number: 1 Of 1 Audit Trail: ISOPROPANOL.DAT sum 1..6 (6) a



ELECTRON MULTIPLIER





Multicollector instrument with zoom lens and multiple electron multiplier detectors.

MATRIX EFFECT

Olivares & Houk, Anal. Chem 1986, 58, 20.

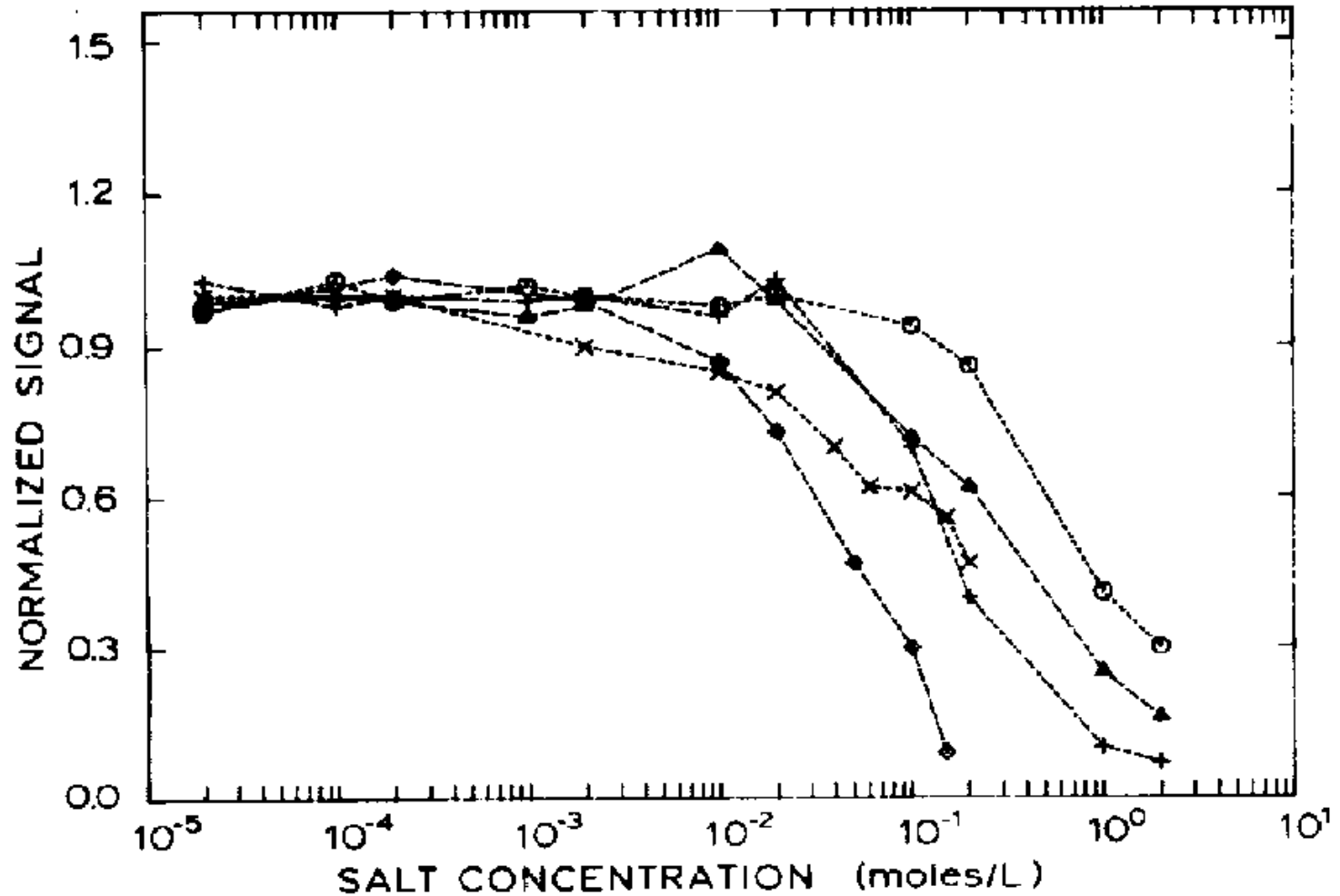


Figure 1. Experimentally determined suppression of cobalt ion signal vs. concomitant salt concentration. The matrix salts used are NaCl (◇), MgCl₂ (×), NH₄I (+), NH₄Br (Δ), and NH₄Cl (O).

VARIATION OF SIGNAL & MATRIX EFFECT WITH NEB. GAS FLOW

Tan & Horlick JAAS 1987, 2, 745.

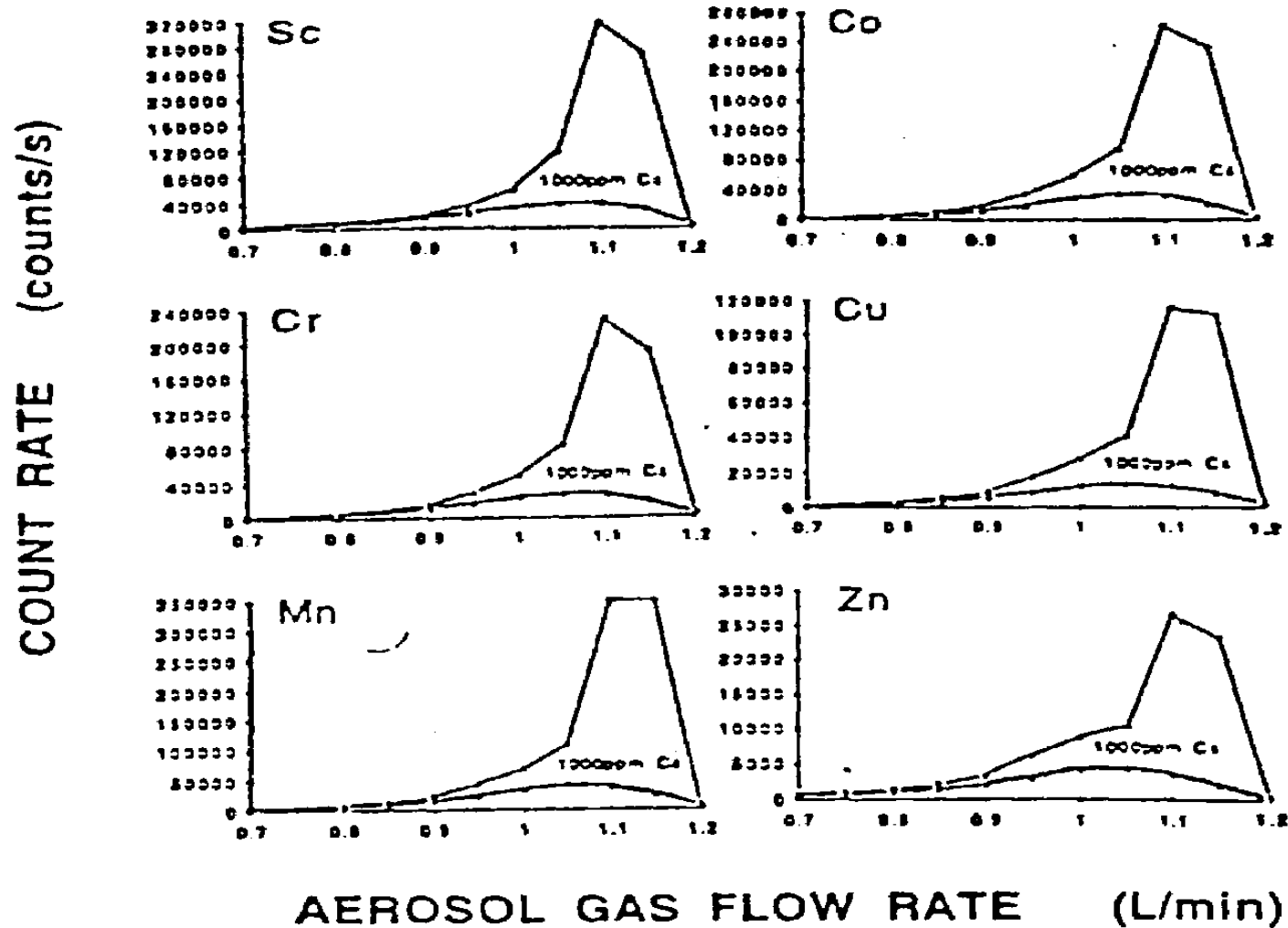


Figure 9b. Matrix interference effect: recovery of signal for Sc, Cr, Mn, Co, Cu, and Zn in the presence of 1000 mg/L Cs (o) relative to analyte signals without Cs

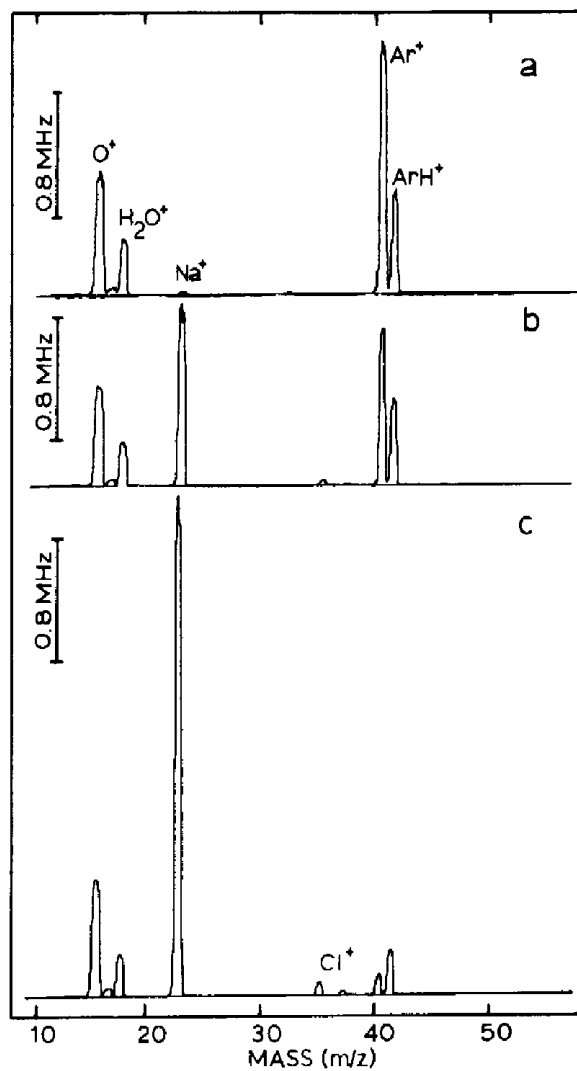


Figure 5. Mass spectra of three solutions of varying NaCl concentration: (a) blank, (b) 0.020 M, (c) 0.20 M.

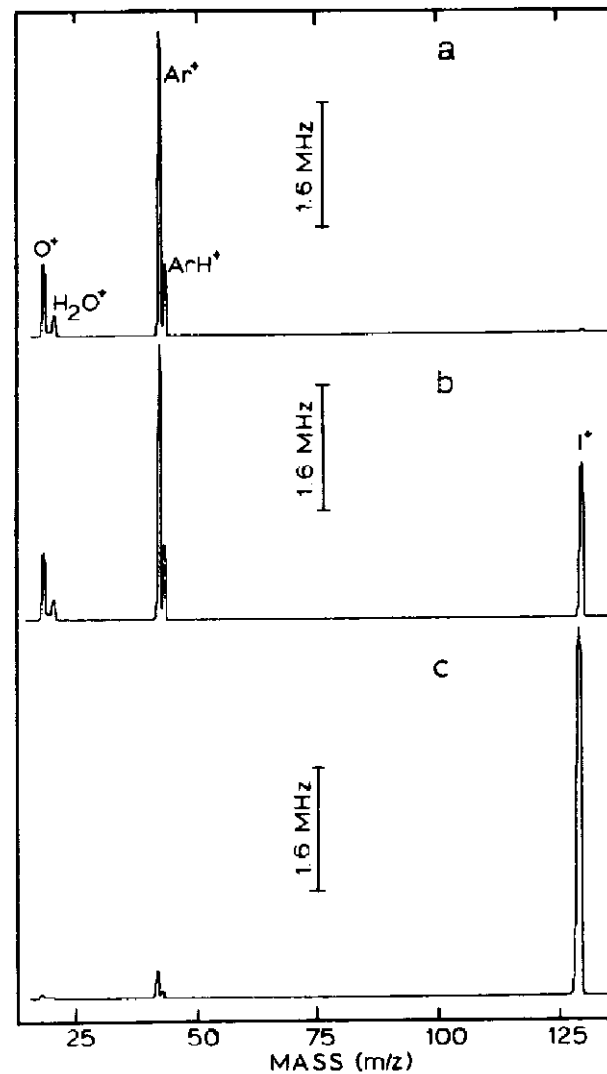
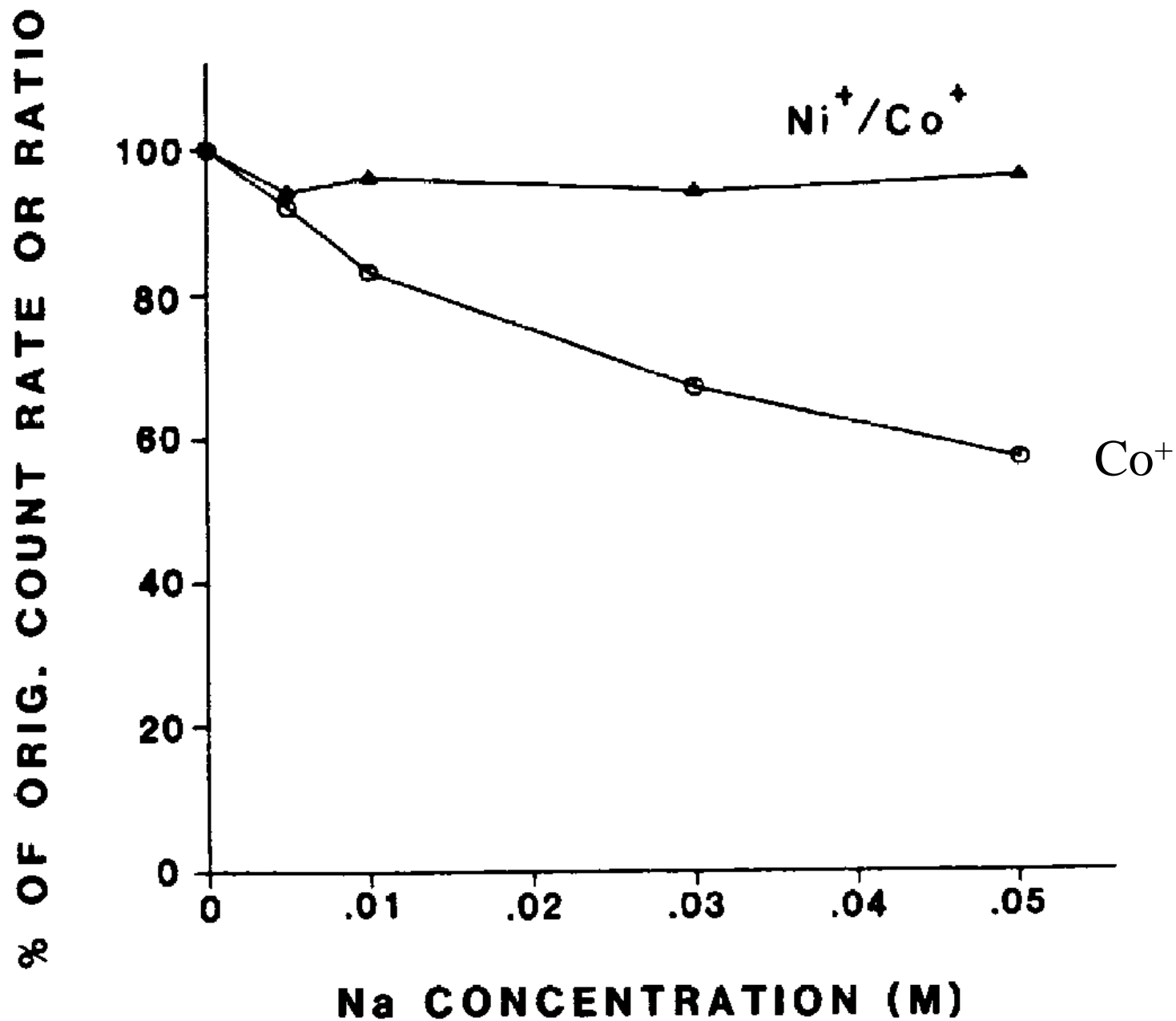


Figure 6. Mass spectra of (a) blank, (b) 0.02 M NH_4I , and (c) 2.0 M NH_4I .

INTERNAL STANDARD

REMOVE POLYATOMIC IONS?

**ALTER ICP:
COOL PLASMA**

SOLVENT REMOVAL

**REMOVE/SEPARATE POLY. IONS
FROM M^+ ANALYTE IONS:**

HIGH RESOLUTION

COLLISION CELLS

GOOD	IE	BAD	IE	D₀
<u>GUYS/GALS</u>	<u>(eV)</u>	<u>GUYS</u>	<u>(eV)</u>	<u>(eV)</u>
S⁺	10.36	O₂⁺	12.063	6.663
Fe⁺	7.87	ArO⁺	~ 13	0.312
		ArN⁺	~14	1.866
Se⁺	9.75	Ar₂⁺	~15	1.25
K⁺	4.34	ArH⁺	~10	4.00*
V⁺	6.74	ClO⁺	11.1	4.65
Ti⁺	6.82	SO⁺	10.0	5.43

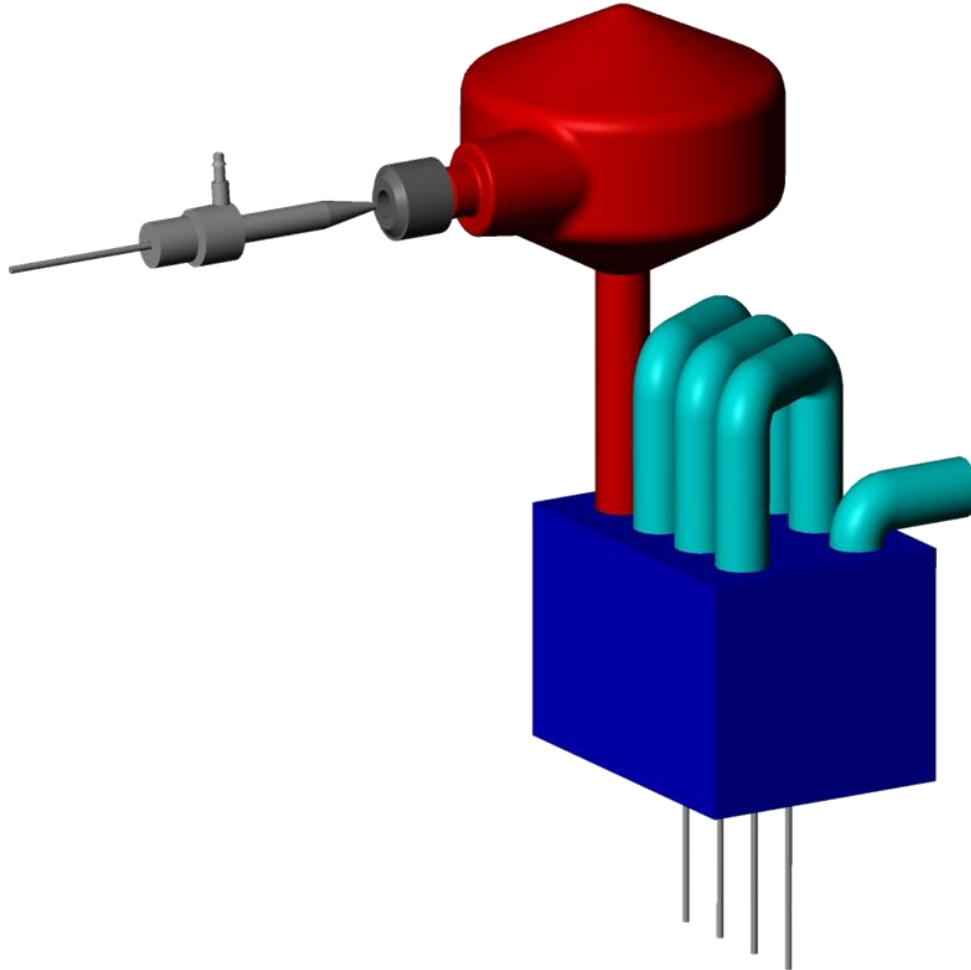
SOLVENT REMOVAL

REDUCE $M0^+$ (also KE discrimination)

**ANALYSIS OF ORGANIC
SOLVENTS**

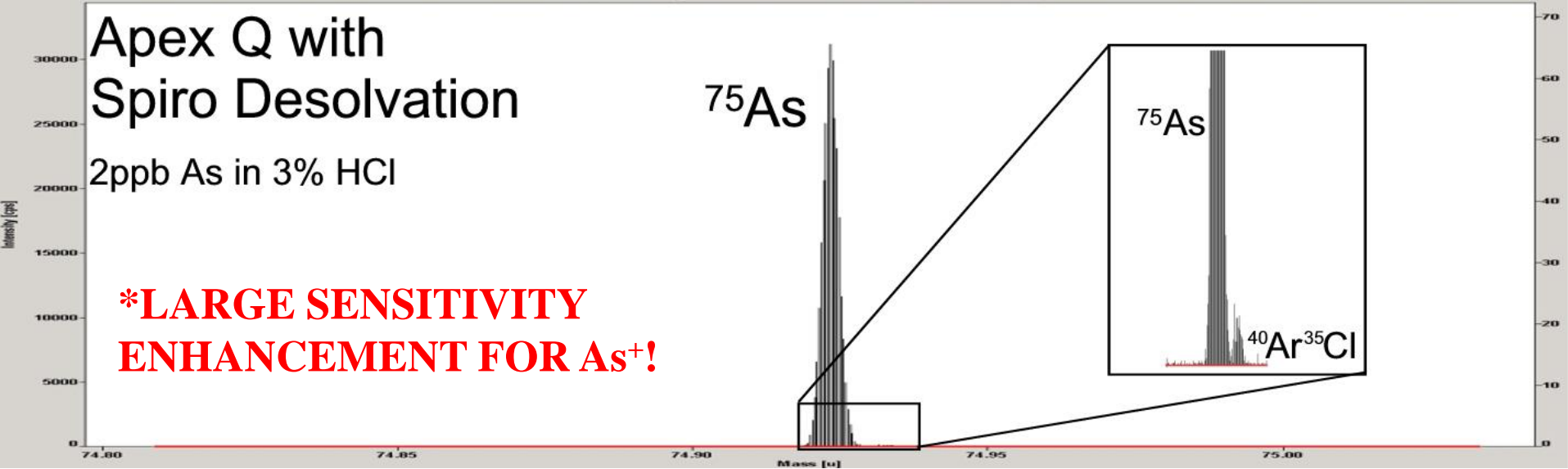
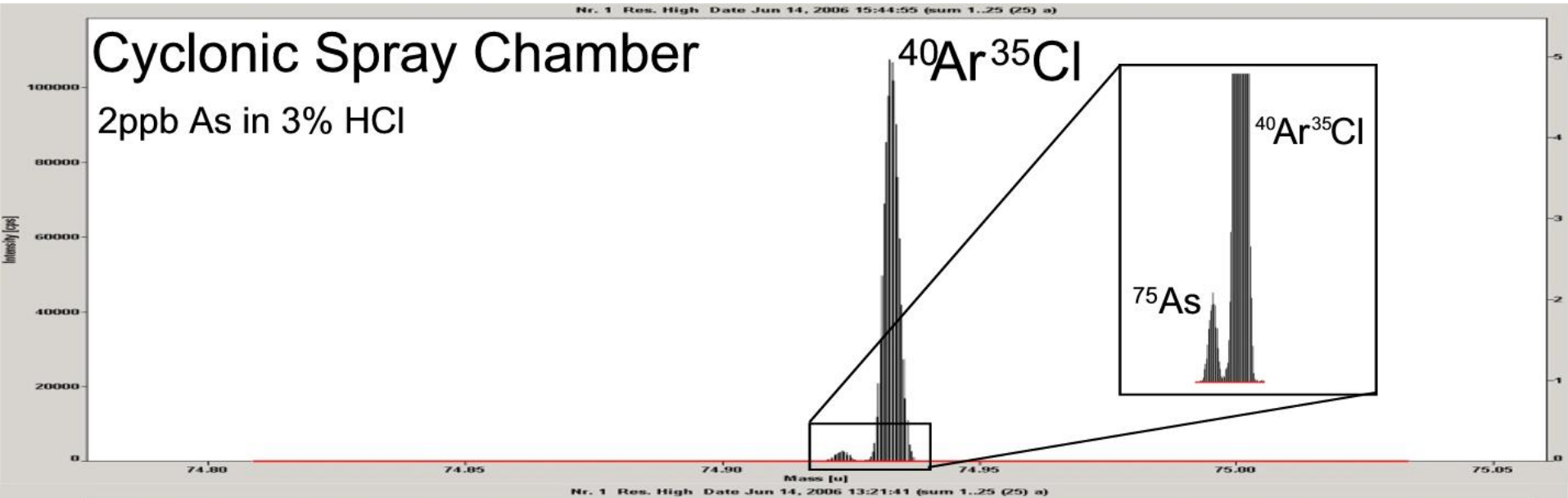
**IMPROVE SENSITIVITY,
ESP. FOR SECTOR
INSTRUMENTS (?)**

Cyclone Spray Chamber + Solvent Removal



Total Internal Volume 180 ml

Membrane Reduction of ArCl⁺ Teflon Membrane Desolvator



COLLISION CELLS

Rowan & Houk, Appl. Spectrosc. 1989, 43, 976.

Douglas, Canad. J. Spectrosc. 1989, 34, 38.

King & Harrison, Int. J. Mass Spectrom. Ion Processes
1989, 89, 171.

Turner, Speakman et al., Plasma Source MS, Developments
& Applications, Royal Society, 1997, p. 28.

Baranov & Tanner, JAAS 1999, 14, 1133

JASMS 1999, 10, 1083.

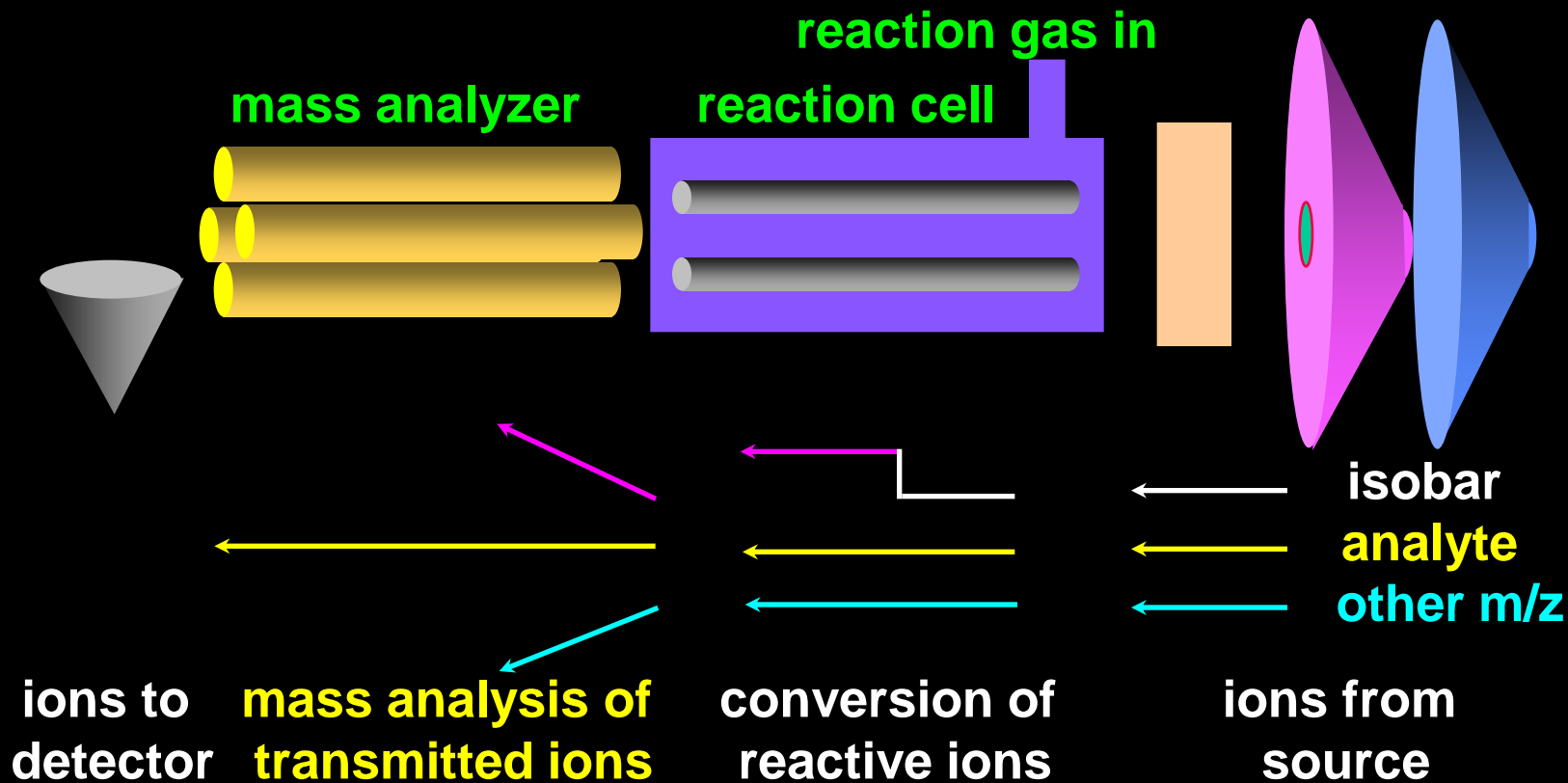
USE COLLISION - INDUCED DISSOCIATION (CID)
&/OR **CHEMICAL REACTION** TO REMOVE POLY. IONS

RETAIN ATOMIC ANALYTE IONS

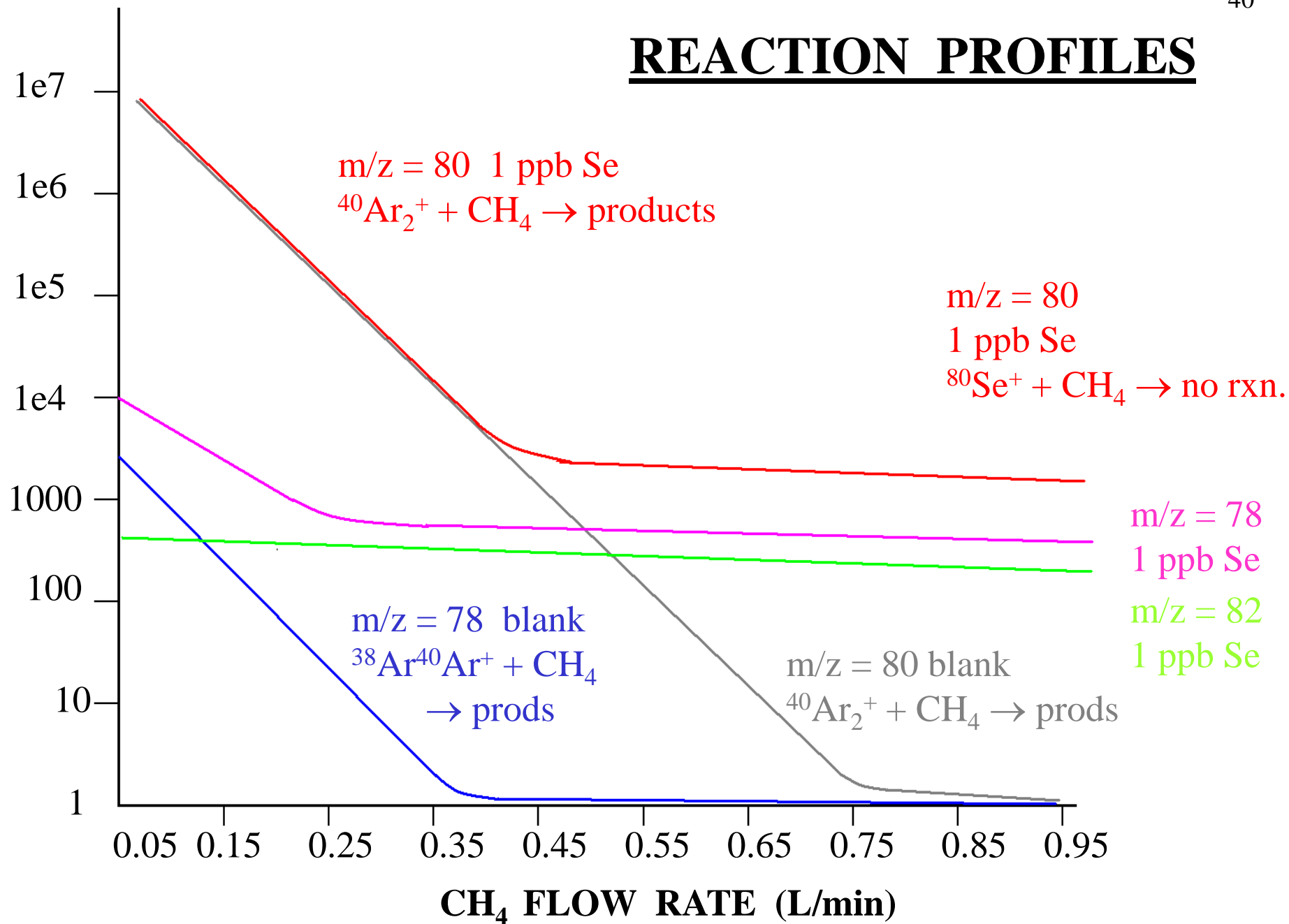
REDUCE KE & SPREAD OF KE OF POLY IONS

GOOD <u>GUYS/GALS</u>	IE <u>(eV)</u>	BAD <u>GUYS</u>	IE <u>(eV)</u>	D₀ <u>(eV)</u>
S⁺	10.36	O₂⁺	12.063	6.663
Fe⁺	7.87	ArO⁺	~ 13	0.312
		ArN⁺	~14	1.866
Se⁺	9.75	Ar₂⁺	~15	1.25
K⁺	4.34	ArH⁺	~10	4.00*
V⁺	6.74	ClO⁺	11.1	4.65
Ti⁺	6.82	SO⁺	10.0	5.43

DYNAMIC REACTION CELL (DRC)



REACTION PROFILES



THERMODYNAMICS OF ION-NEUTRAL RXNS



EXOTHERMIC RXN USUALLY RAPID, EXTENSIVE



**ENDOTHERMIC RXN, SLOWER
KEEP COLLISION ENERGY LOW**

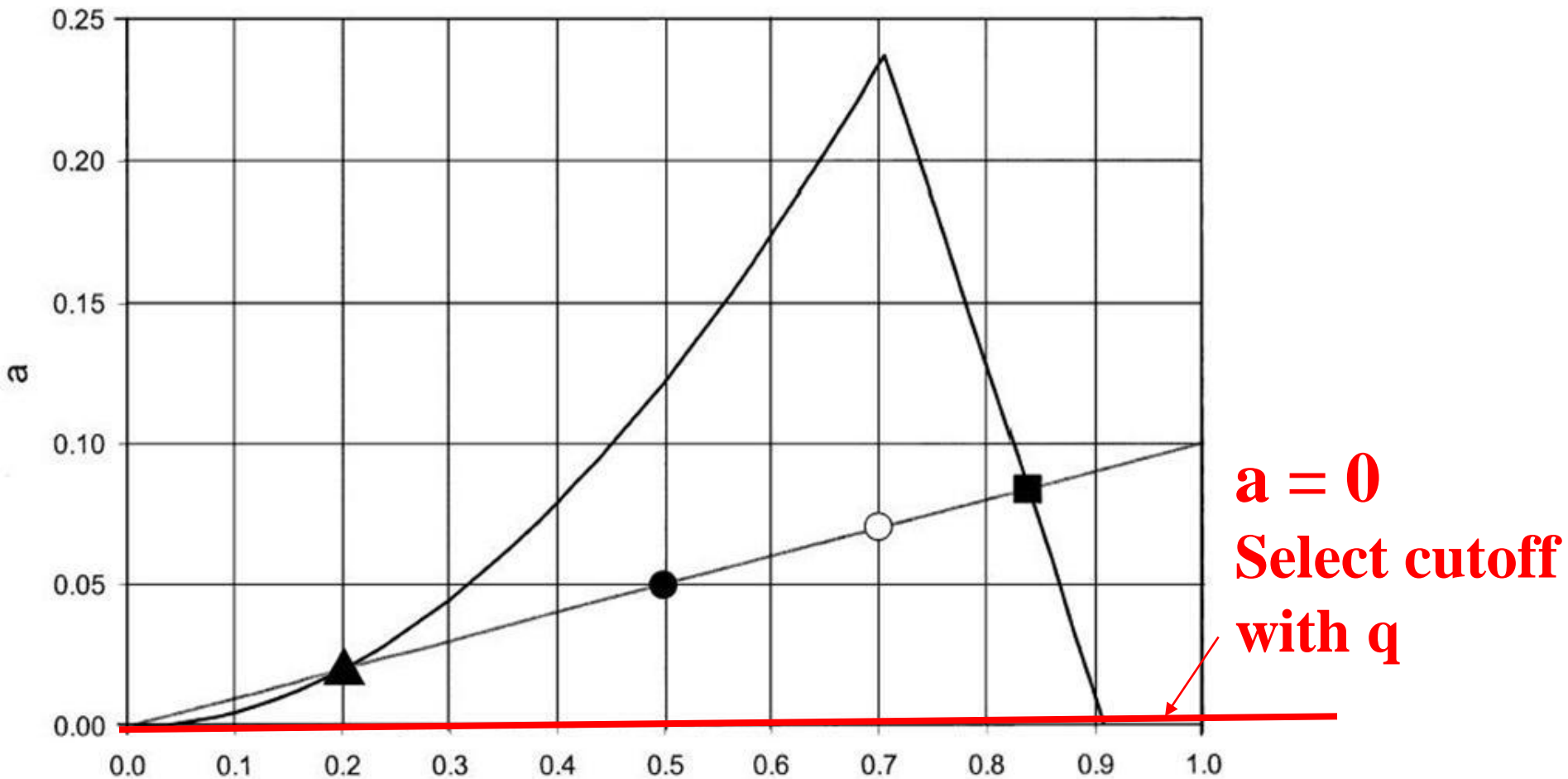
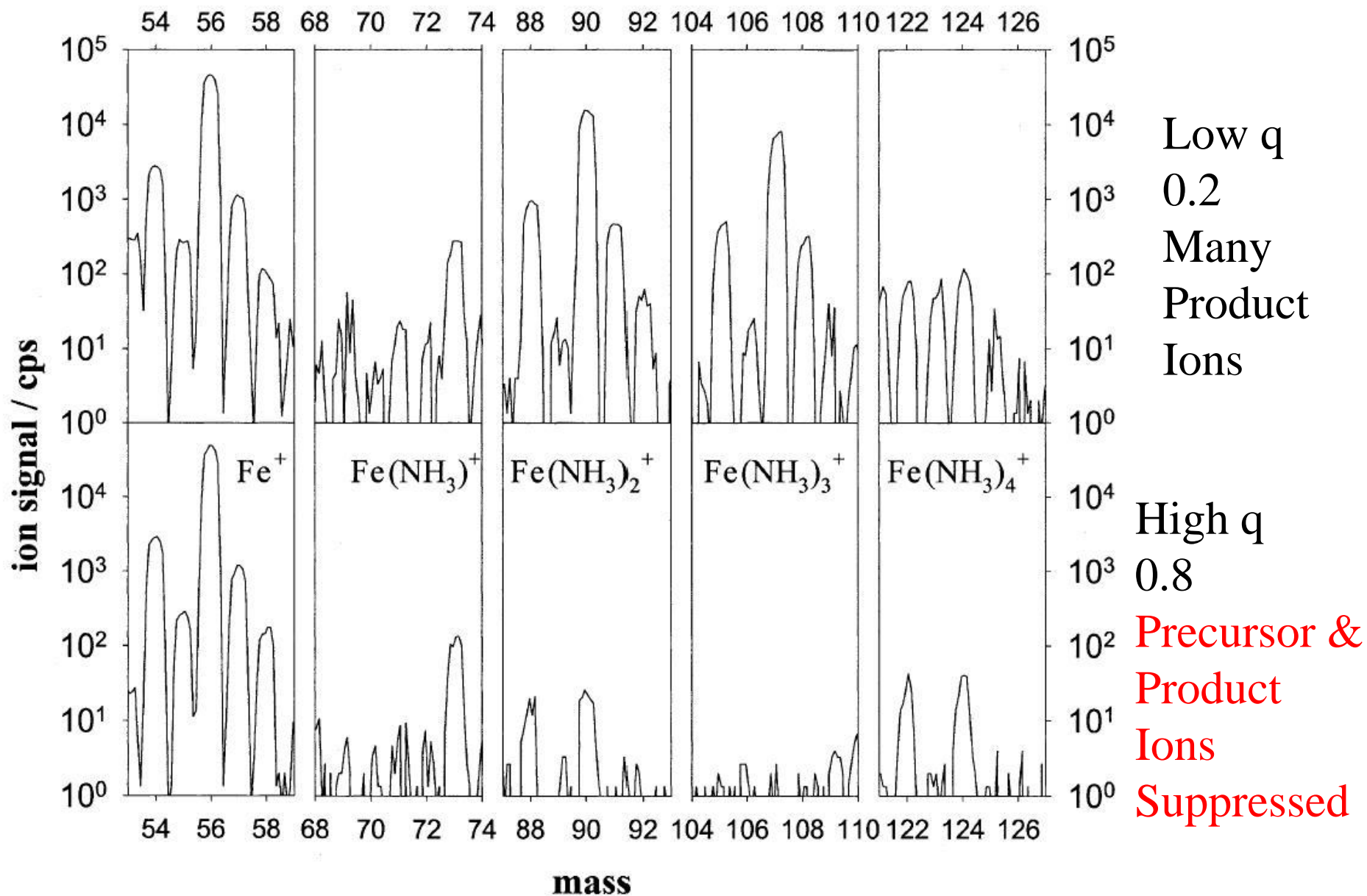


Fig. 30. Quadrupole stability diagram with hypothetical scan line. (\blacktriangle) Denotes the high mass cut-off, and (\blacksquare) denotes the low mass cut-off. The bandpass includes a lower mass range when operated at (\bullet) than at (\circ), and this can affect the formation of secondary interferences if the precursor ion is included/excluded under these conditions.

$$q = 2V/(m/z)r_0^2\omega^2$$

$\text{Fe}(\text{NH}_3)_n^+$ CLUSTERS



KINETIC ENERGY DISCRIMINATION

COLL CELL LENGTH $L = 10$ cm

GAS DENSITY n

ION HAS CROSS SECTION Ω (cm²)

NUMBER OF COLLISIONS = $L/\lambda = L n \Omega$

λ = mean free path (cm)

EXPECT ~ 5 TO 10 COLLISIONS

POLY ION IS LARGER

LARGER Ω

MORE COLLISIONS IN SAME LENGTH L

KE LOSSES & KE DISCRIMINATION

$$\text{Fraction of KE remaining per coll} = \alpha \sim \frac{m_{\text{coll gas}}^2 + m_{\text{ion}}^2}{(m_{\text{coll gas}} + m_{\text{ion}})^2}$$

$$\alpha \sim \frac{4^2 + 56^2}{(4 + 56)^2} = 0.88 \text{ for coll of Fe}^+ \text{ and ArO}^+ \text{ with He}$$

SAY Fe⁺ HAS 5 COLLS

ArO⁺ HAS 10 COLLS

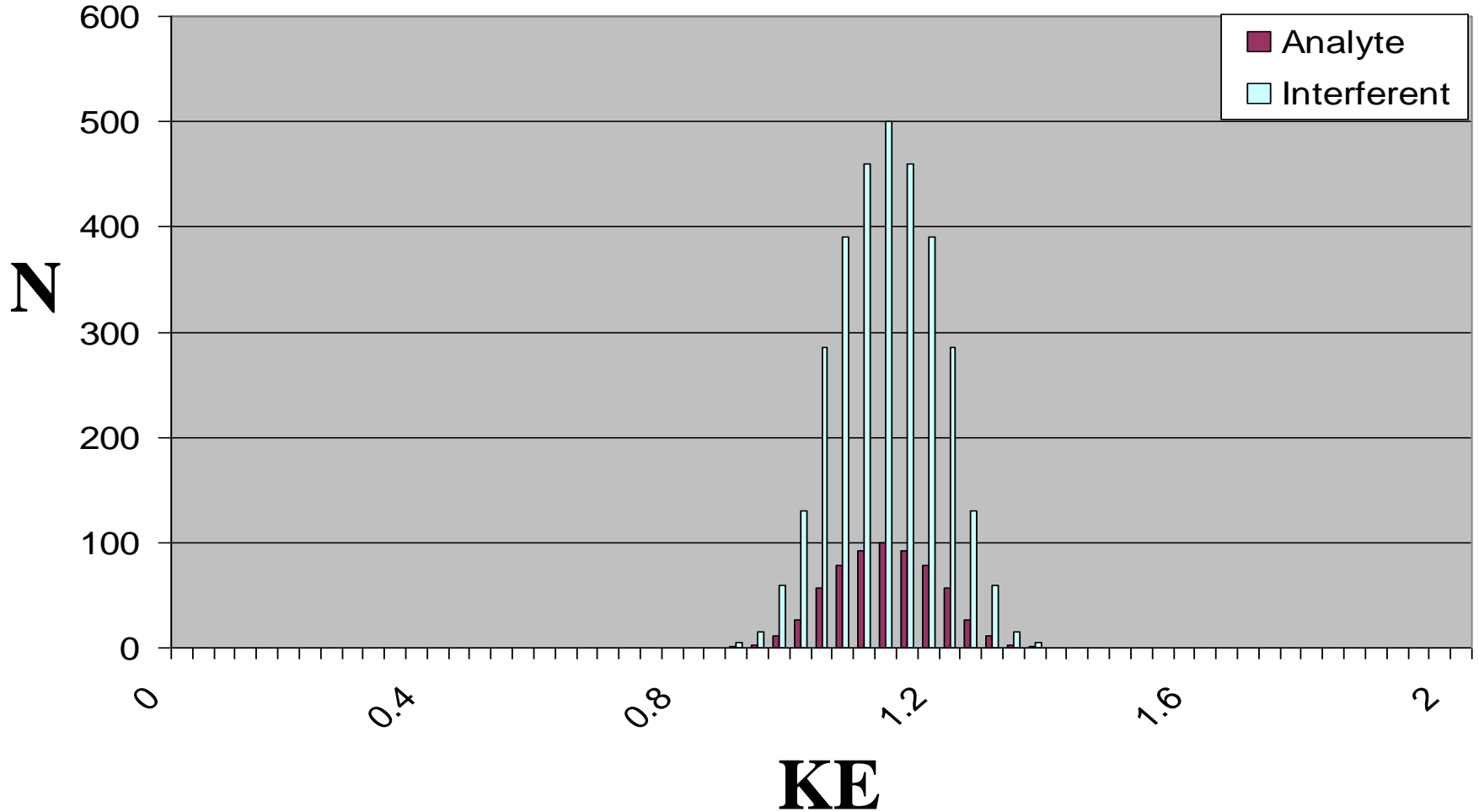
Fe⁺ HAS $\alpha^5 = 0.88^5 = 0.52$ OF INITIAL KE REMAINING

ArO⁺ HAS $\alpha^{10} = 0.88^{10} = 0.28$ OF INITIAL KE

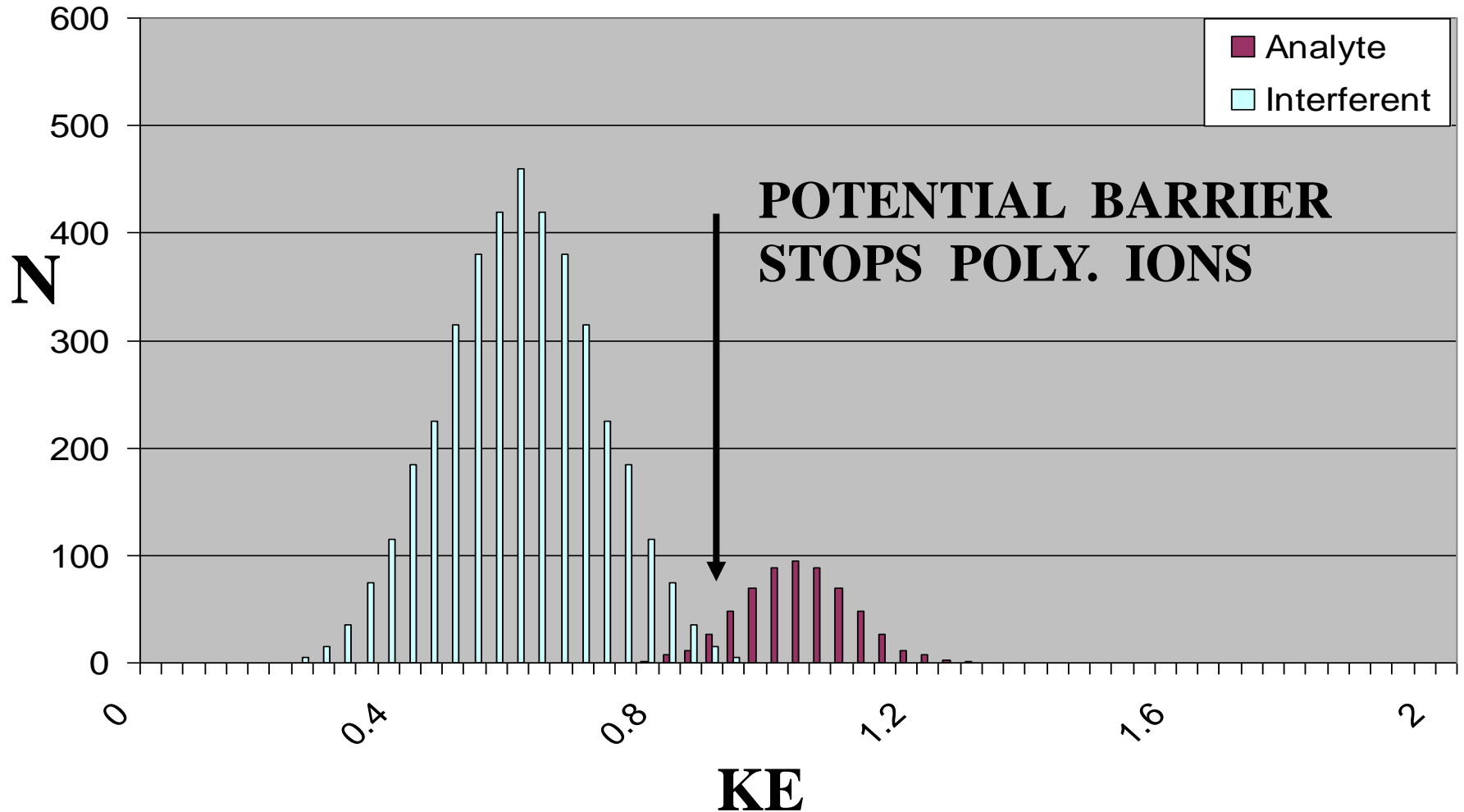
Covey & Douglas JASMS 1993 p 616

KINETIC ENERGY DISCRIMINATION

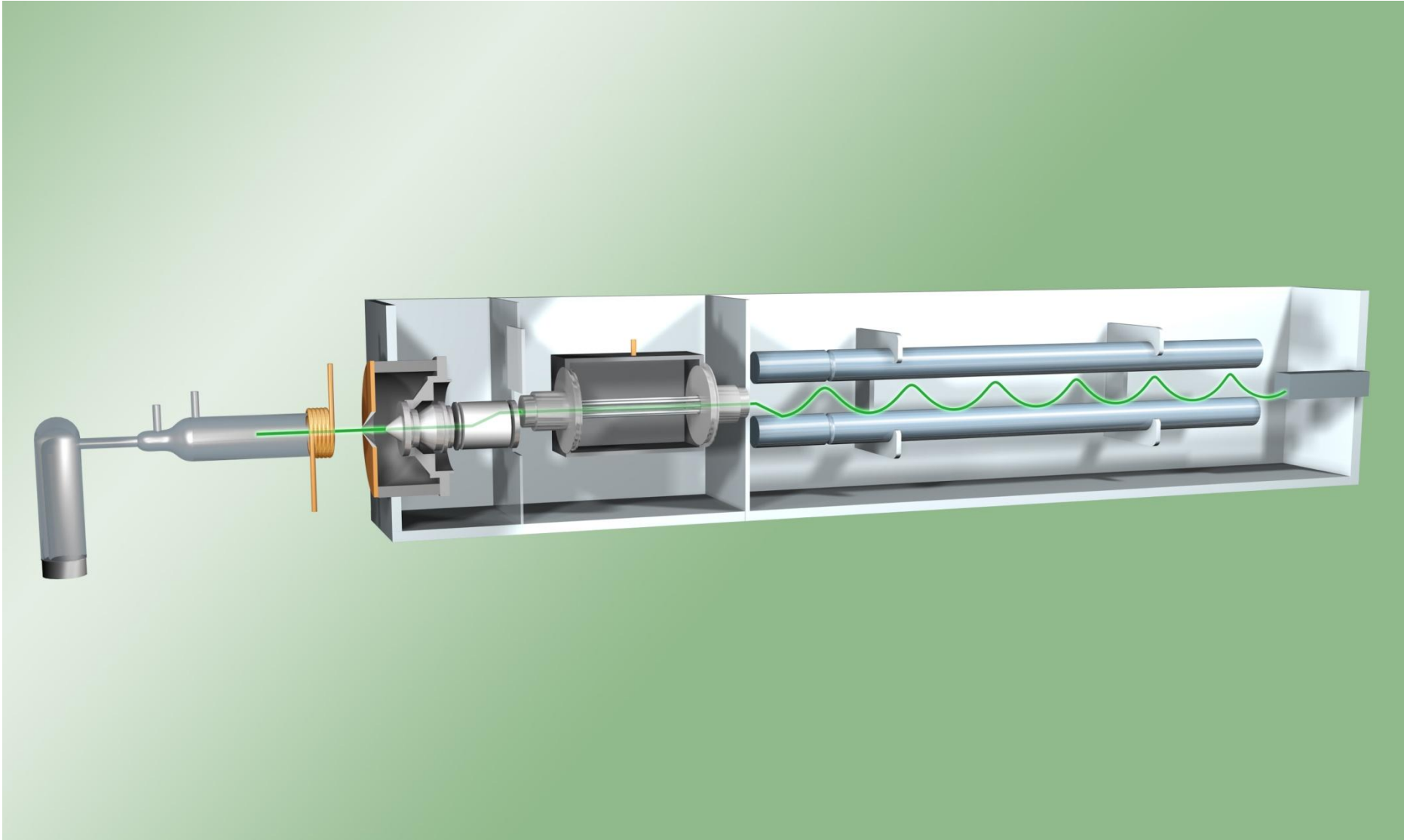
NO COLL. GAS



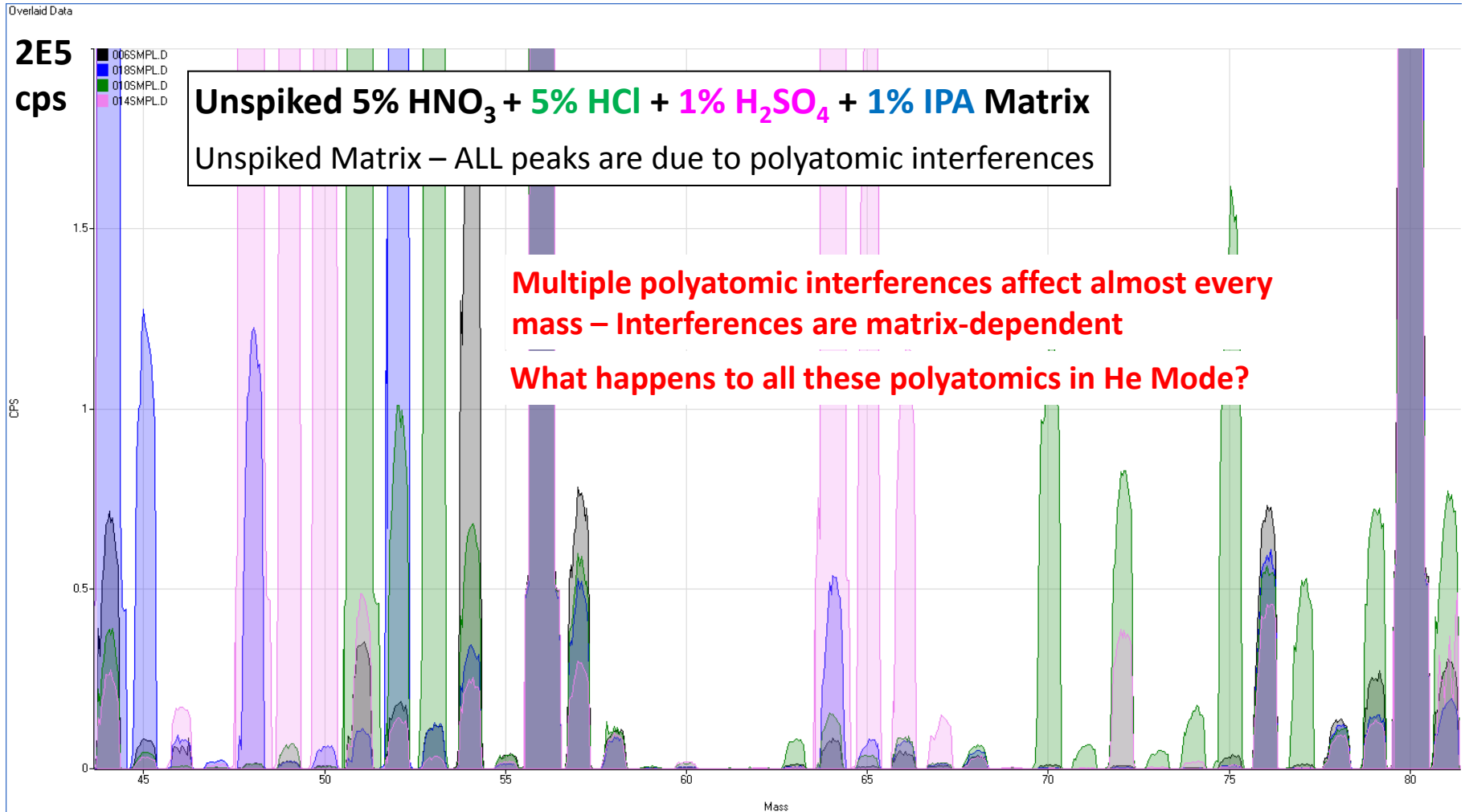
POLY. ION HAS LARGER CROSS SECTION FOR KE LOSS



OCTOPOLE COLLISION CELL



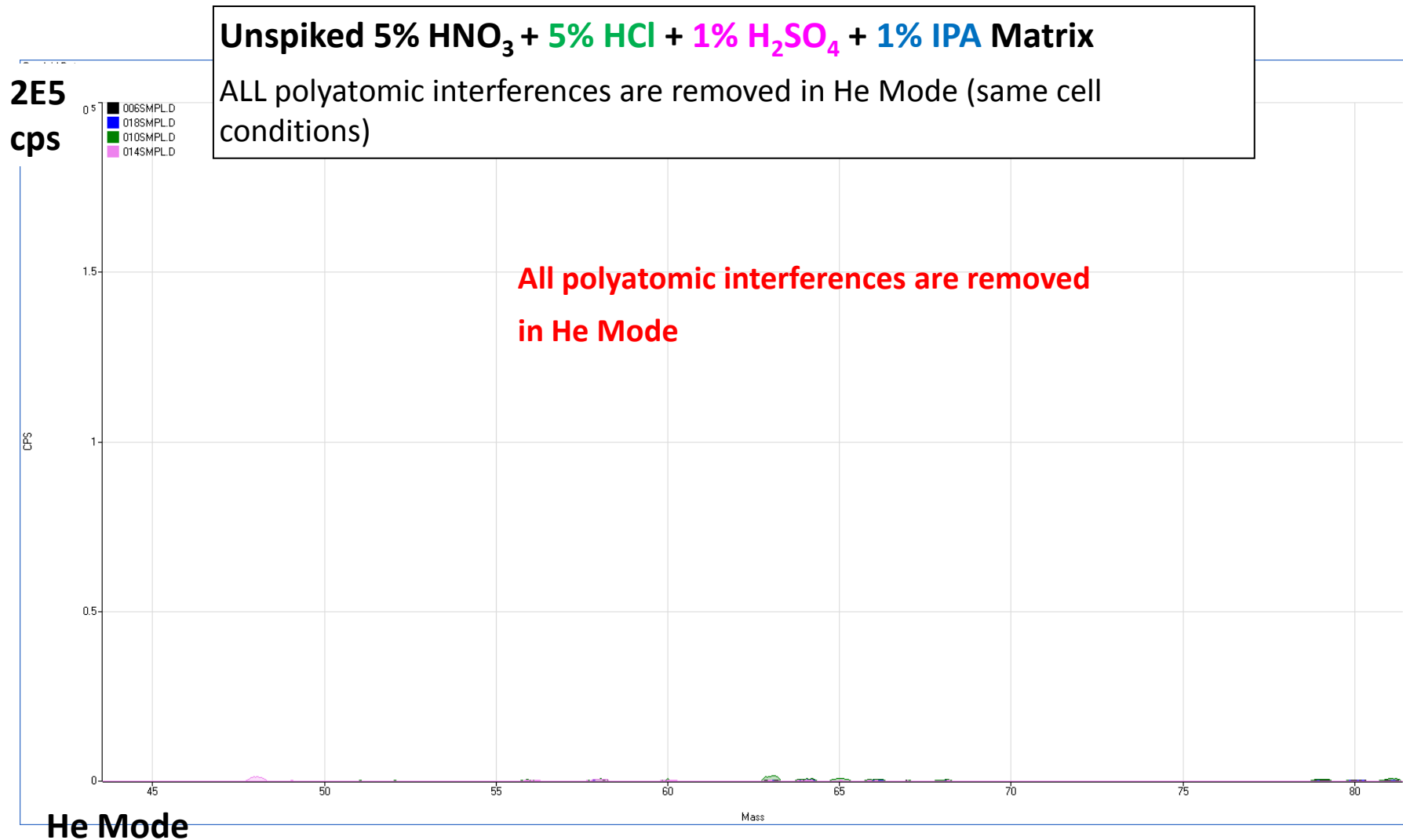
Acid Matrices & IPA in NoGas Mode ($\text{HNO}_3 + \text{HCl} + \text{H}_2\text{SO}_4 + \text{IPA}$)



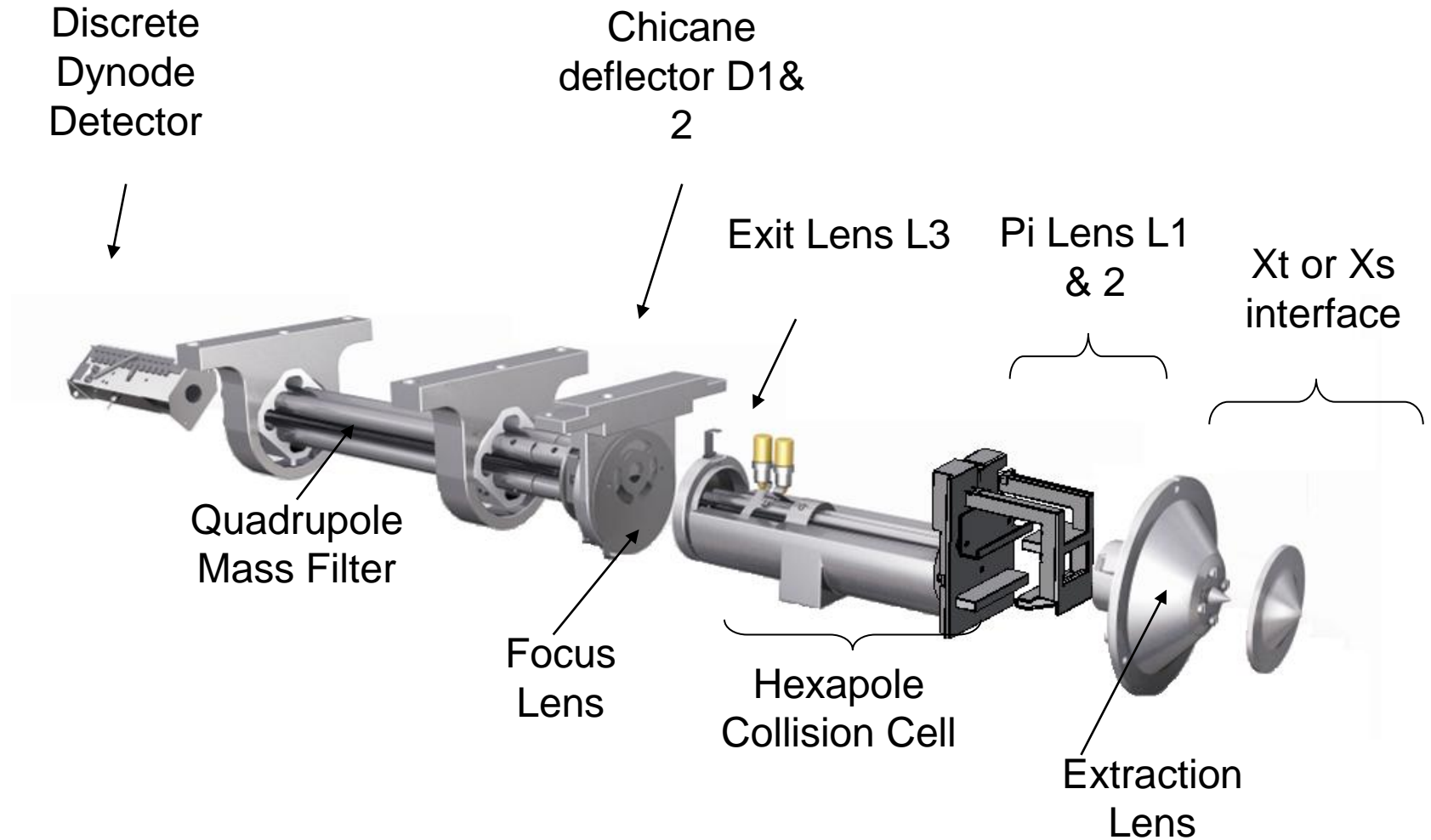
NoGas Mode

Single Acid Matrices and IPA in He Mode

($\text{HNO}_3 + \text{HCl} + \text{H}_2\text{SO}_4 + \text{IPA}$)



Hexapole Collision Cell



QUESTIONS

Type your question in the
“Submit Question”
box below your slide window

THANK YOU FOR ATTENDING

We Need Your Feedback!

Please complete the post-webcast evaluation form that will immediately appear in your browser window.