

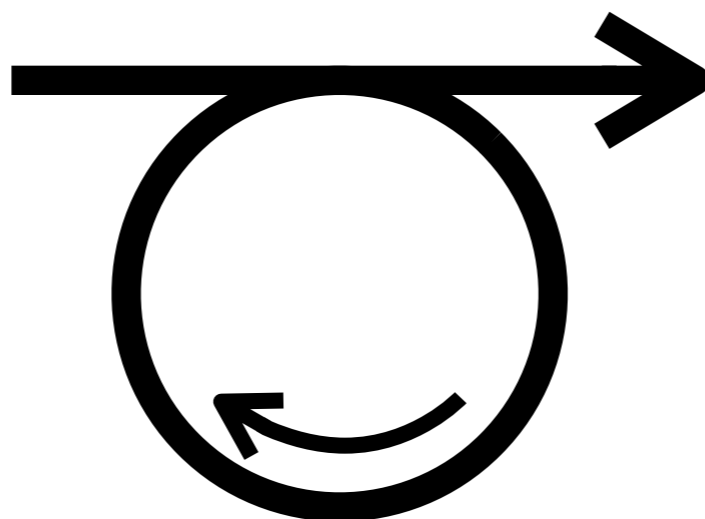
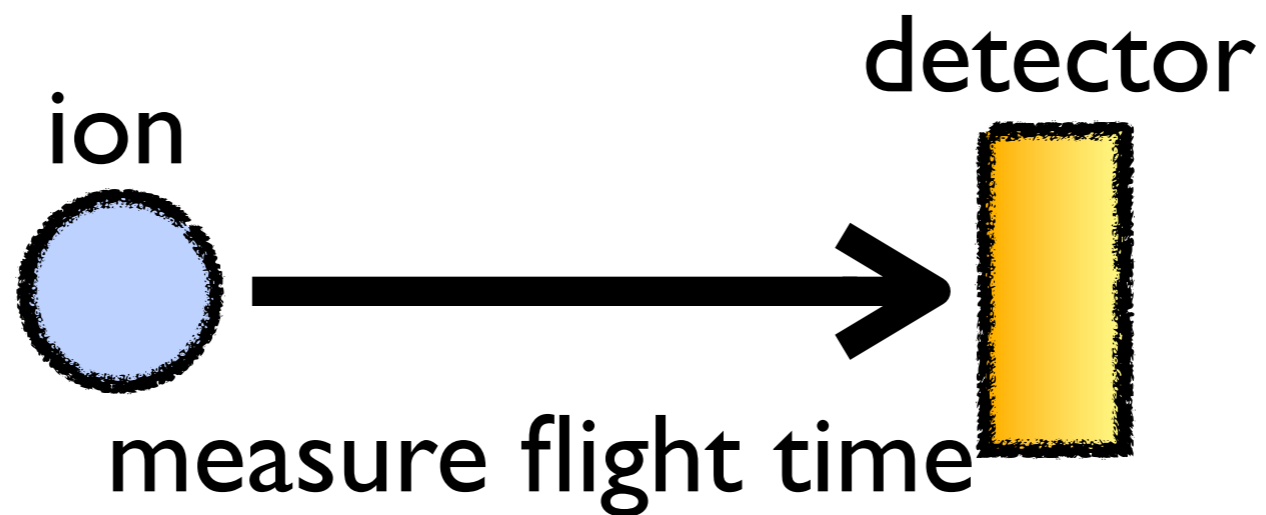
# Development of multi-turn time-of-flight mass spectrometers

**Jun Aoki, Michisato Toyoda**  
**Osaka University**

# Outlines

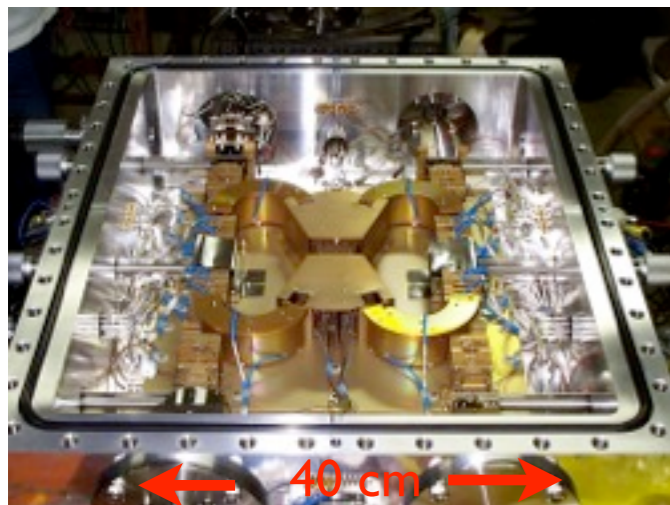
1. Introduction
2. Ion Optics
3. Applications
4. Conclusion

# Multi-turn time-of-flight (TOF) mass spectrometer



# First laboratory model for ROSETTA

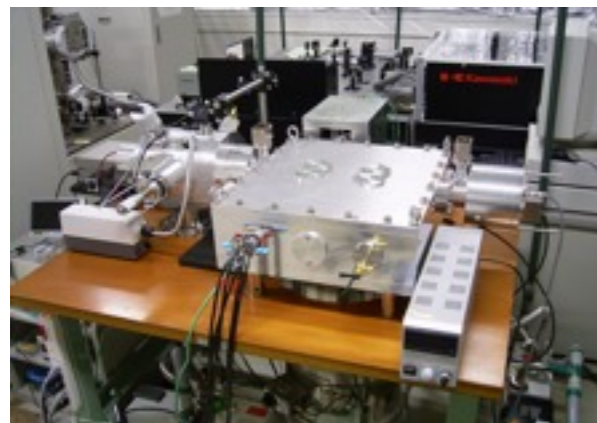
1996 - 2001 Grant in Aid for Scientific Research (B)



“MULTUM Linear plus”

J. Mass Spectrom., 38 (2003), 1125-1142.

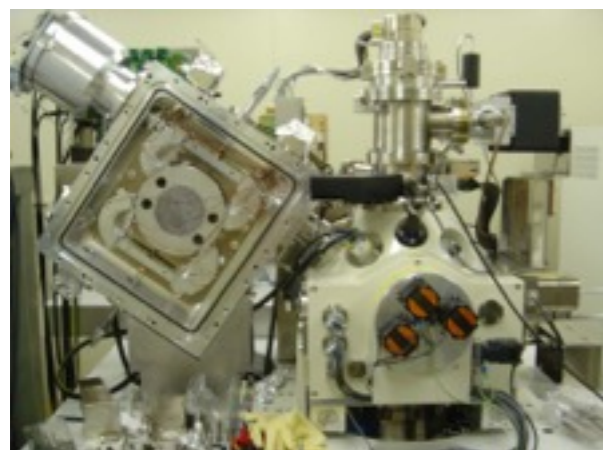
For imaging mass spectrometry  
2005~2010 CREST



“MULTUM-IMG”

J. Biomed. Opt., 16 (2011), 046007.

2005 - 2008 Grant-in-Aid for Creative Scientific Research

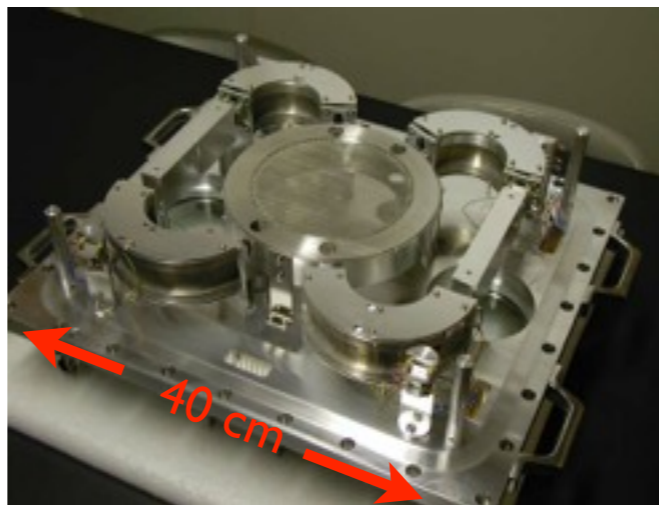


“MULTUM-SIMS”

Surf. Interface Anal., 42 (2010), 1598-1602.

# Second laboratory model for ROSETTA

1999 - 2002 Grant in Aid for Scientific Research (B)



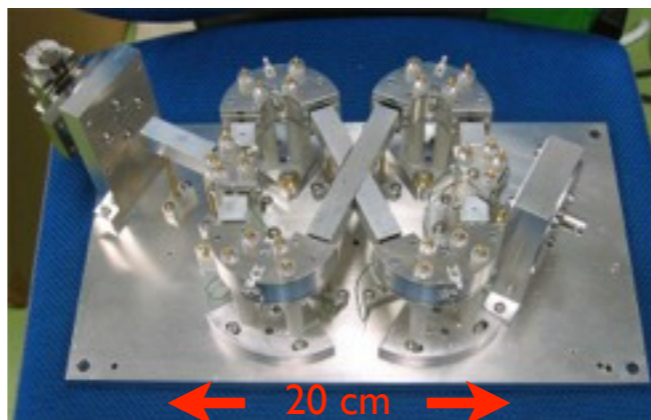
“MULTUM II”

J. Mass Spectrom., 38 (2003), 1125-1142.

Miniaturize

Smaller instrument

2003 - 2005 constructed in workshop of Osaka Univ.



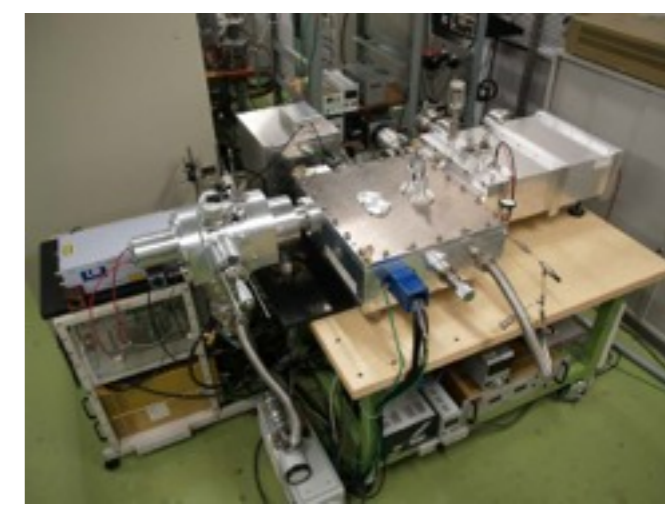
“MULTUM-S”

J. Mass Spectrom. Soc. Jpn., 55 (2007), 363-368.

For future space missions

# Tandem TOF mass Spectrometer

2004 - 2006 Grant in Aid for Young Scientists (A)



“MULTUM TOF/TOF”

Rev. Sci. Instrum., 78 (2007), 074101

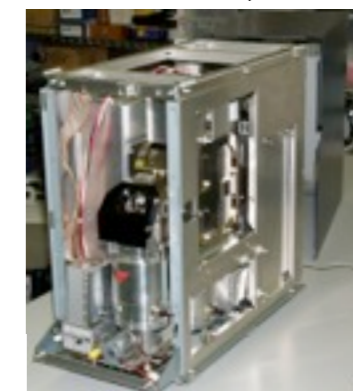
2008~

Innovative Project for Advanced Instruments,  
Renovation Center of Instruments for Science Edu  
and Technology, Osaka University

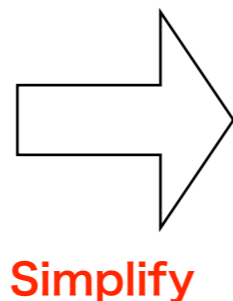


2007 - 2008 JST Supporting Program for  
Creating University Ventures

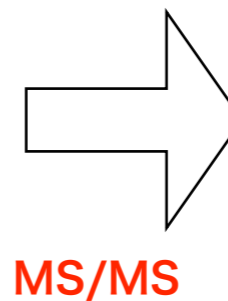
University Venture  
MSI.TOKYO, Inc.



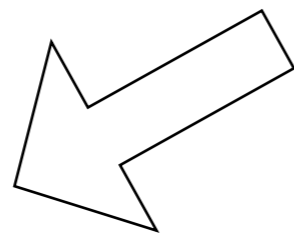
“MULTUM-S II” -> infiTOF  
Anal. Chem., 82 (2010), 8456.



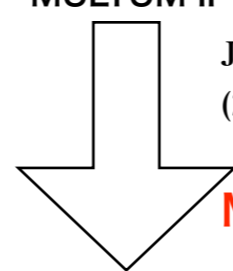
Simplify



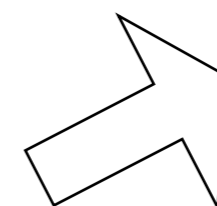
MS/MS



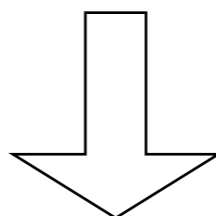
Imaging MS



Miniaturize

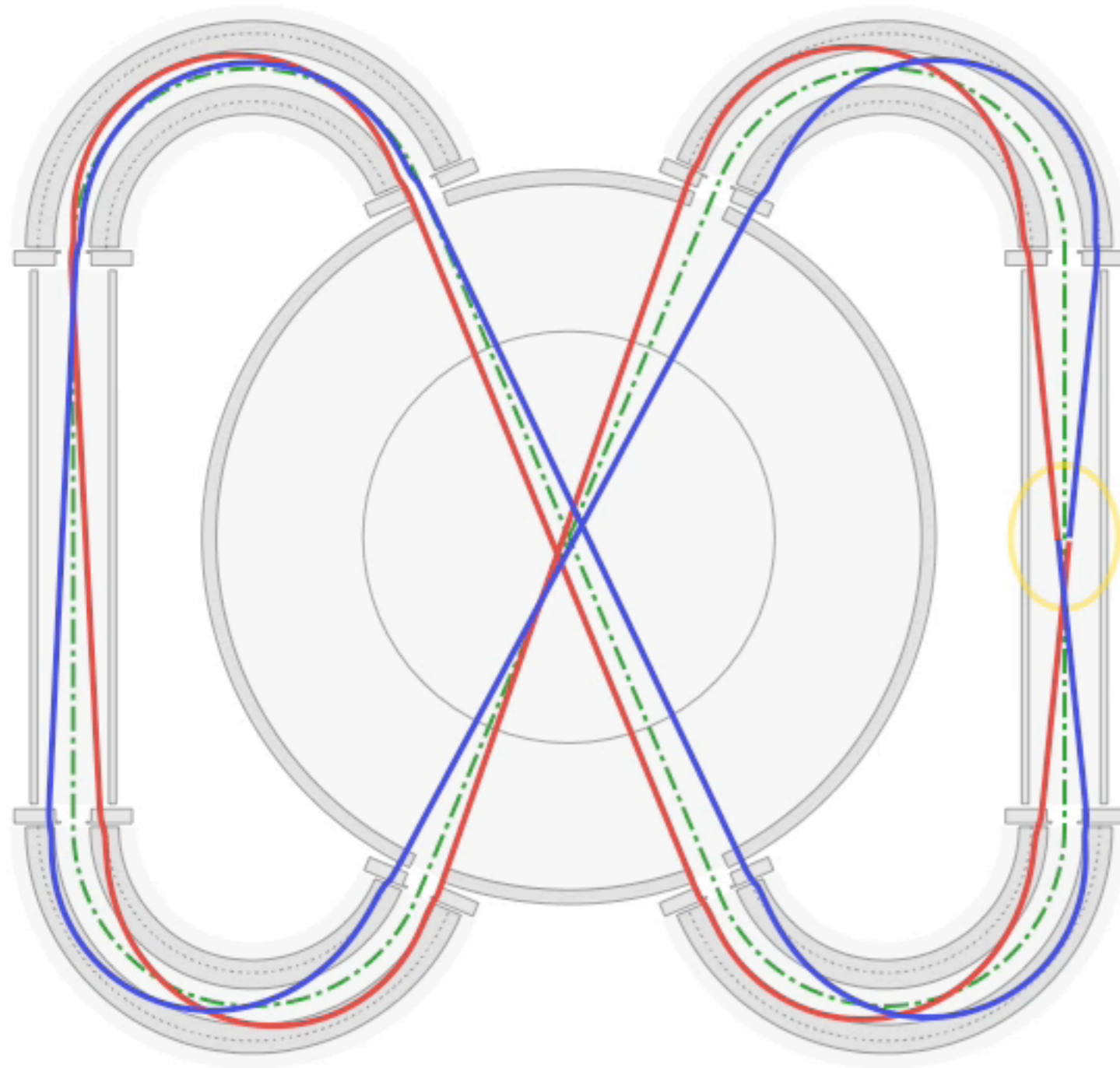


Compact instrument

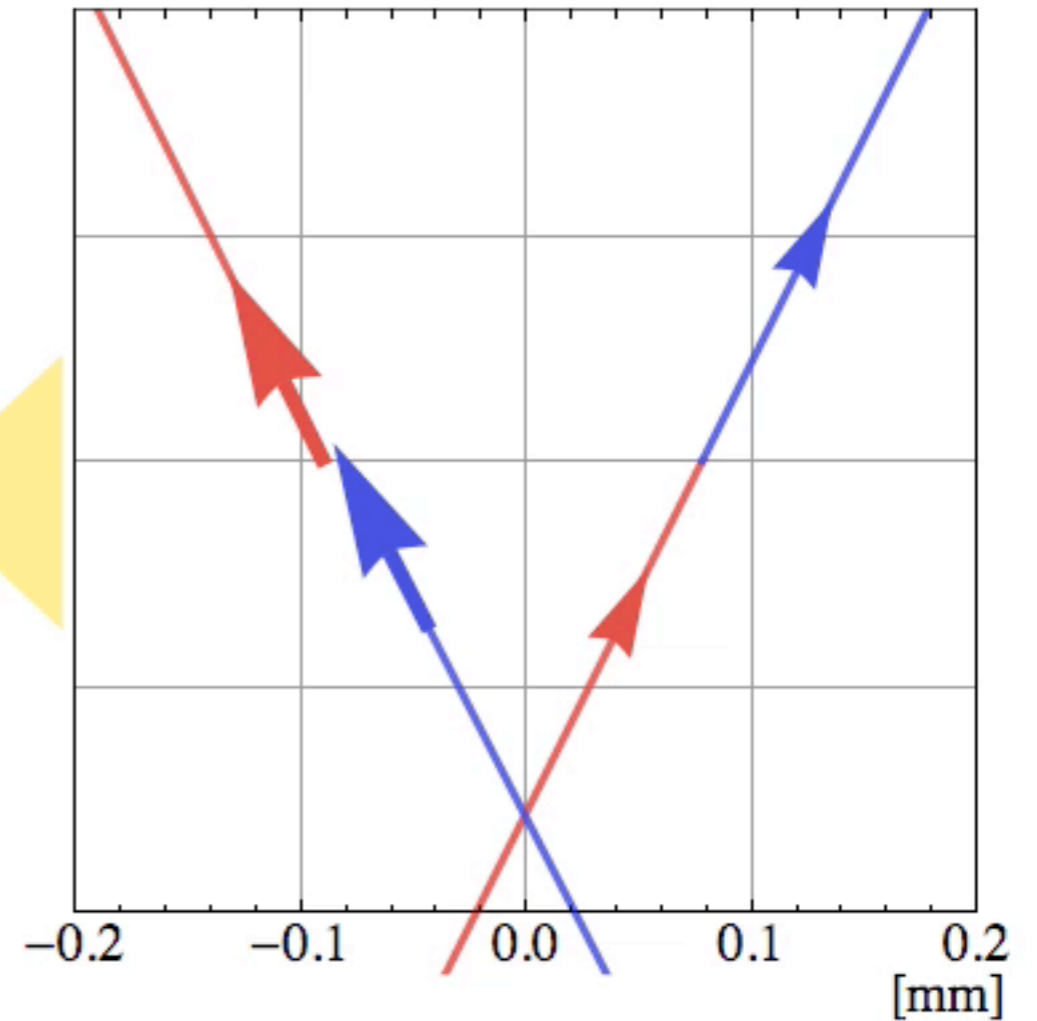


For future space missions

# MULTUM's optics



## Spatial Focus

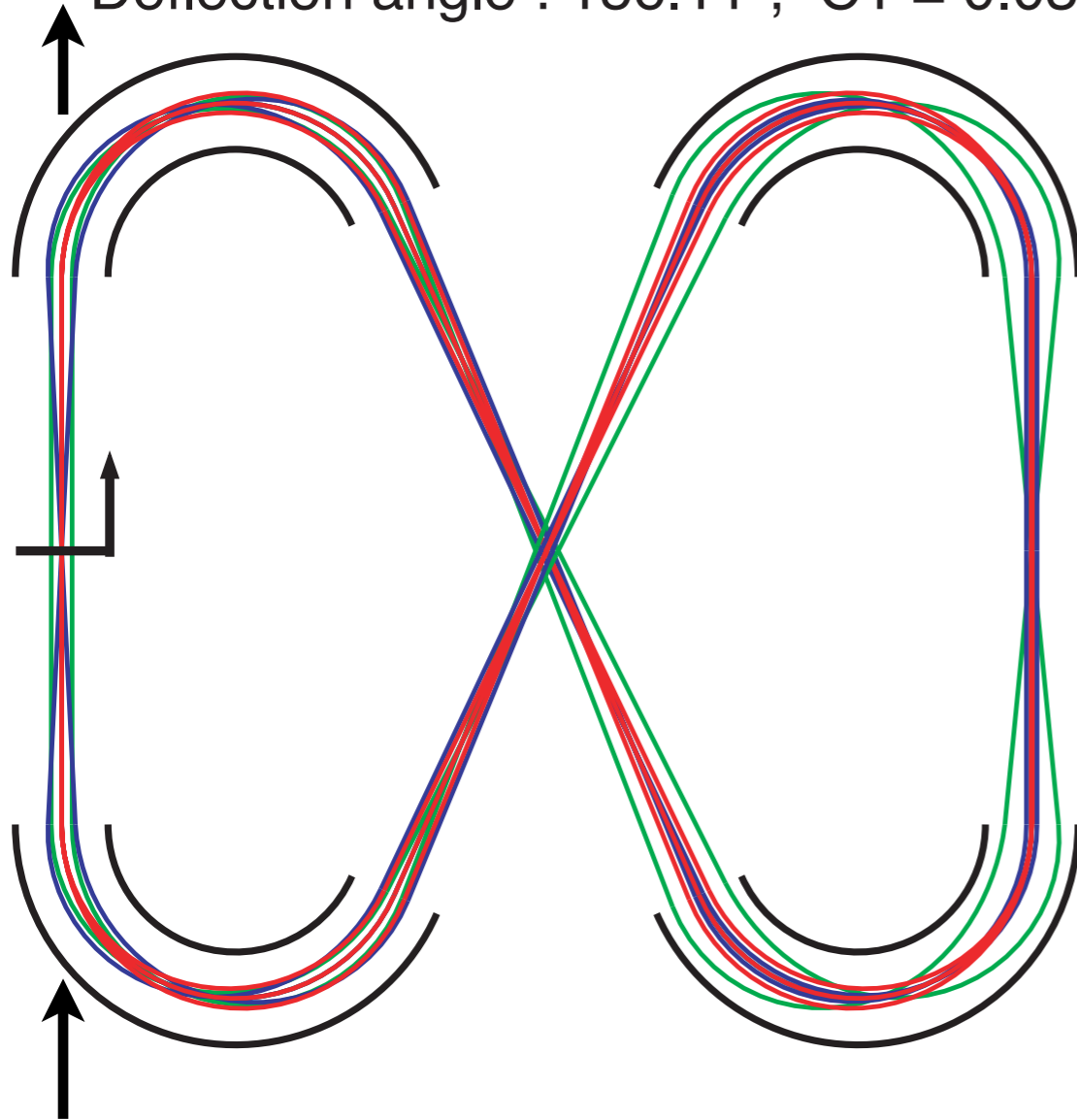


Ions return in same position and angle after 2 cycles.

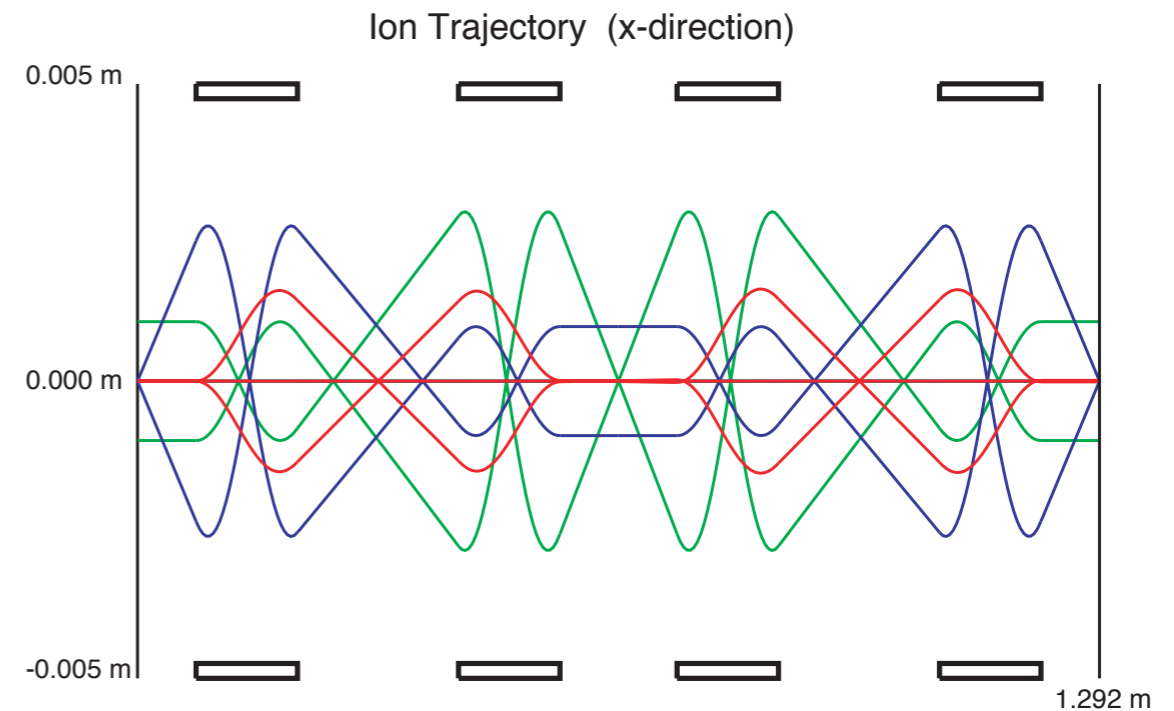
# Ion Trajectories of 'MULTUM II'

## Toroidal Electric Sector

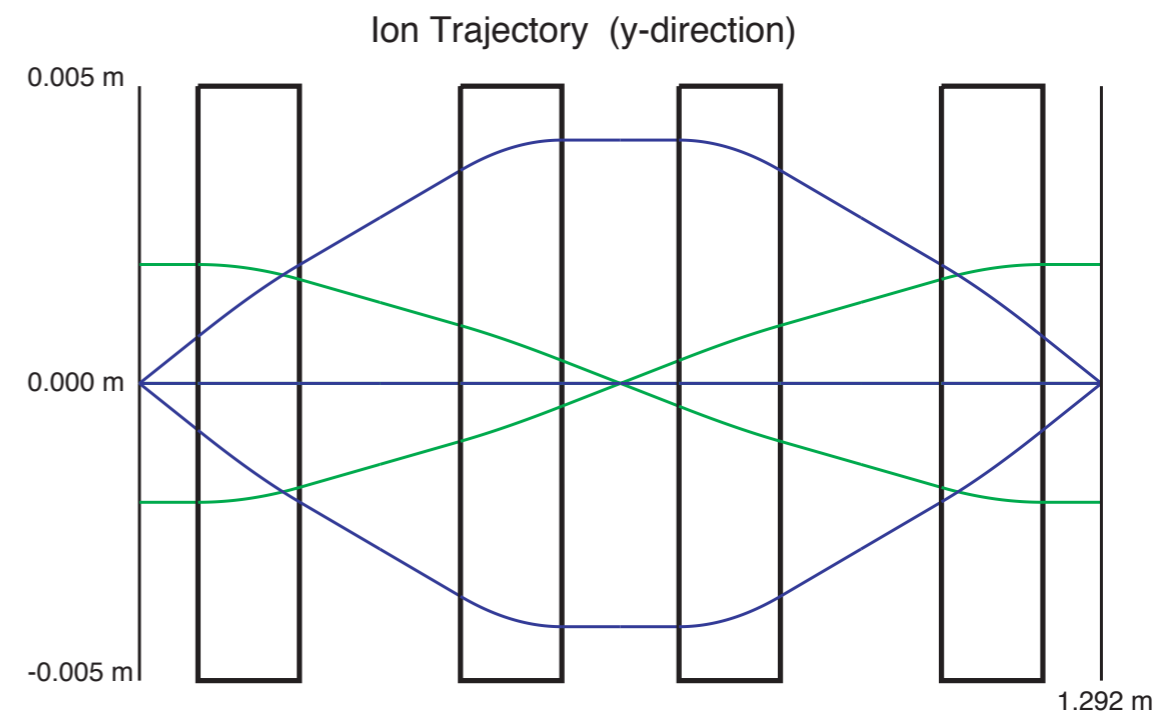
Deflection radius : 50 mm,  
Deflection angle :  $156.11^\circ$ ,  $C1 = 0.0344$



$x_{\max} = 0.0030 \text{ m}$ ,  $\alpha_{\max} = 0.0500$   
 $\gamma_{\max} = 0.0000$ ,  $\delta_{\max} = 0.0700$



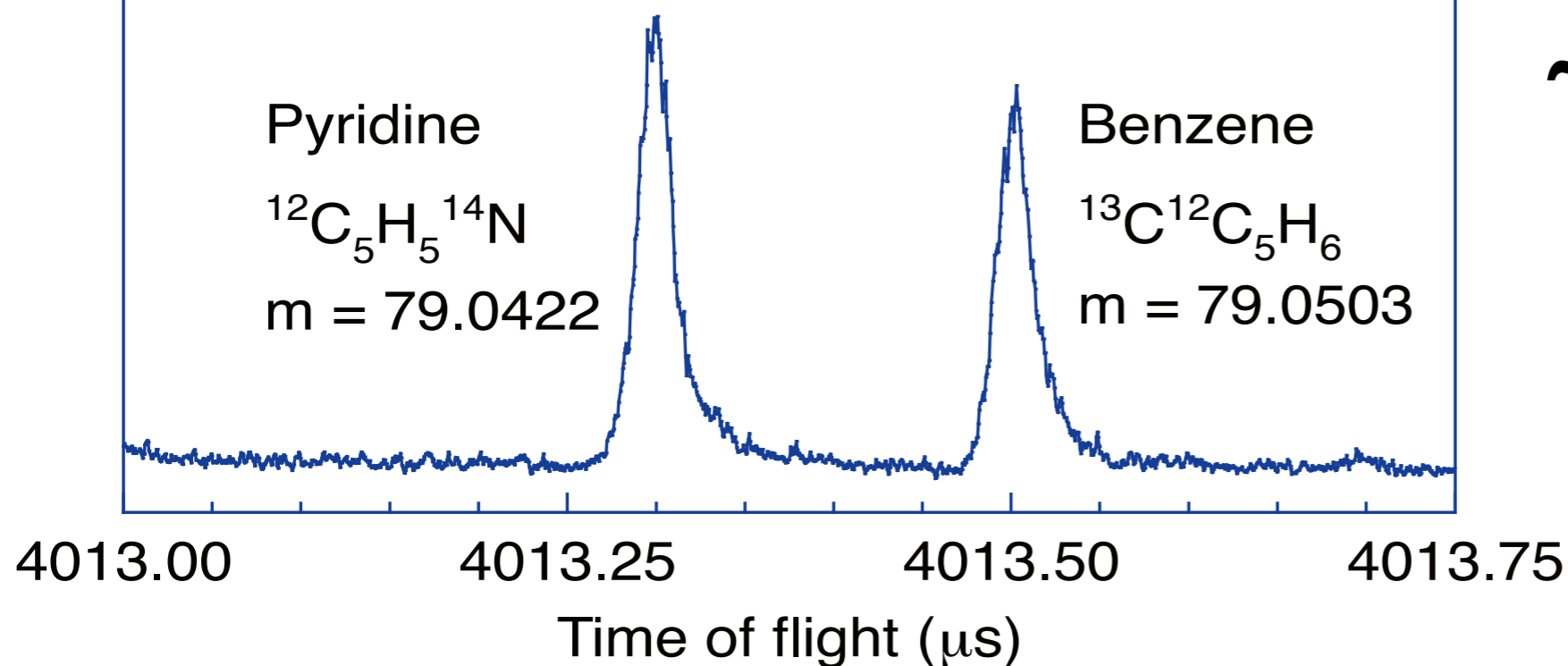
$x_{\max} = 0.0010 \text{ m}$ ,  $\alpha_{\max} = 0.0300$ ,  $\gamma_{\max} = 0.0000$ ,  $\delta_{\max} = 0.0300$



$y_{\max} = 0.0020 \text{ m}$ ,  $\beta_{\max} = 0.0100$

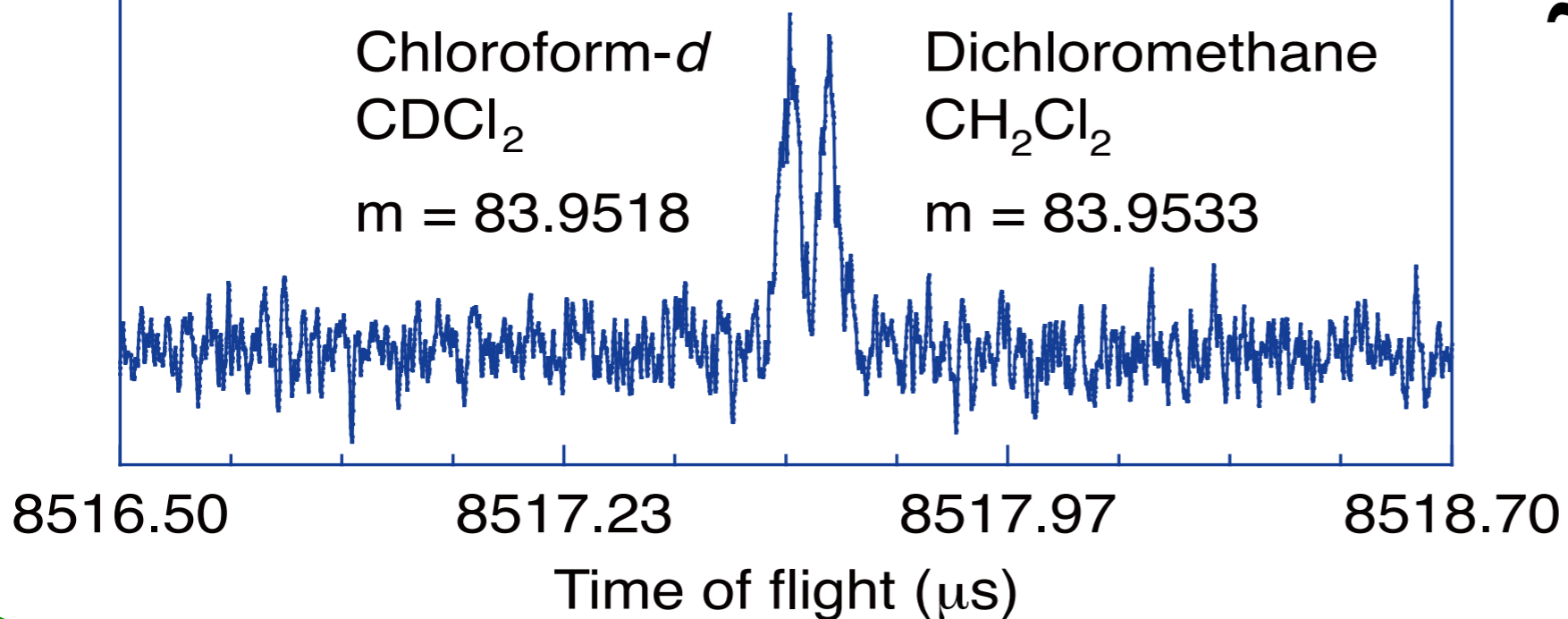
# High resolution EI TOF Spectra

**Resolution (FWHM) = 91,000**



**~300 cycles**

**Resolution (FWHM) = 115,000**



**~660 cycles**

D. Okumura, et al.,  
*Eur. J. Mass Spectrom.*,  
**11** (2005), 261.

# Applications

- MULTUM-S II
- MULTUM-IMG



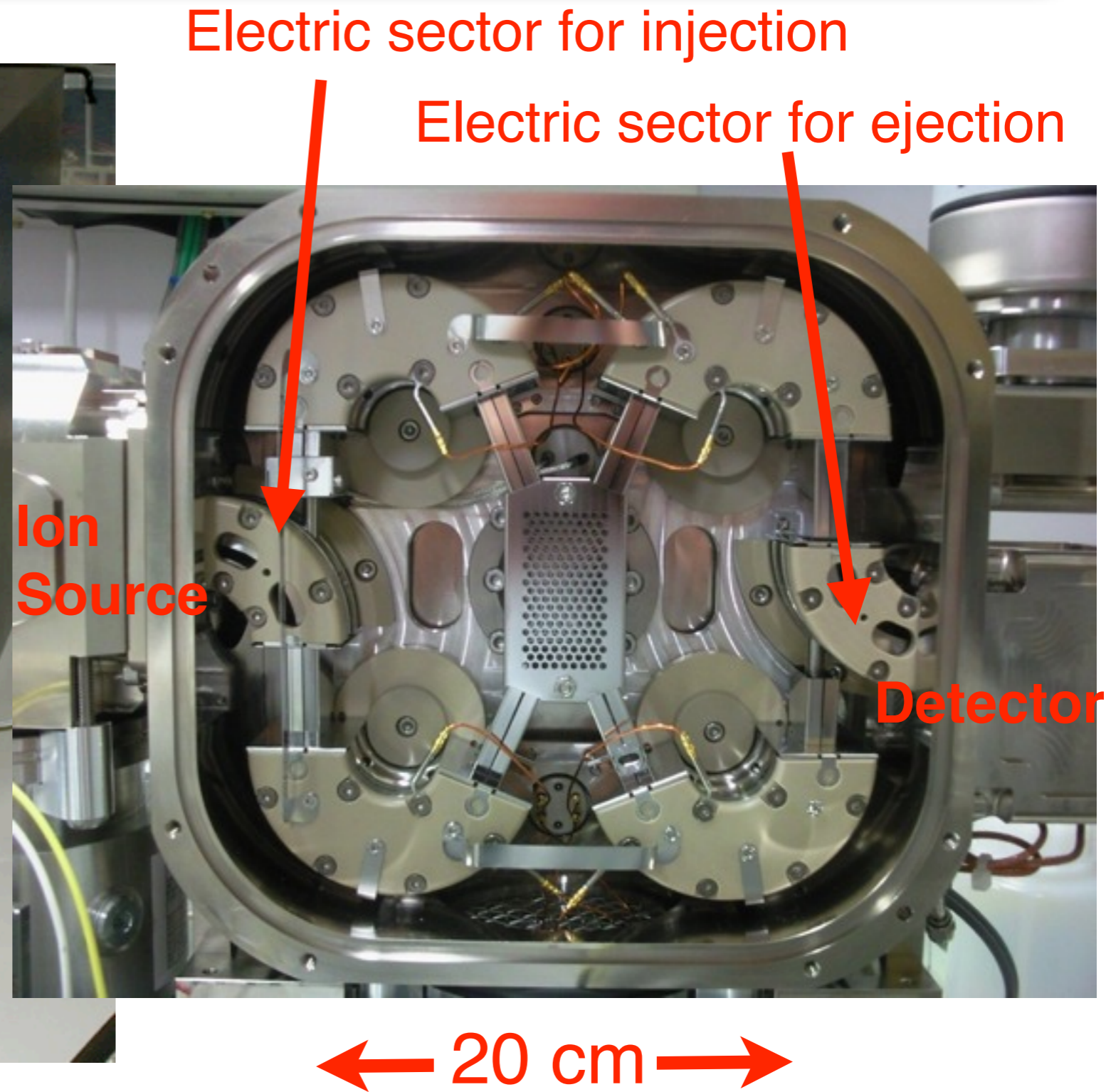
# Miniature Multi-turn TOF Mass Spectrometer

## “MULTUM-S II”

supported by University Venture Project,  
Japan Science and Technology Agency (JST)

S. Shimma, et al., *Anal. Chem.*, **82** (2010), 8456-8463

# Photograph of improved instrument "MULTUM -S II"

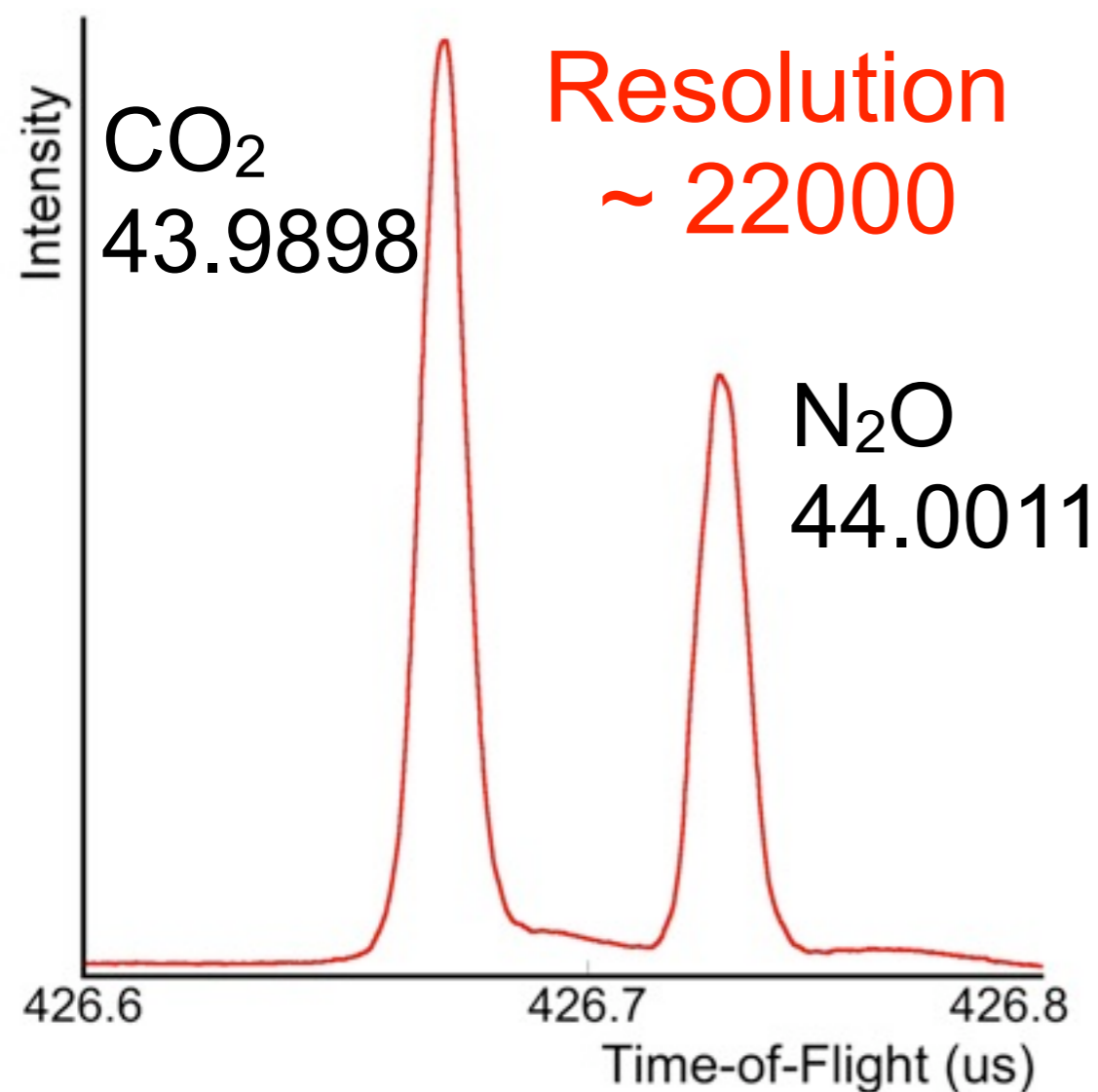


**50 (H) cm × 30 (W) cm × 60 (D) cm, 35kg**

# Results of MULTUM-S II

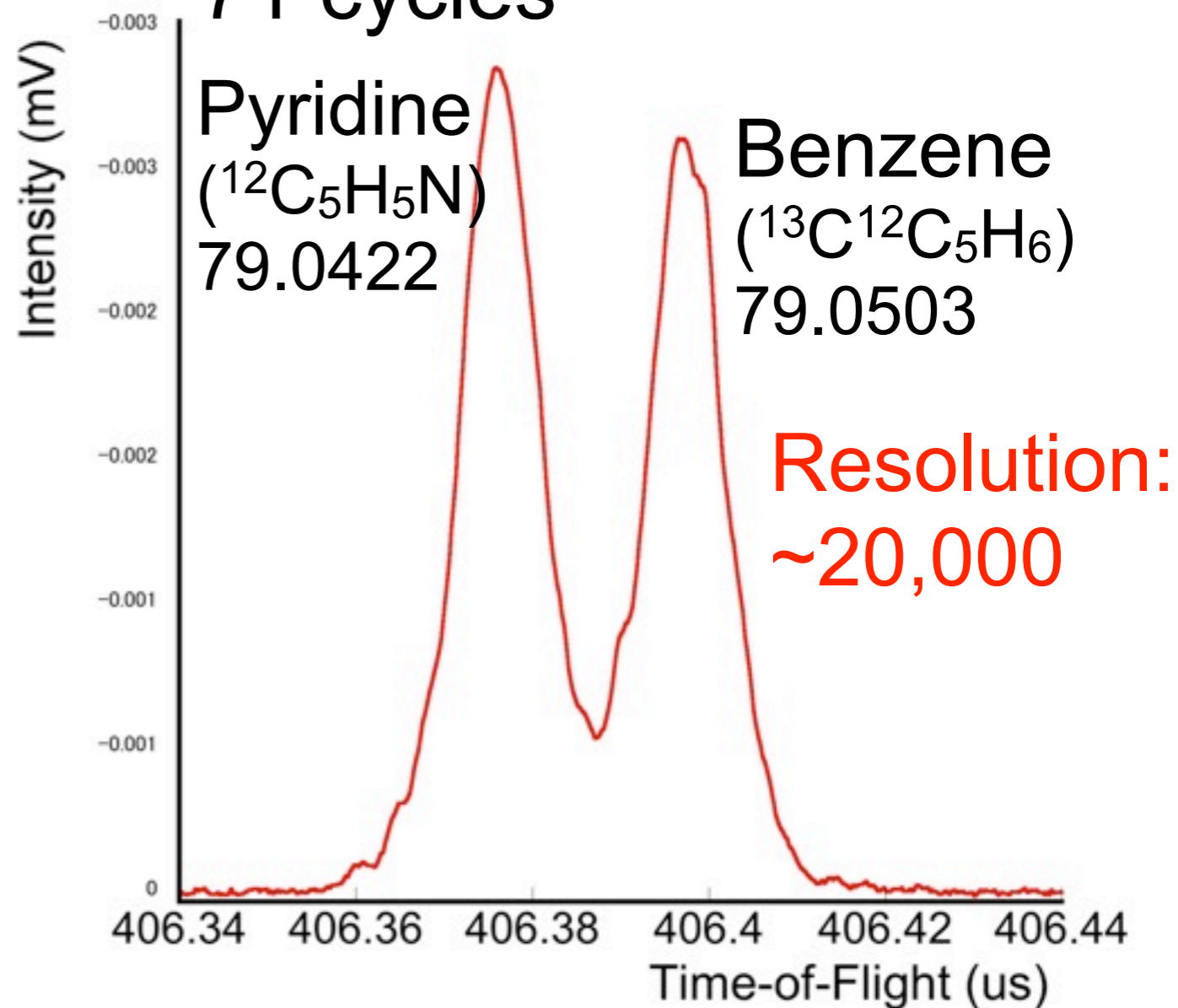
## CO<sub>2</sub> - N<sub>2</sub>O doublet

98 cycles



## Pyridine - Benzen doublet

71 cycles



This instrument will become a powerful analytical tool for portable or on-site analysis

# Multi-turn Imaging TOF Mass Spectrometer

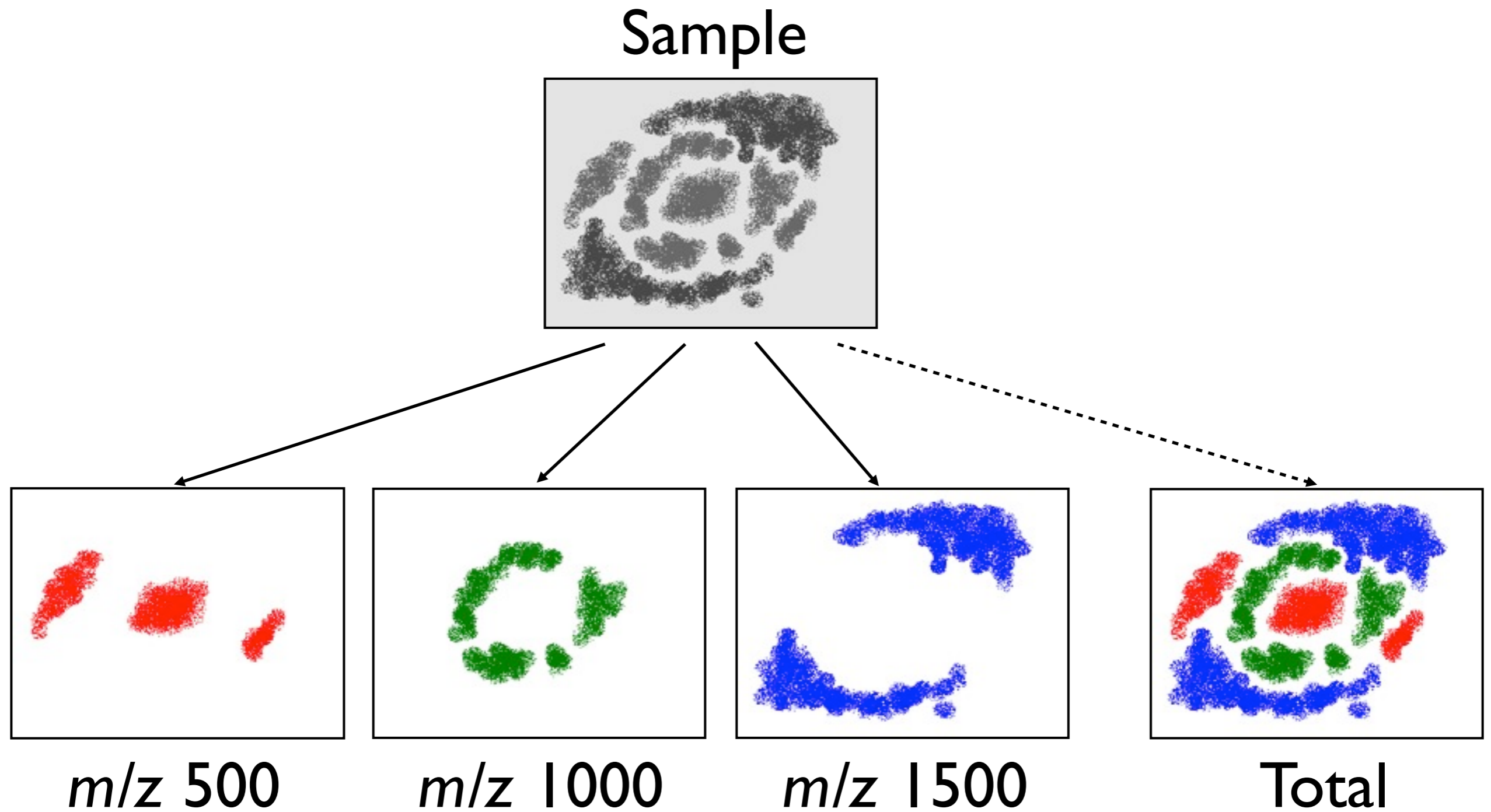
## “MULTUM-IMG”

supported by Core Research for Evolutional Science and Technology  
(CREST), JST

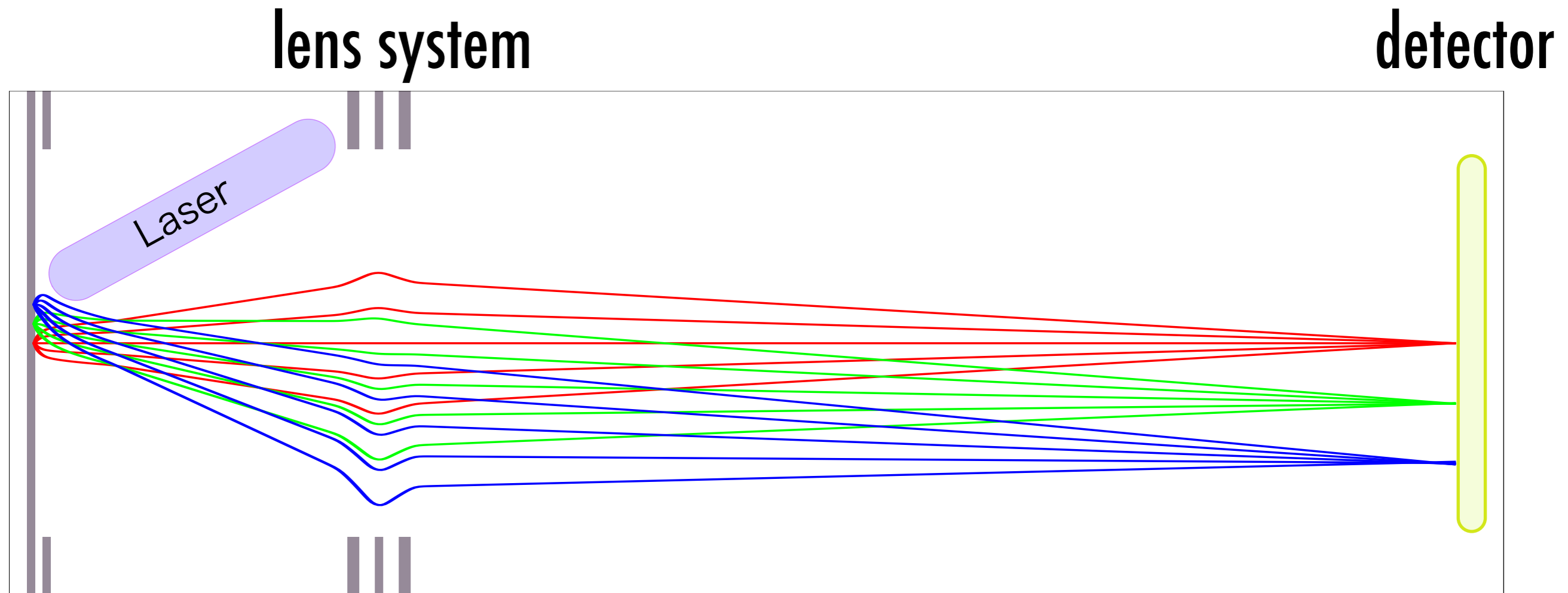
H. Hazama, et.al , *Appl. Surf. Sci.* **255** (2008), 1257.

H. Hazama, et.al , *J. Biomed. Opt.*, **16** (2011), 046007.

# What is imaging mass spectrometry ?



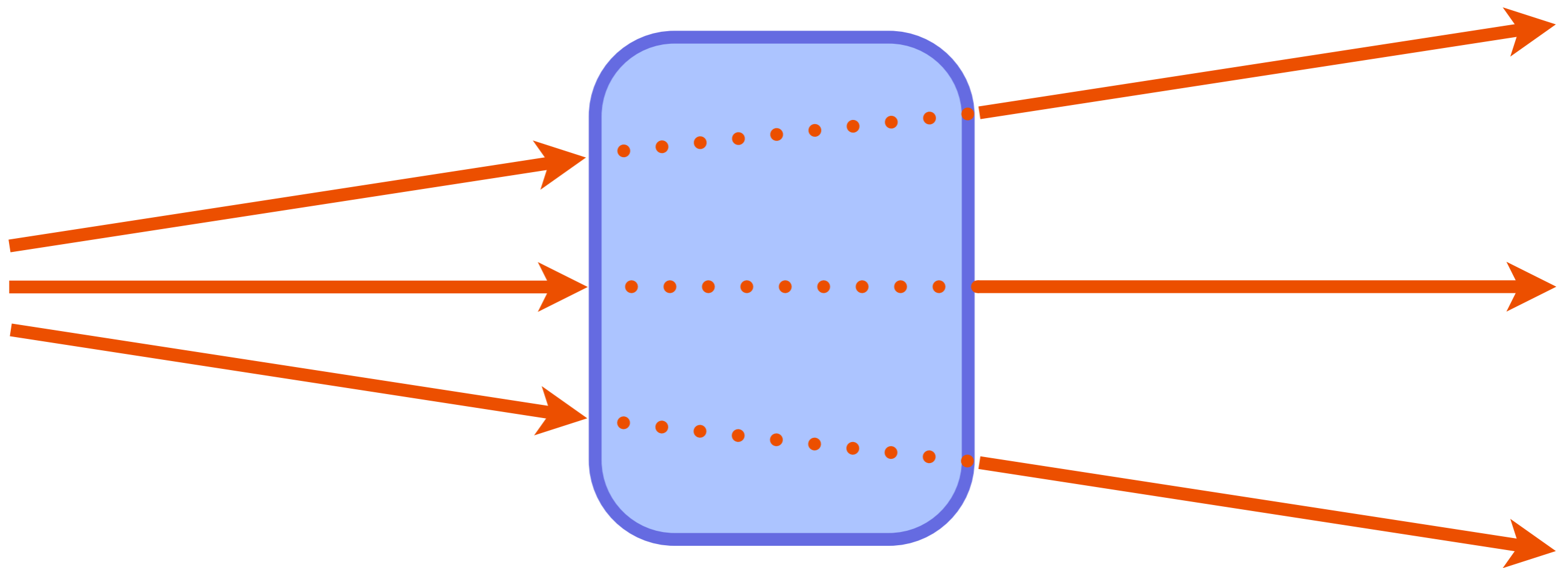
# Basic ion optics for stigmatic mass microscope



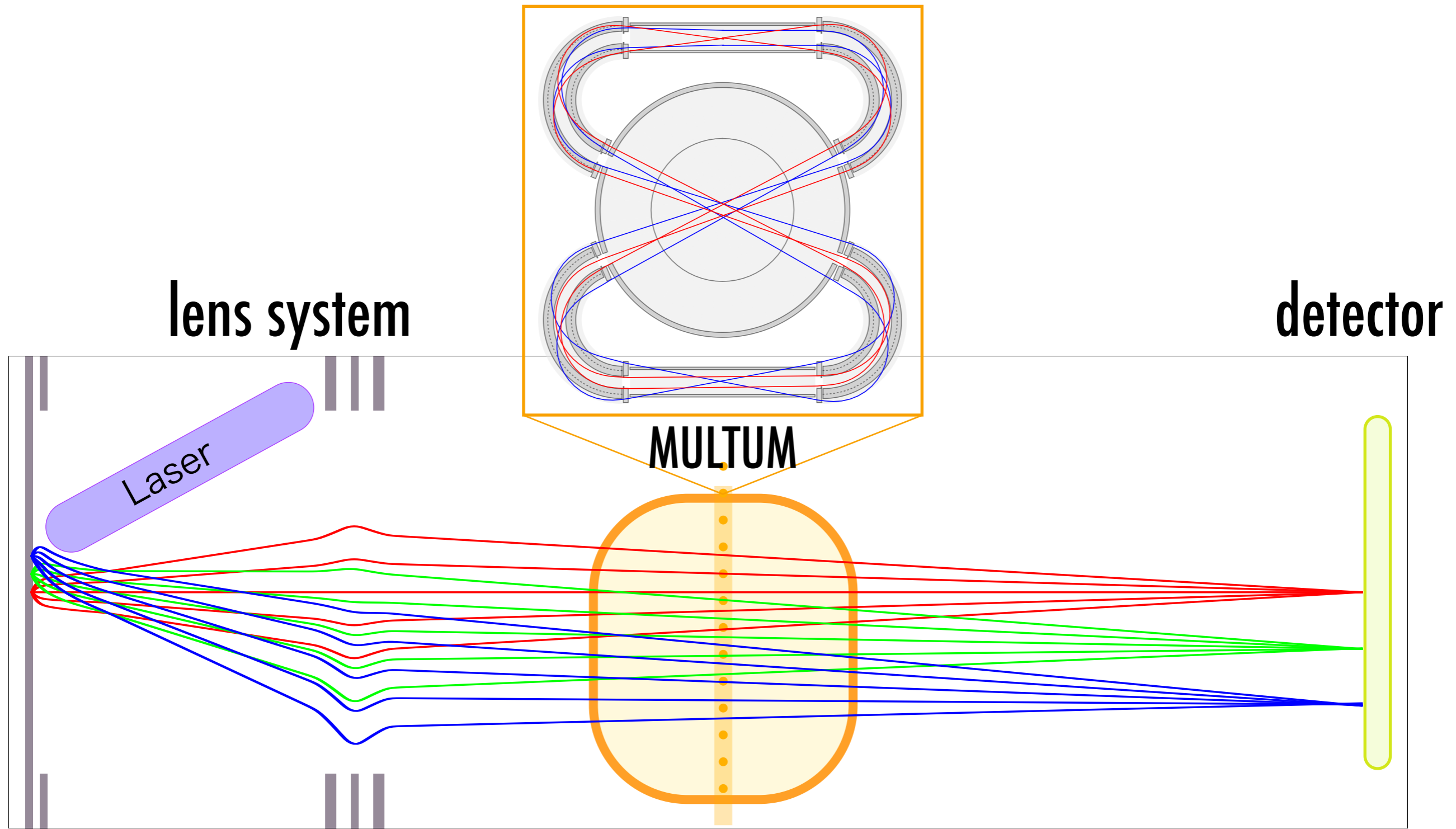
flight pass for time-of-flight measurement

# MULTUM's optics

MULTUM

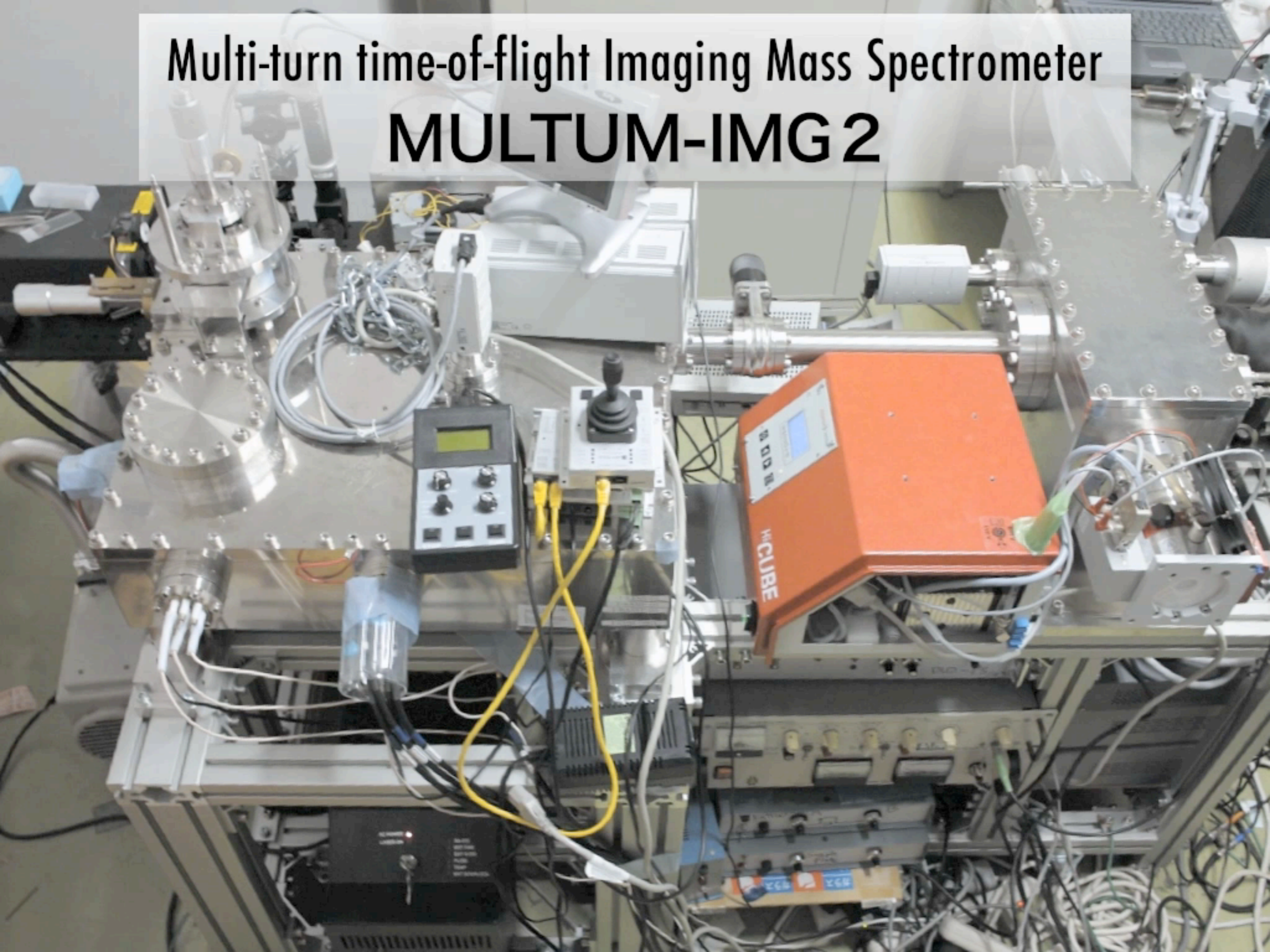


# Advanced ion optics for stigmatic mass microscope



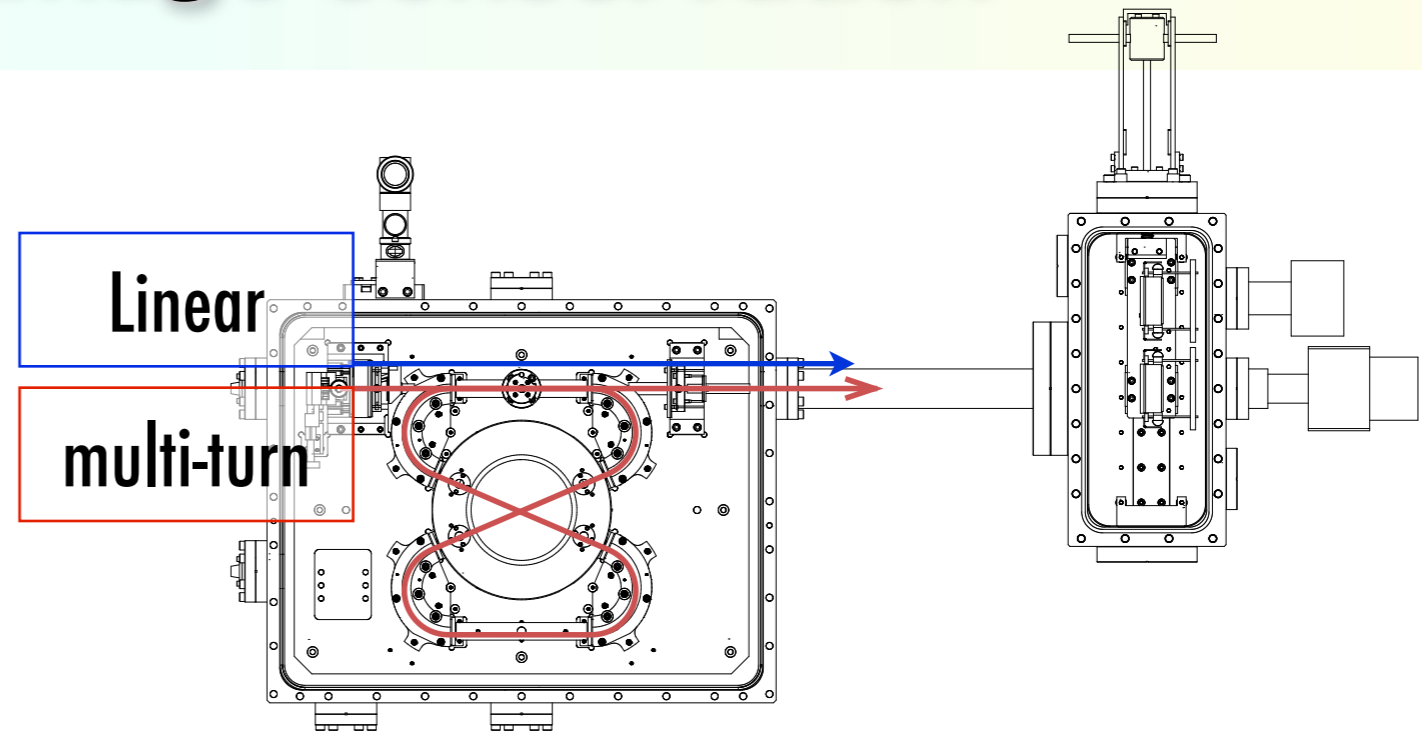
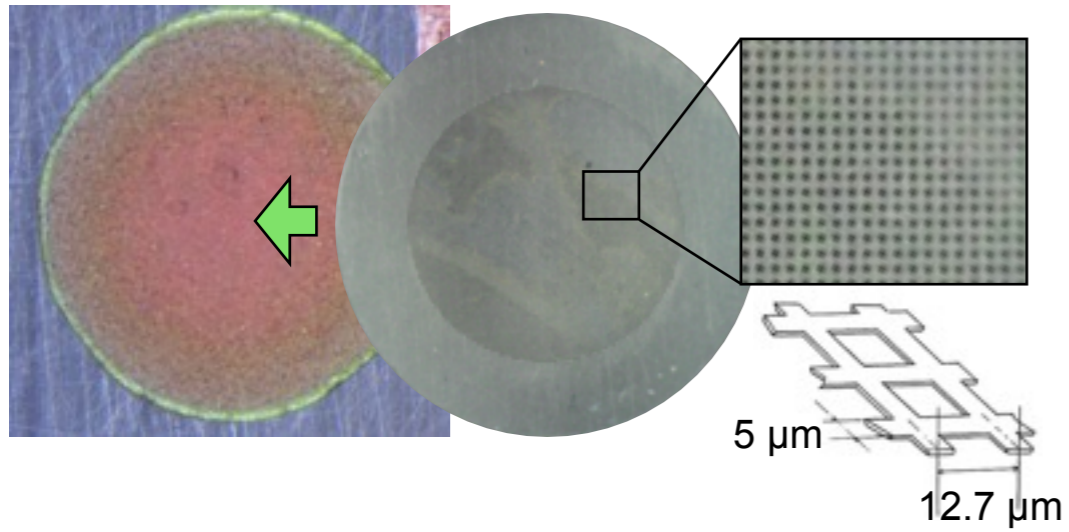


# Multi-turn time-of-flight Imaging Mass Spectrometer **MULTUM-IMG 2**

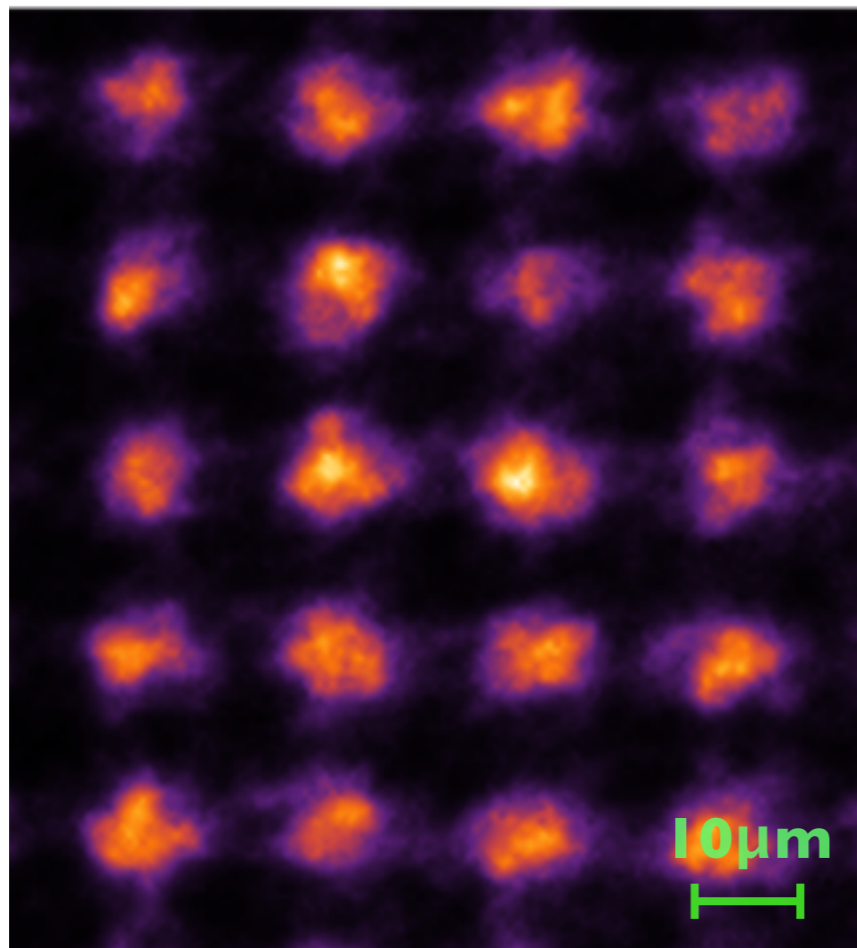


# Evaluation for image conservation

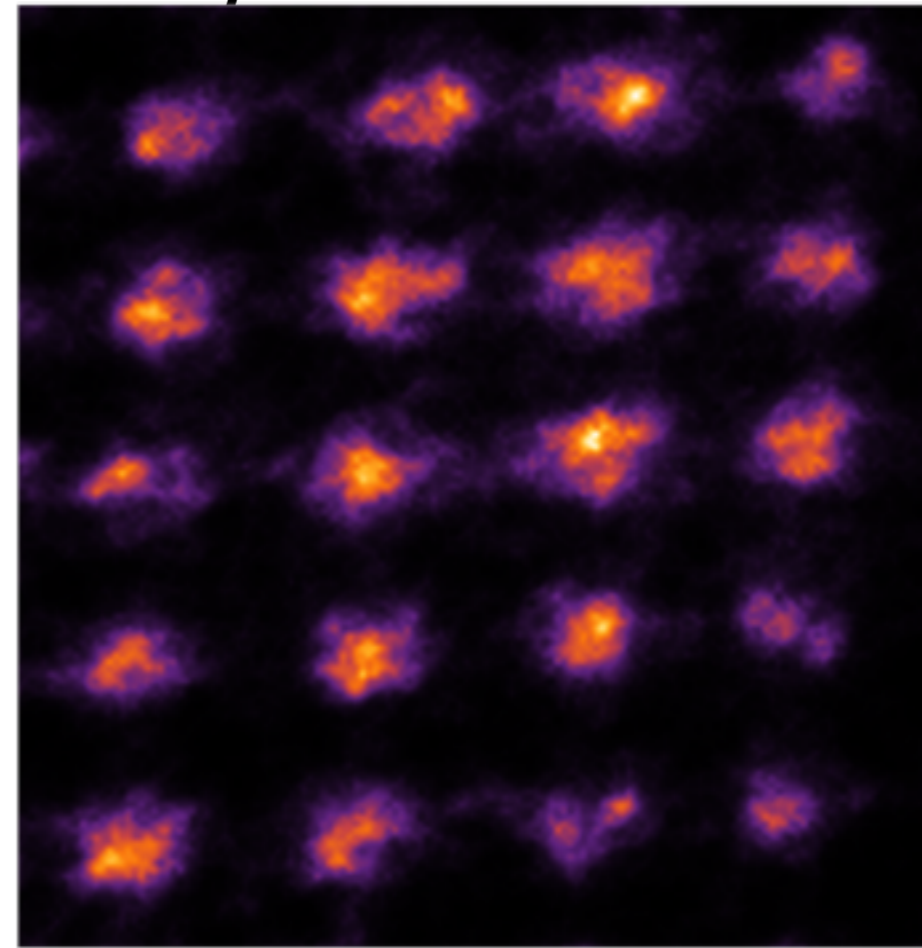
metal mesh of  $12.7\ \mu\text{m}$  pitch on crystal violet dye



**Linear** (flight length of  $0.8\ \text{m}$ )



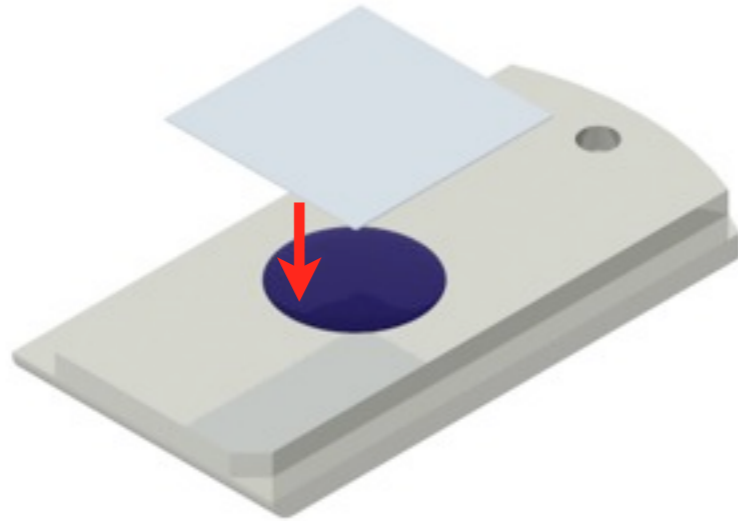
**8 cycles** (flight length of  $11.5\ \text{m}$ )



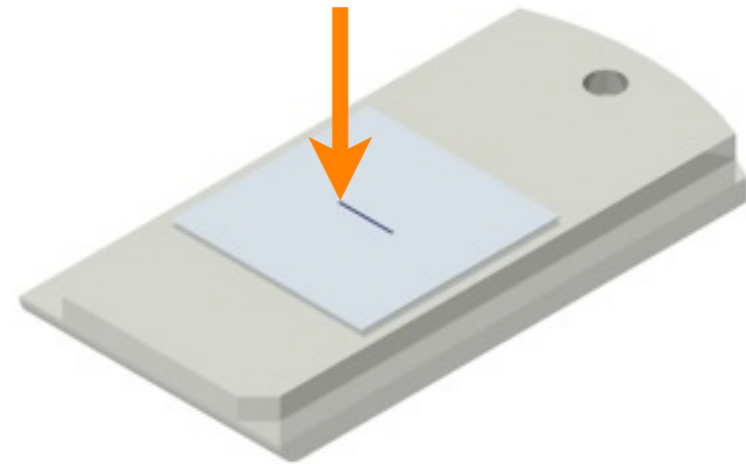
# Evaluation for spatial resolution

## Making evaluation sample

① A dried droplet of crystal violet dye is covered by thin aluminum foil of  $1.5 \mu\text{m}$  thickness.

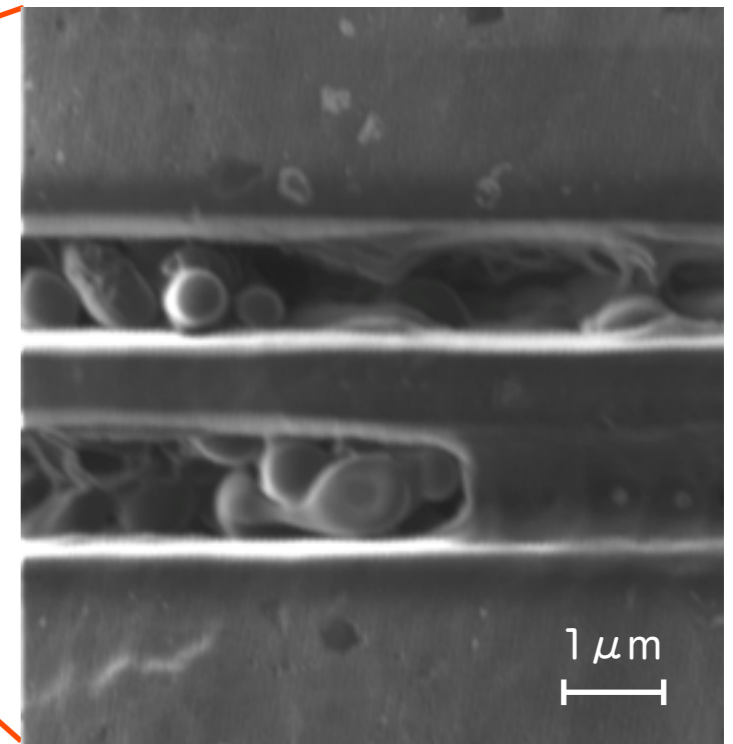
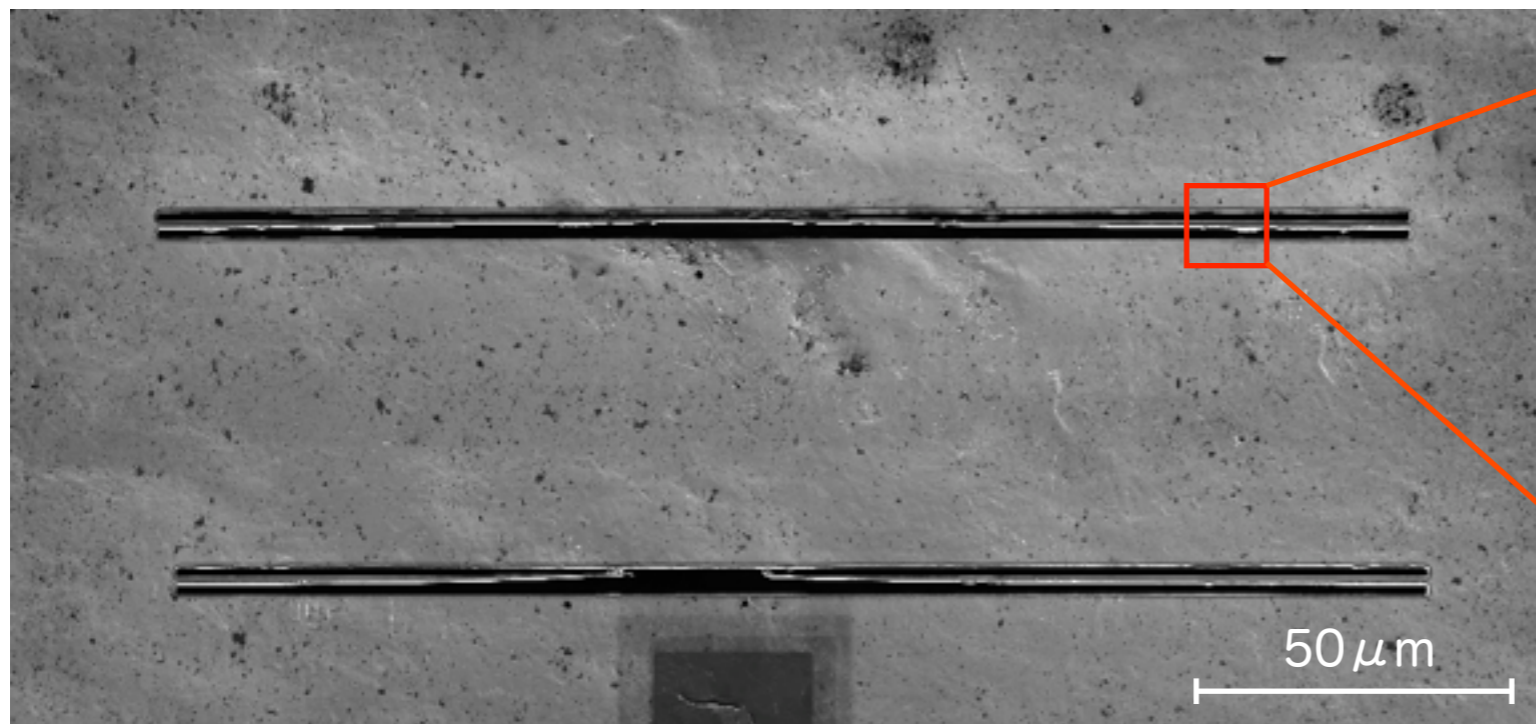


② Etching with focused ion beam to form fine slits

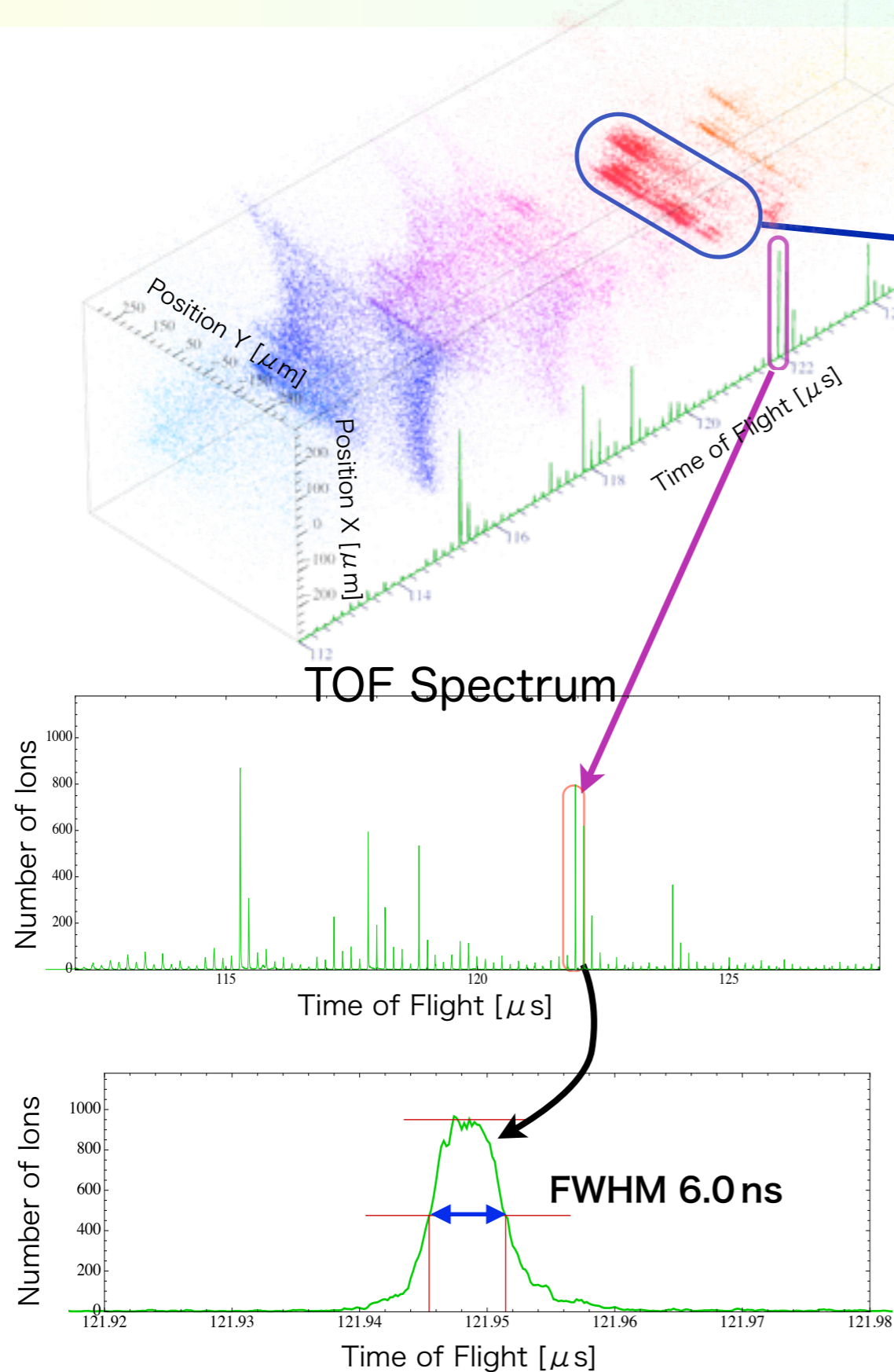


SEM image

Two slits of  $1 \mu\text{m}$  width are aligned with  $1 \mu\text{m}$  gap.

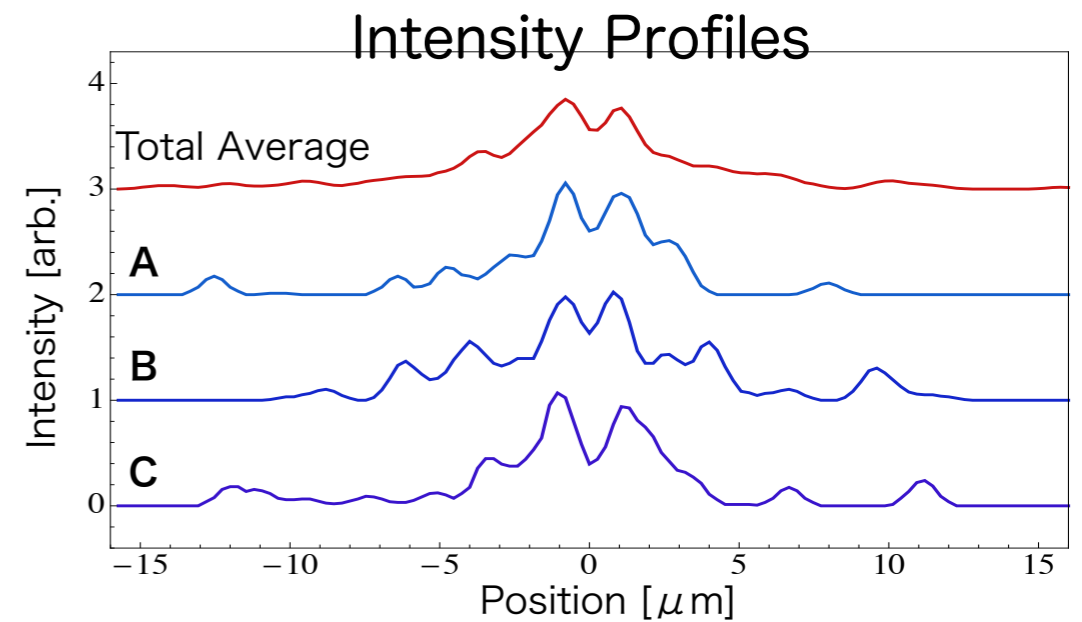
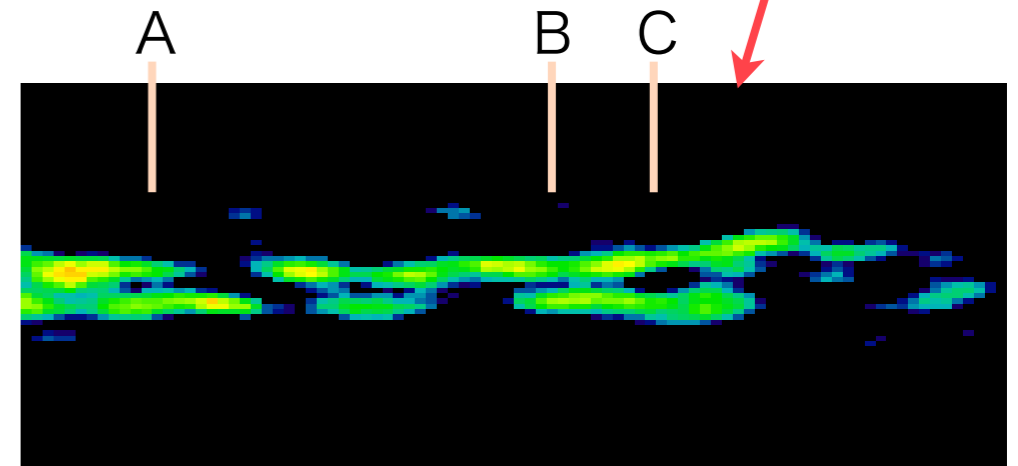
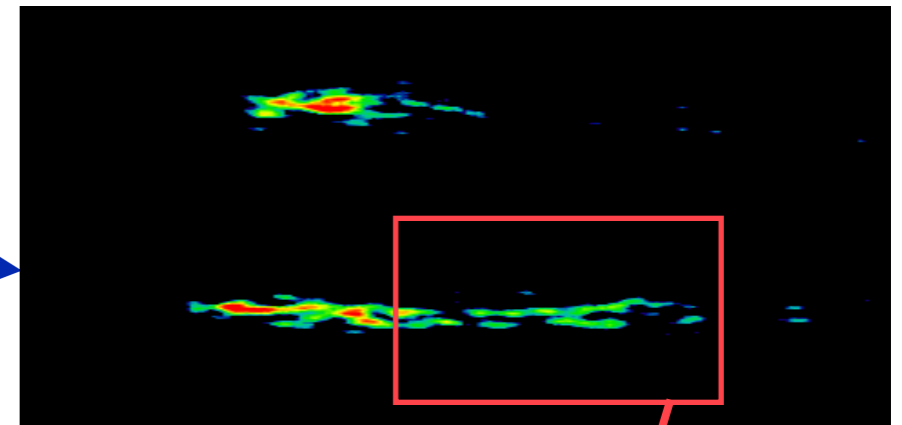


# Evaluation for spatial resolution



mass resolution  $m/\Delta m > 10000$

Ion Image



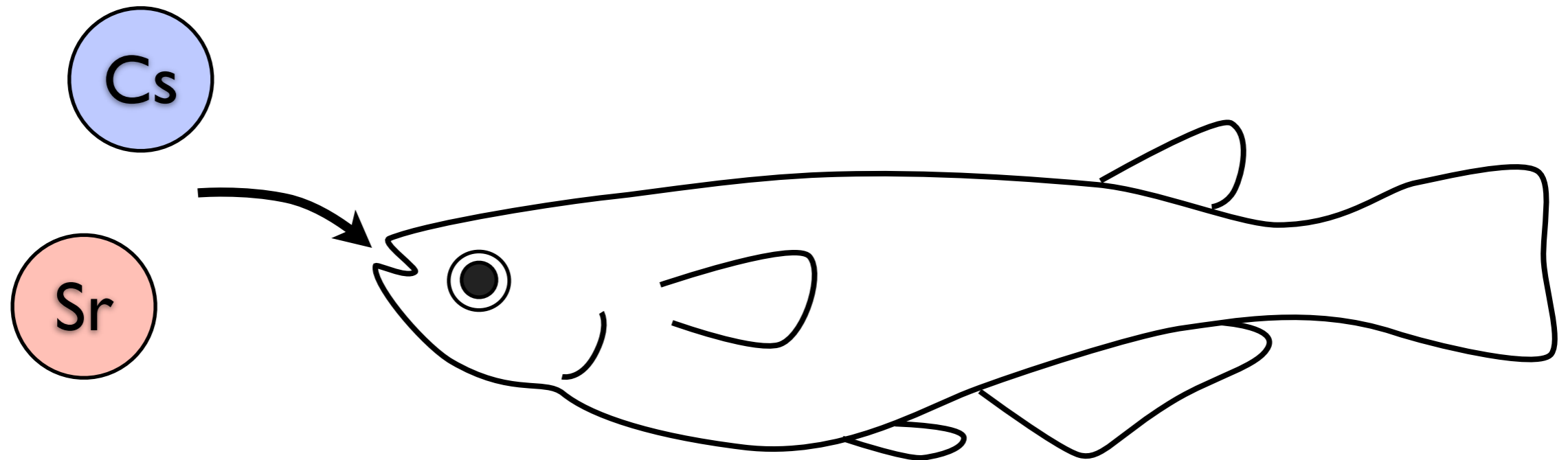
spatial resolution  $1\ \mu\text{m}$

# Imaging Applications

- Observation of accumulated metal cation in fish

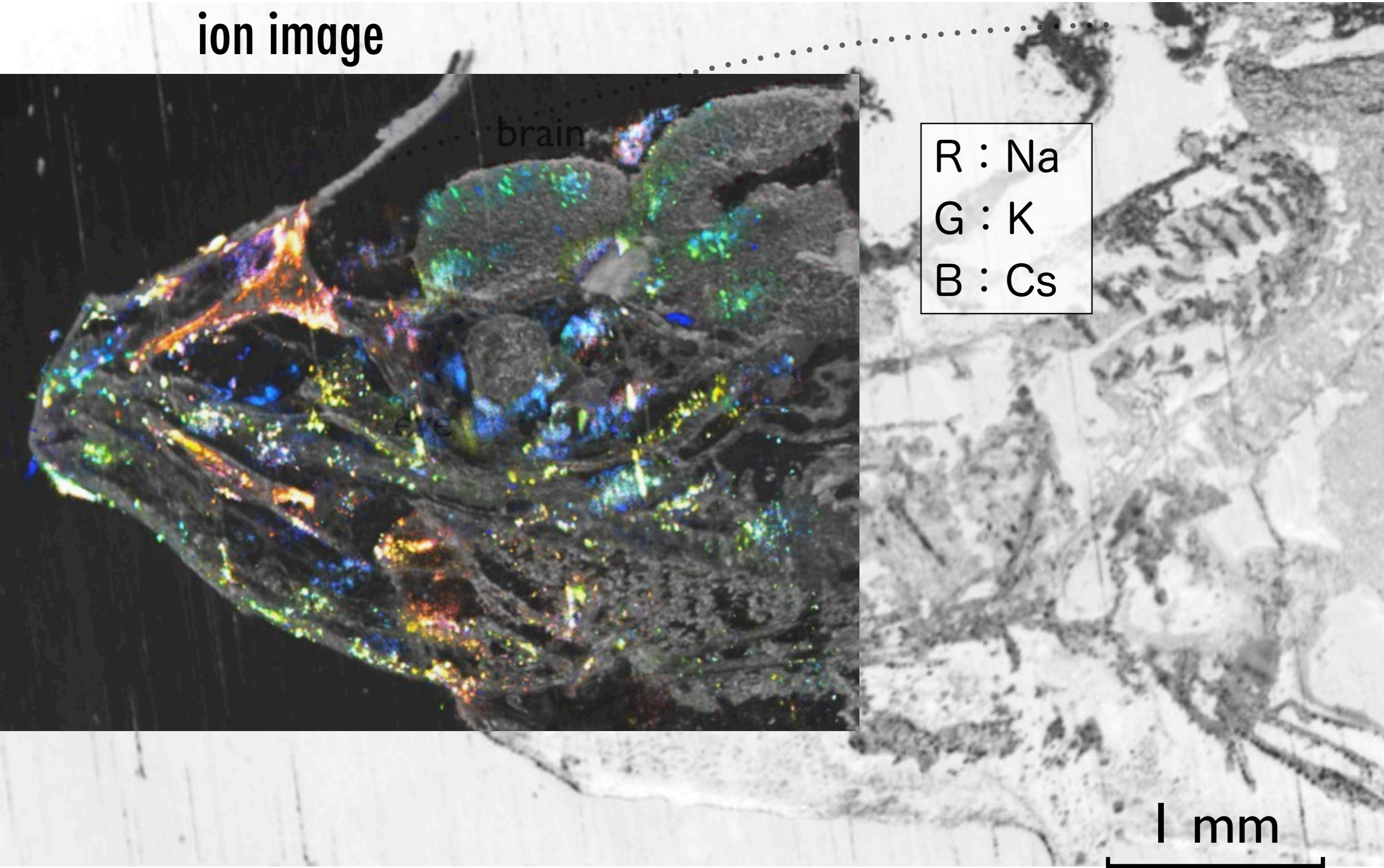
# Observation of accumulated metal cation in fish

Small fish (medaka; *Oryzias latipes*) was raised for two weeks in water containing Cs and Sr.



# Observation of accumulated metal cation in fish

ion image



brain

eye

R : Na  
G : K  
B : Cs

1 mm

# Conclusion

- We developed multi-turn time of flight mass spectrometer.
- High mass resolving power were achieved with compact size instrument.
- Applications of MULTUM are in progress.

