Prototype coded aperture miniature mass spectrometer using a cycloidal sector mass analyzer, a carbon nanotube (CNT) field emission electron ionization source, and an array detector

11th Harsh-Environment Mass Spectrometry Workshop

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Charles B. Parker,[†] Jason J. Amsden,[†] Philip J. Herr,[†] David M. W. Landry,[†] William Kim,[†] Raul Vyas,[†] Matthew P. Kirley,[†] Adam D. Keil,[@] Kristin H. Gilchrist,[‡] Erich J. Radauscher,[†] Stephen D. Hall,[‡] James B. Carlson,[‡] Nicholas Baldasaro,[‡] David Stokes,[‡] Shane T. Di Dona,[†] Zachary E. Russell,[†,&] Sonia Grego,[‡] Steven J. Edwards,[*] Roger P. Sperline,[*] M. Bonner Denton,[*] Brian R. Stoner,[‡,†] Michael E. Gehm,[†] and Jeffrey T. Glass[†]

† Department of Electrical and Computer Engineering, Duke University, Durham, NC, USA 27708
‡ Discovery Science and Technology, RTI International, Research Triangle Park, NC, USA 27709
@ Broadway Analytical, LLC Monmouth, IL USA 61462
* Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ USA 85721
& Present Address: Ion Innovations, Norcross, GA USA 30092

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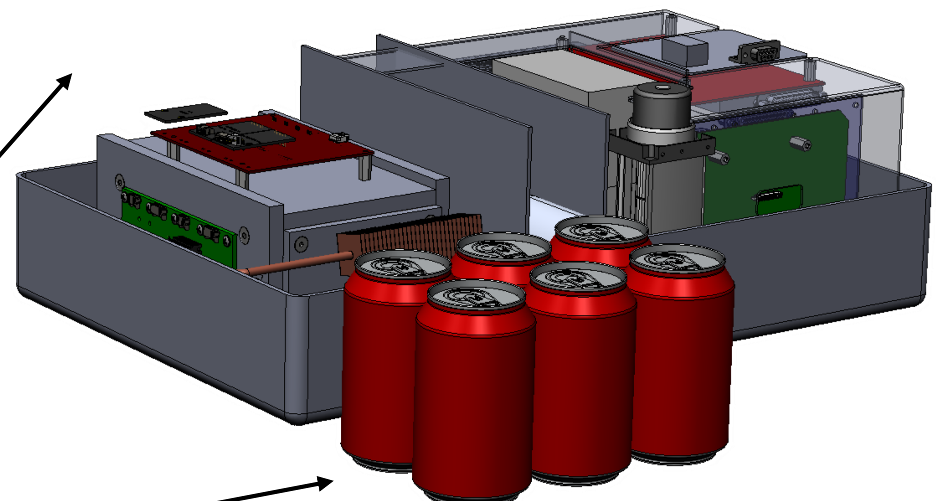
CAMMS-ES Vision

- **CAMMS-ES**: **C**oded **A**perture **M**iniature **M**ass **S**pectrometer for **E**nvironmental **S**ensing
- Traditional miniature mass spectrometers suffer from a throughput vs. resolution tradeoff
- CAMMS-ES employs coded apertures to break this throughput vs. resolution tradeoff
- CAMMS-ES will enable the production of portable instruments with high sensitivity and resolution

Portable high performance mass spectrometer



CAMMS-ES mini
prototype concept

CAMMS-ES and ARPA-E MONITOR

ARPA-E MONITOR

- **Methane Observation Networks with Innovative Technology to Obtain Reductions (MONITOR**) program is developing innovative technologies to cost-effectively and accurately locate and measure methane emissions associated with natural gas production.

CAMMS-ES

- *Portable mass spectrometer with high resolution and high sensitivity for VOC leak detection*
  - *Detection of not only methane, but other compounds of interest including*
    - *Butane, propane, ethane, benzene, ethylbenzene, toluene, xylene*
    - *Thermogenic/biogenic differentiation using higher order alkyl chains*
- *Applications*
  - *Ad hoc leak detection at refineries*
  - *Fence line monitoring at refineries*

People have been trying for 60 years!

Cycloidal mass analyzer advertisement in 1956 issue of Analytical Chemistry

mass spectrometry

out of the laboratory....into the plant

CEC's two companion instruments . . . Types 21-610 and 21-620 . . . have taken mass spectrometry out of the purely laboratory-instrument class and made the inherent speed and accuracy of this analytical method practical for industrial use. As a process-stream analyzer, the mass spectrometer is exceptionally versatile, provides stream-composition information *on the spot* for regulating plant start-up procedures, optimizing operations and products, and minimizing process interruptions.

SEVERAL MODES OF OPERATION

Both 21-610 and 21-620, together with available accessory systems, work on either a batch or continuous basis, permit . . .

- *continuous determination of a single component*
- *alternate determination of several components*
- *automatic scanning of a complete spectrum*
- *programming up to six mass numbers for automatic, repetitive monitoring*
- *alternate monitoring of more than one process stream through automatic manifolding, valving, and timing systems.*

APPLICATION . . . INSTALLATION

CEC's Application Engineers offer without charge experienced help in fitting the mass spectrometer to your specific application. In addition, all mass spectrometers are installed and put into initial operation by a skilled CEC Field Service Engineer. Send today for Bulletin CEC 1824B-X1.

COMPANION INSTRUMENTS

Both the 21-610 and 21-620 Mass Spectrometers are flexible and simplified, need only 115 volts and a small supply of cooling water, are easily moved around the plant. The Type 21-610 is useful for monitoring streams with components to mass 80. The Type 21-620 employs the newly developed "Cycloidal Focusing" principle, is usable for accurate readings from mass 2 to mass 150.

Consolidated Electrodynamics Corporation
formerly Consolidated Engineering Corporation

300 North Sierra Madre Villa, Pasadena, California • SALES AND SERVICE OFFICES IN: *Albuquerque, Atlanta, Boston, Buffalo, Chicago, Dallas, Detroit, New York, Pasadena, Philadelphia, San Francisco, Seattle, Washington, D.C.*

ELECTRONIC INSTRUMENTS FOR MEASUREMENT AND CONTROL

For further information, circle number 15 A on Readers' Service Card, page 63 A

VOLUME 28, NO. 4, APRIL 1956

15 A

Our 4 technologies will finally make this possible!

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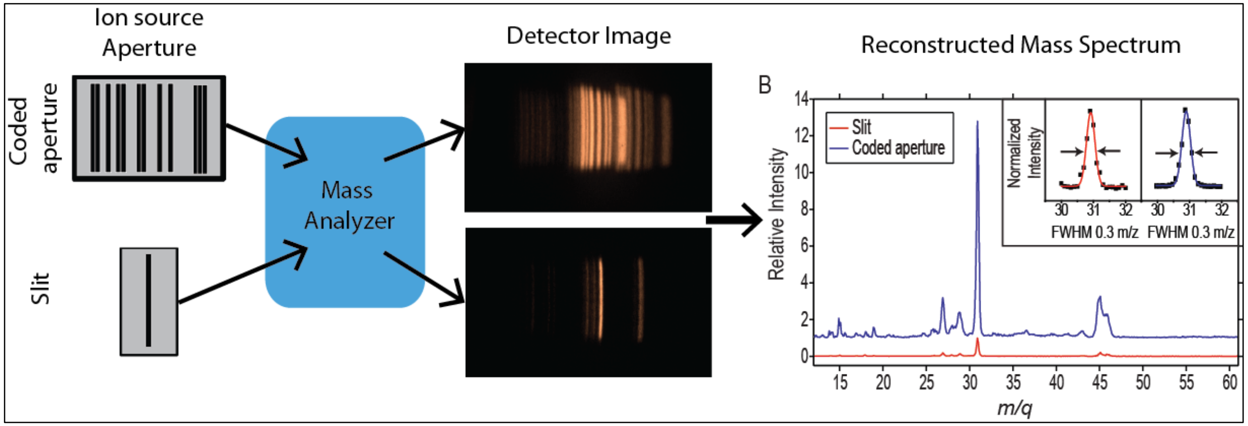
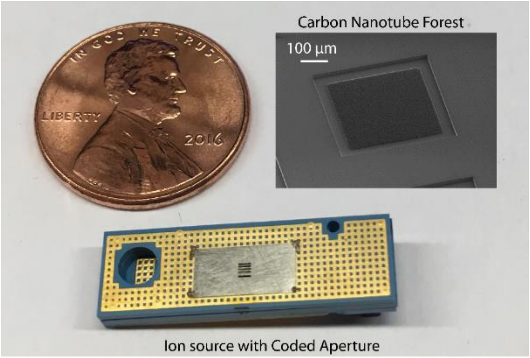
Four Enabling Miniaturization Technologies

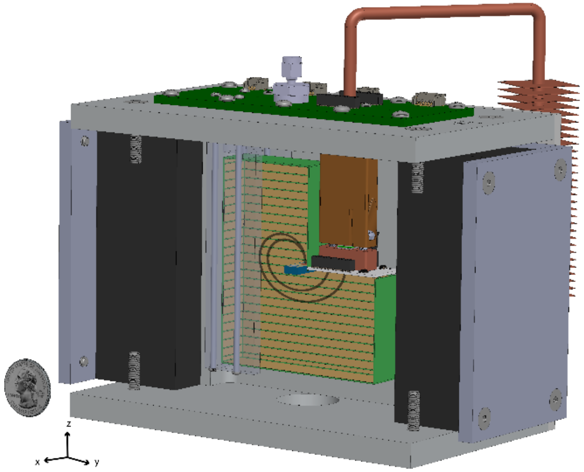


Aperture Coding: increased throughput, no loss in resolution

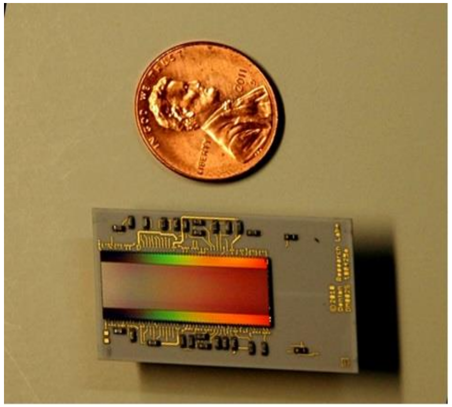
Microfabricated CNT field emission ion source



Cycloidal mass analyzer

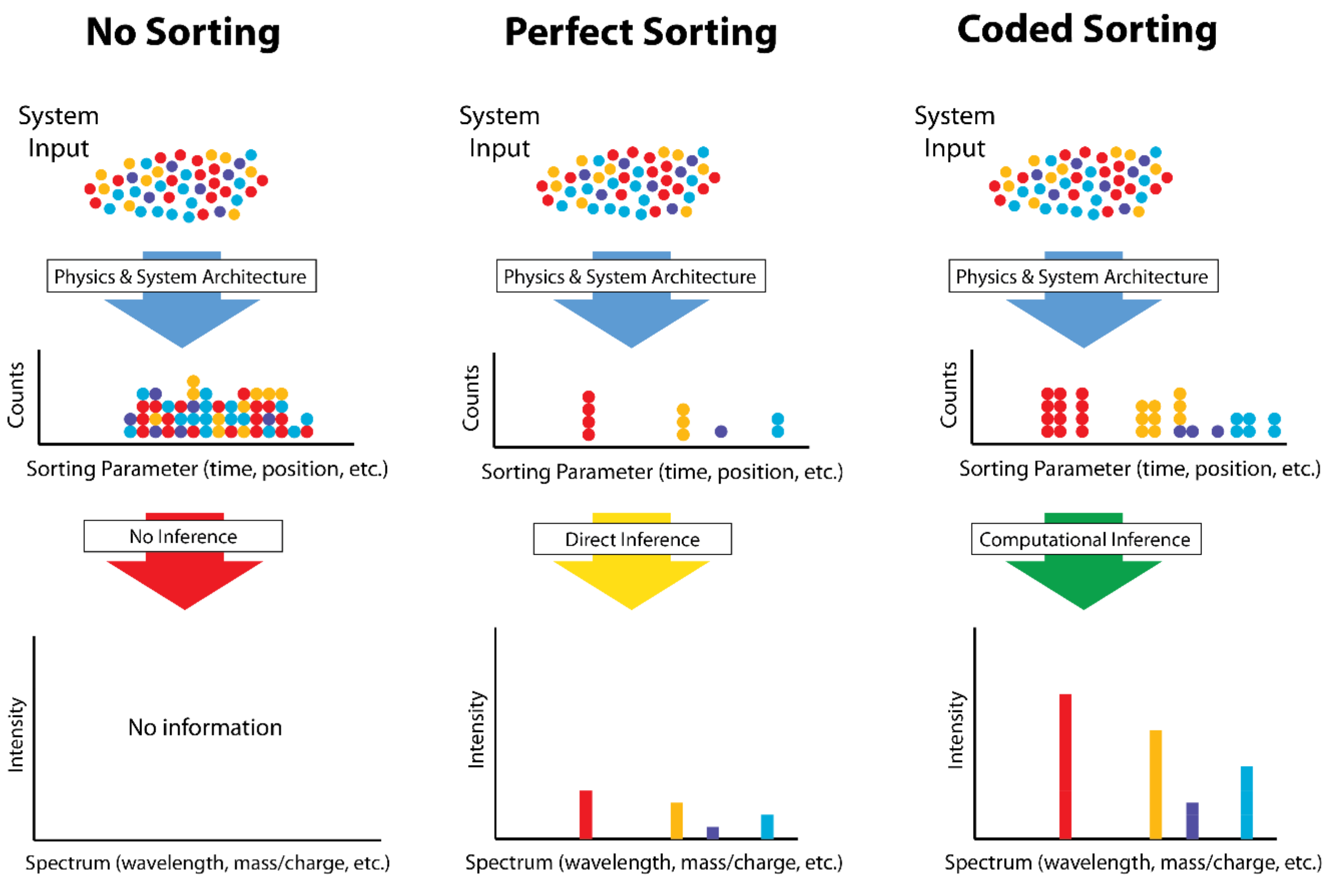


Focal plane array detector



What is Aperture Coding?

- Conventional instruments act as sorters
- Input is sorted via a system architecture and relevant physics
- In the absence of sorting the system throughput is large, however no information can be inferred
- In a conventional system, the architecture is designed using the relevant physics to achieve near perfect sorting
    - Spectra can be obtained via a simple calibration of the sorting parameter
    - Architecture choices limit performance and



- There is a continuum between no sorting and perfect sorting
- With appropriately structured sorting, the ability to discern the spectrum is maintained via a computational inference eliminating the throughput vs. resolution tradeoff

Aperture coding breaks the throughput vs. resolution tradeoff

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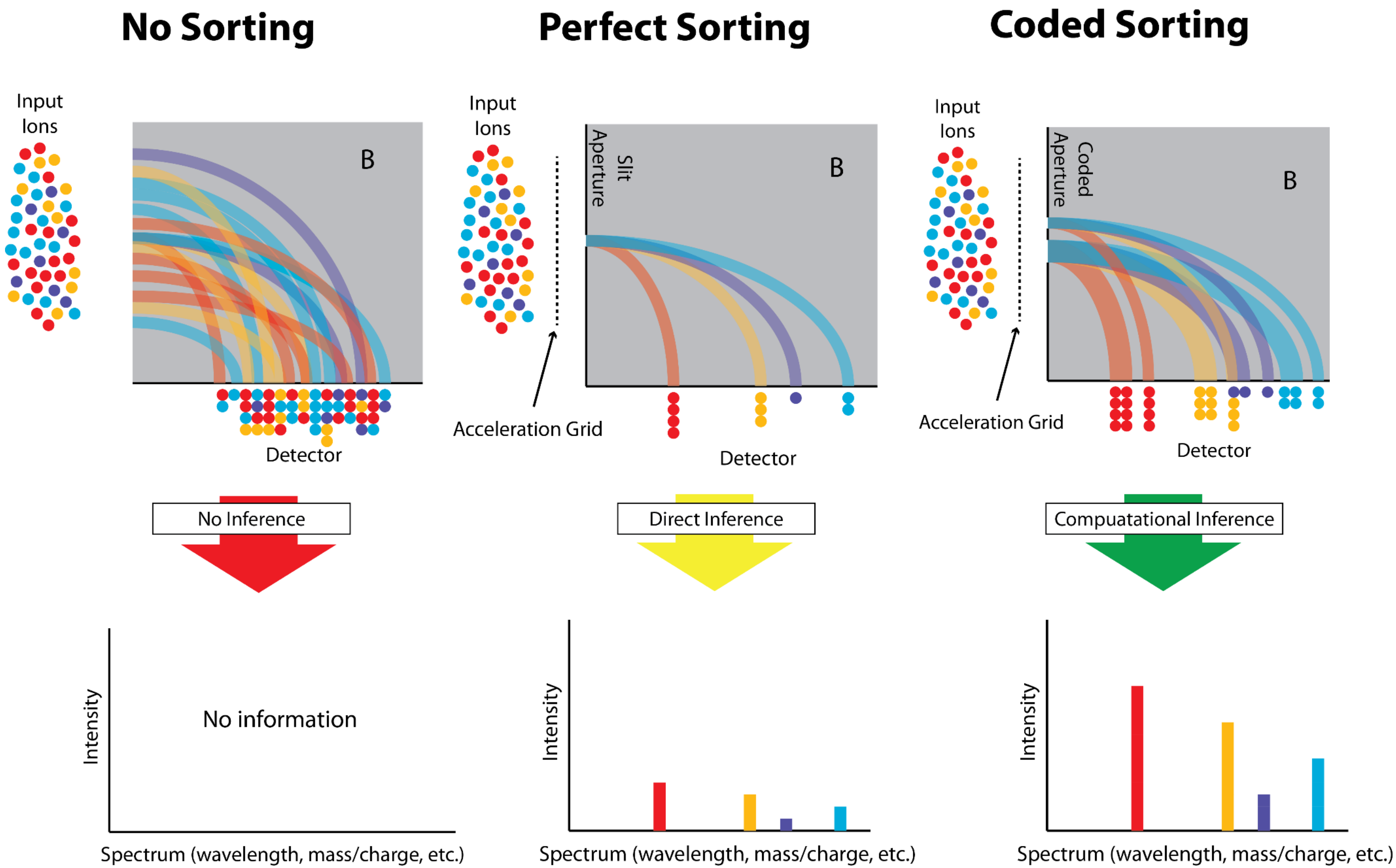
Coded Aperture Sector



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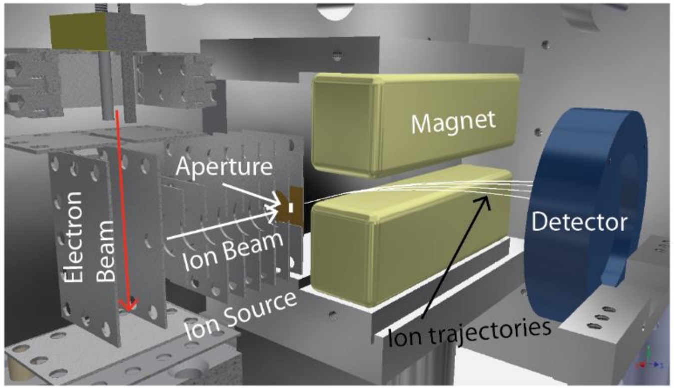
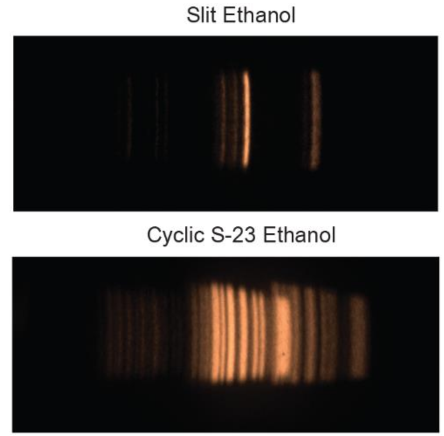
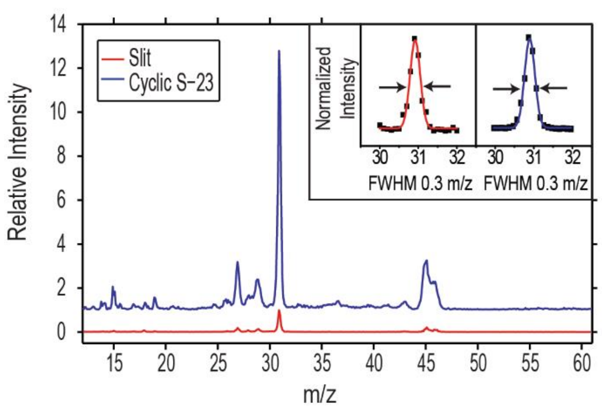
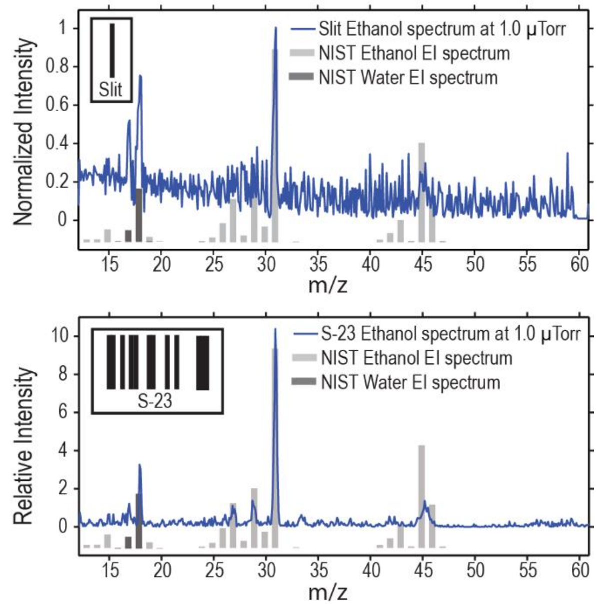
Aperture Coding Proof of Concept: a simple 90-degree magnetic sector









Aperture coding works in a simple 90-degree sector

Chen EX, Russell ZE, Amsden JJ, Wolter SD, Danell RM, et al. 2015. Order of magnitude signal gain in magnetic sector mass spectrometry via aperture coding. J. Am. Soc. Mass Spectr. 26: 1633-40

Spatial coding in the Mattauch-Herzog Mass Analyzer

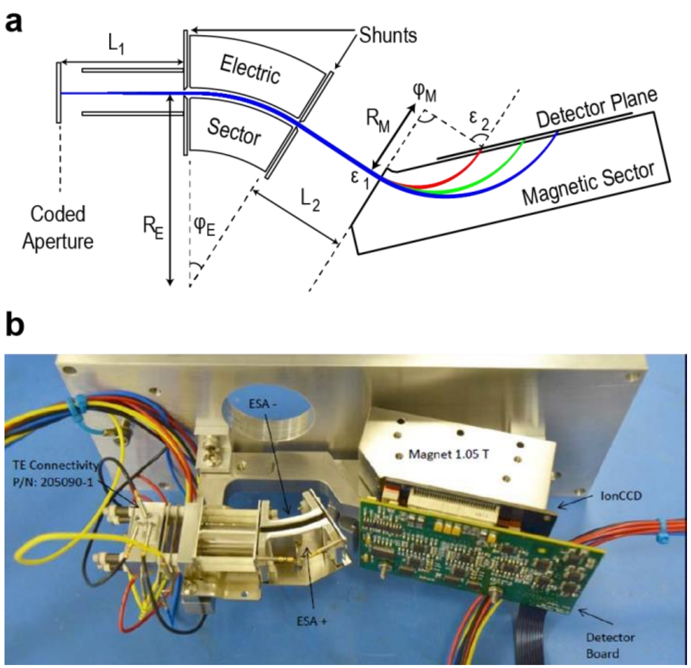
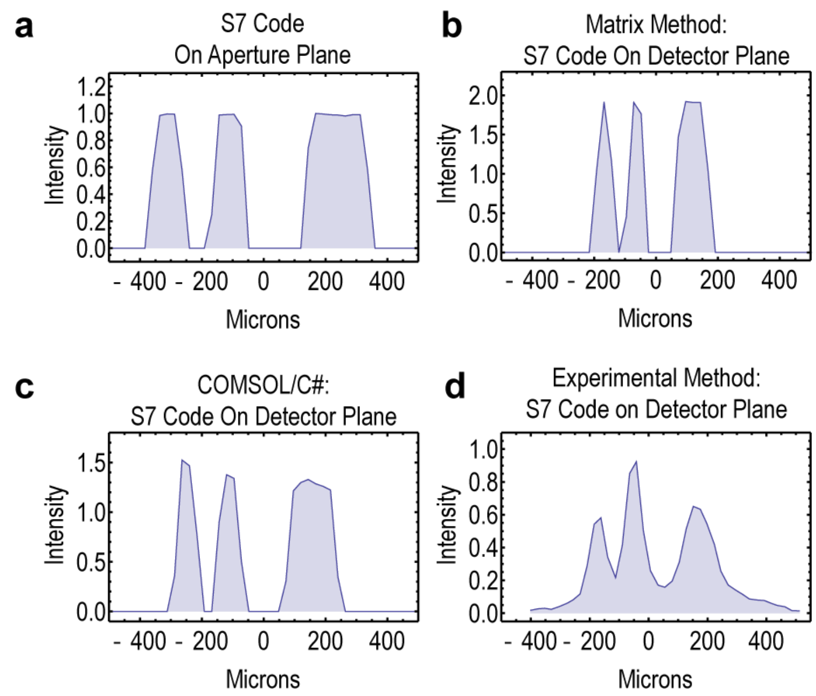


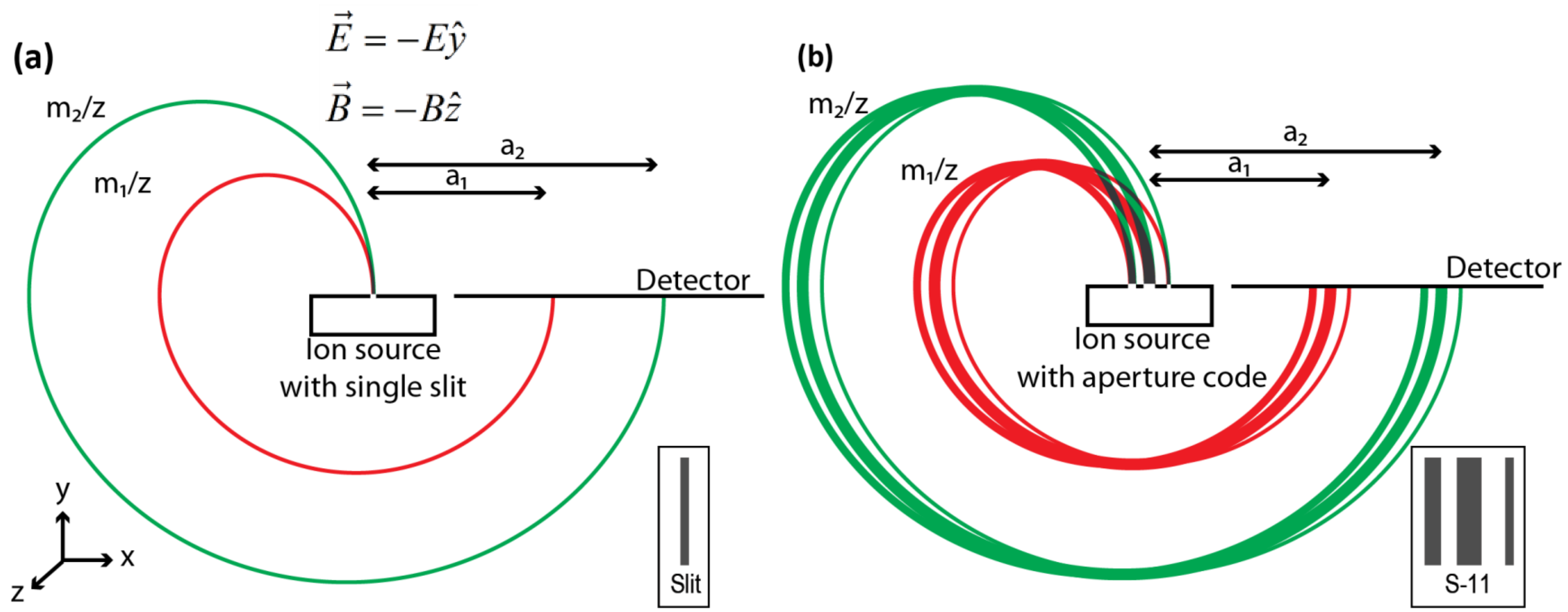
Image courtesy of OI Analytical, a Xylem Brand



- Matrix method shows excellent pattern mapping with demagnification
- COMSOL/particle tracing shows good pattern mapping with similar demagnification and distortion of larger aperture patterns due to sector width
- Experiment showed transfer of pattern, however modifications are necessary to reduce the effects of fringing fields at the entrance and exit of the sectors.

Russell, Z. E.; DiDona, S. T.; Amsden, J. J.; Parker, C. B.; Kibelka, G.; Gehm, M. E.; Glass, J. T., Compatibility of Spatially Coded Apertures with a Miniature Mattauch-Herzog Mass Spectrograph. Journal of The American Society for Mass Spectrometry 2016, 27 (4), 578-584.

Cycloidal mass analyzer and spatial coding



The distance along this x-axis, known as the pitch, is described by the following equation:

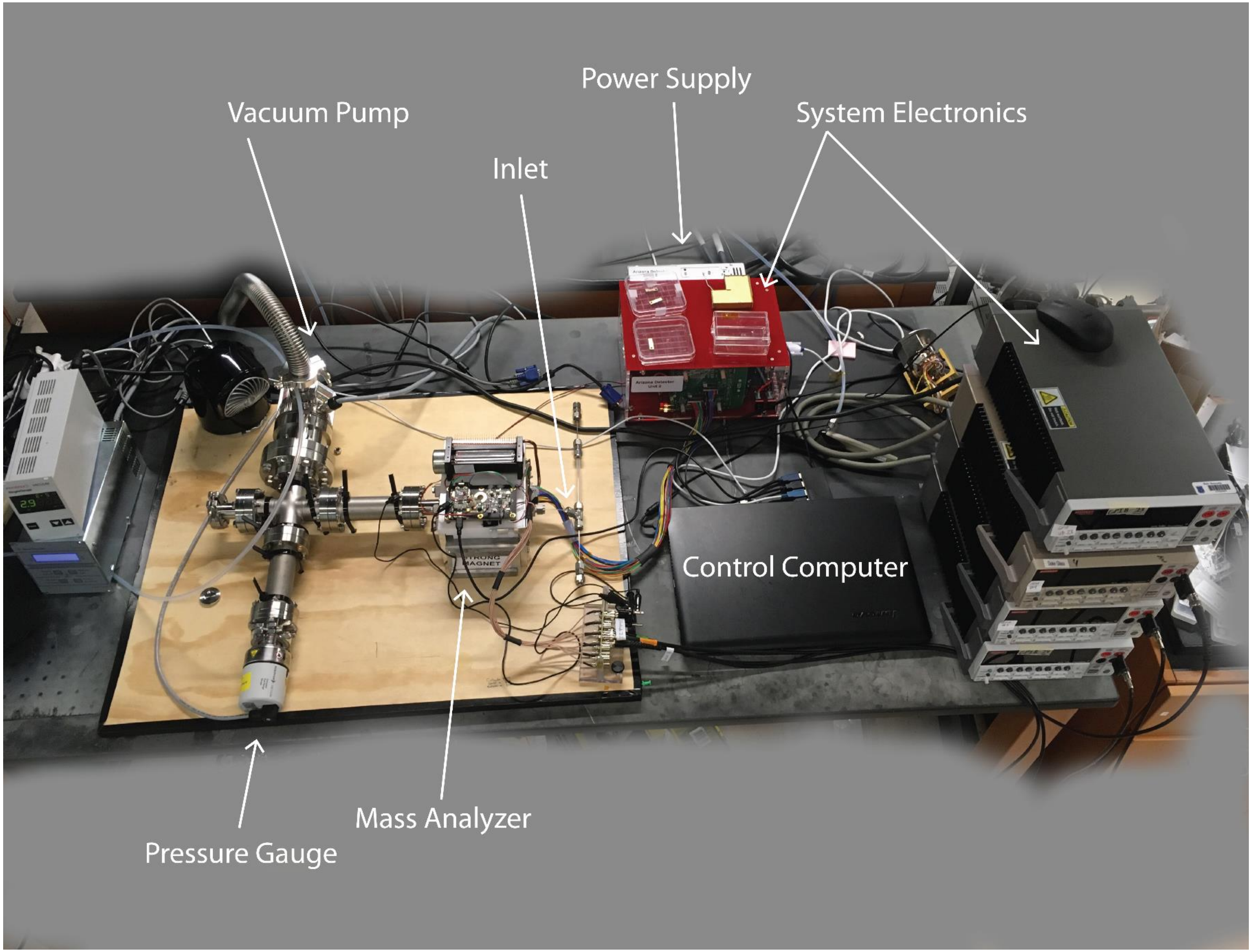
a_i = distance along x - axis
E = electric field strength
B = magnetic field strength
m_i = mass of ion
q = charge on ion
d = position of the aperture

$$a_i = \frac{m_i}{z}\frac{2\pi E}{B^2}$$

Compatible with aperture coding!

Bleakney, W.; Hipple, J. A., Jr., A New Mass Spectrometer with Improved Focusing Properties. Physical Review 1938, 53 (7), 521-529.
Amsden, J.J., Gehm, M.E., Russell, Z.E., Chen, E.X., Dona, S.T.D., Wolter, S.D., Danell, R.M., Kibelka, G., Parker, C.B., Stoner, B.R., Brady, D.J., Glass, J.T.: Coded apertures in mass spectrometry. Annu. Rev. Anal. Chem. 10, 141-156 (2017).

CAMMS-ES Laboratory prototype



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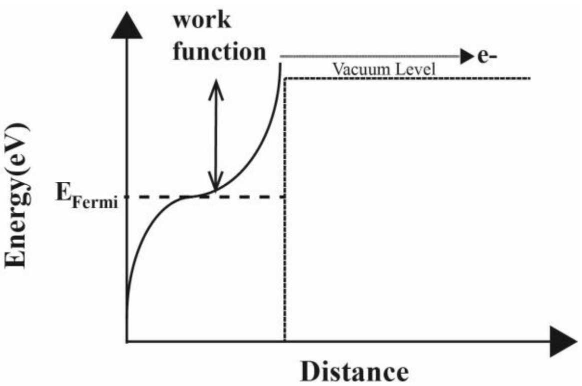
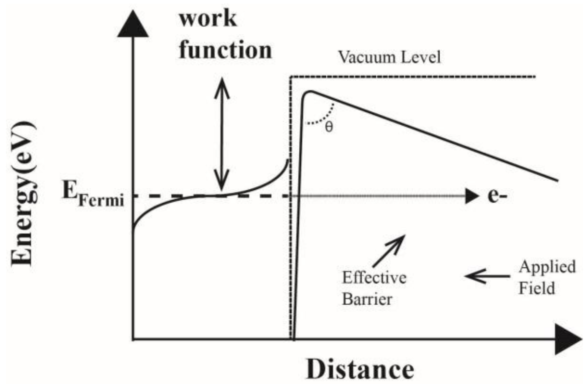
Thermionic electron emission vs Field emission: Why CNTs?

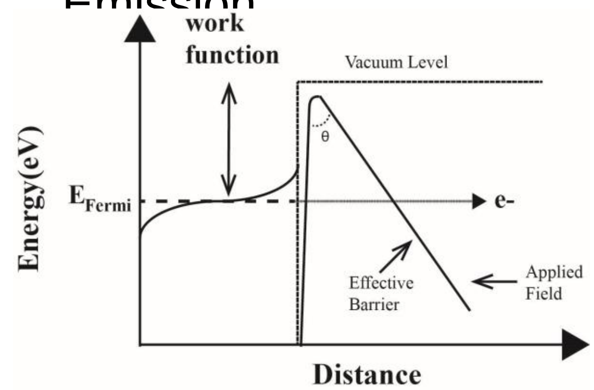
Thermionic Emission



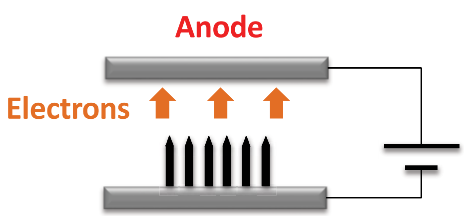
Planar Field Emission

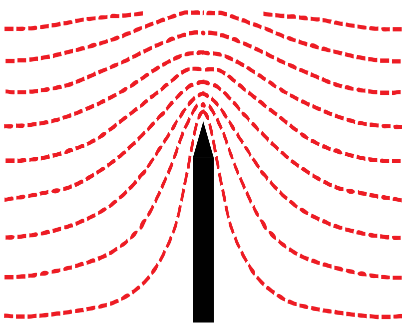


Micro-tip field Emission



	Thermionic	Field emission
Stability	Good	Fluctuating
Pulsing	No	Yes
Lifetime	Short (1 month, no pulsing possible)	Long (1 year of pulsed operation at operating pressure)
Power	High (10 W)	Low (<2 mW)





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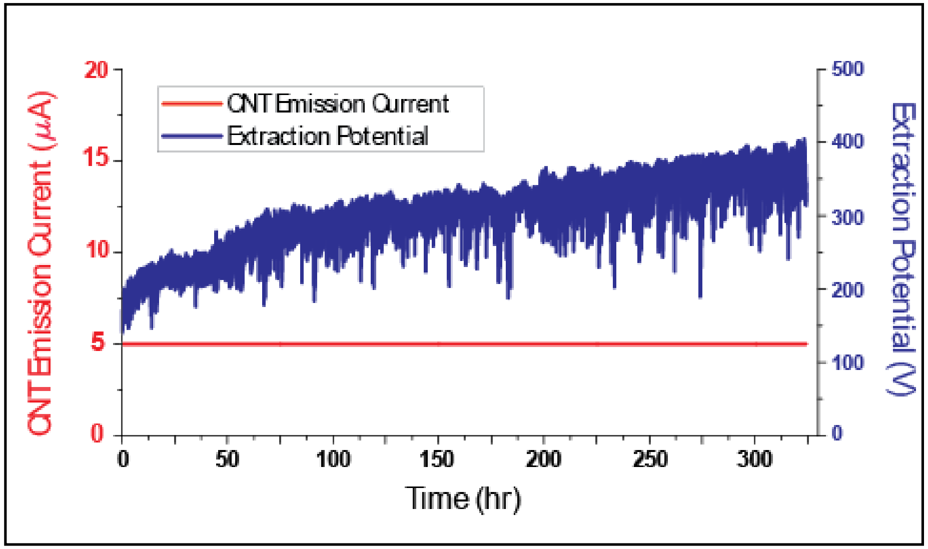
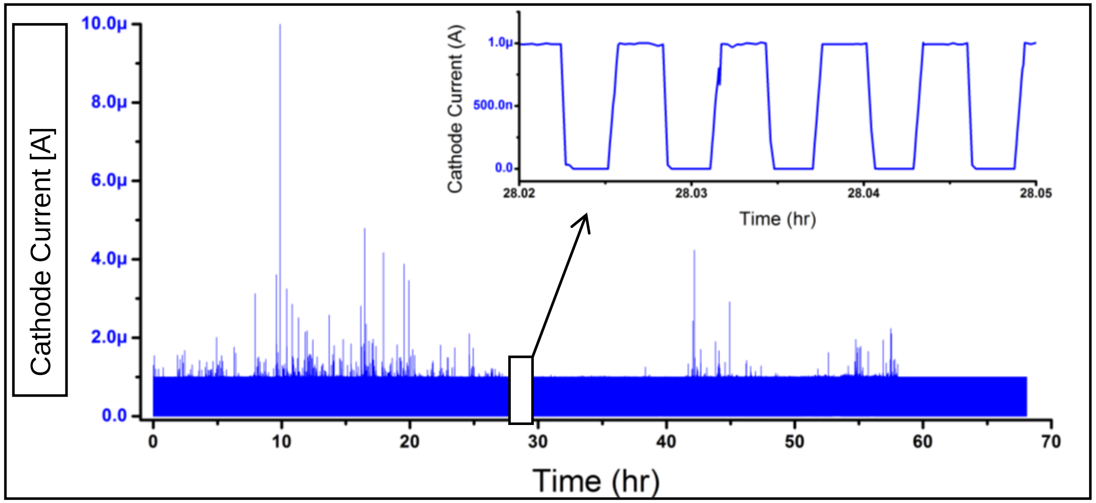
High pressure (1 x 10^{-4} Torr room air) lifetime



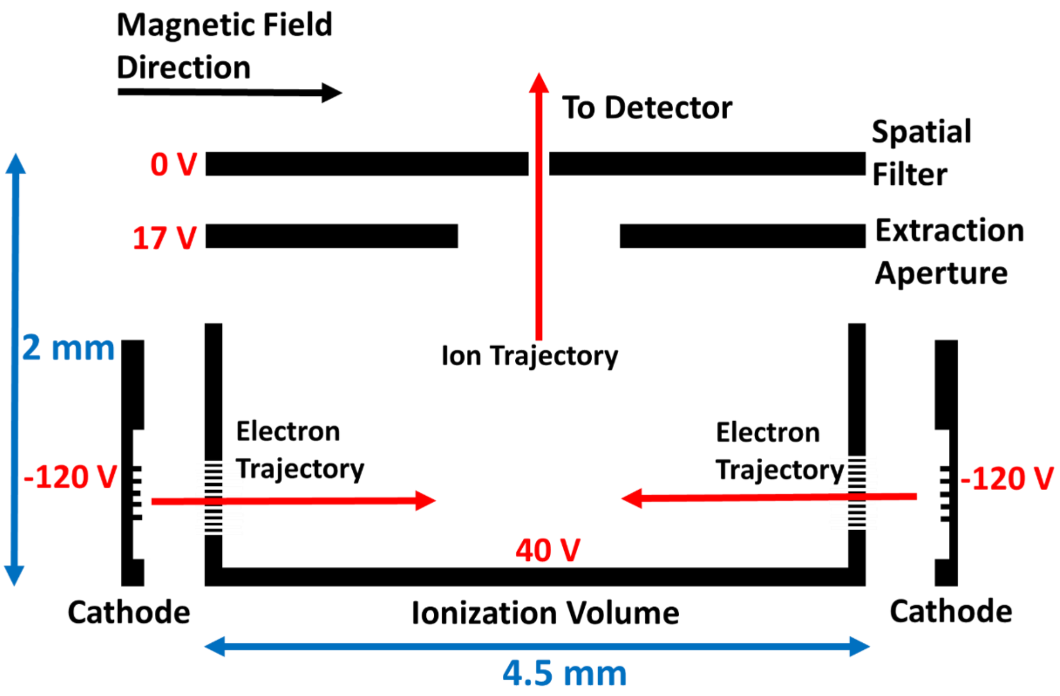
Continuous operation: >300 hours



Pulse Parameters:
- 2 sec ramp
- 10 sec ON
- 8 sec OFF
- Total: >11,000 pulses

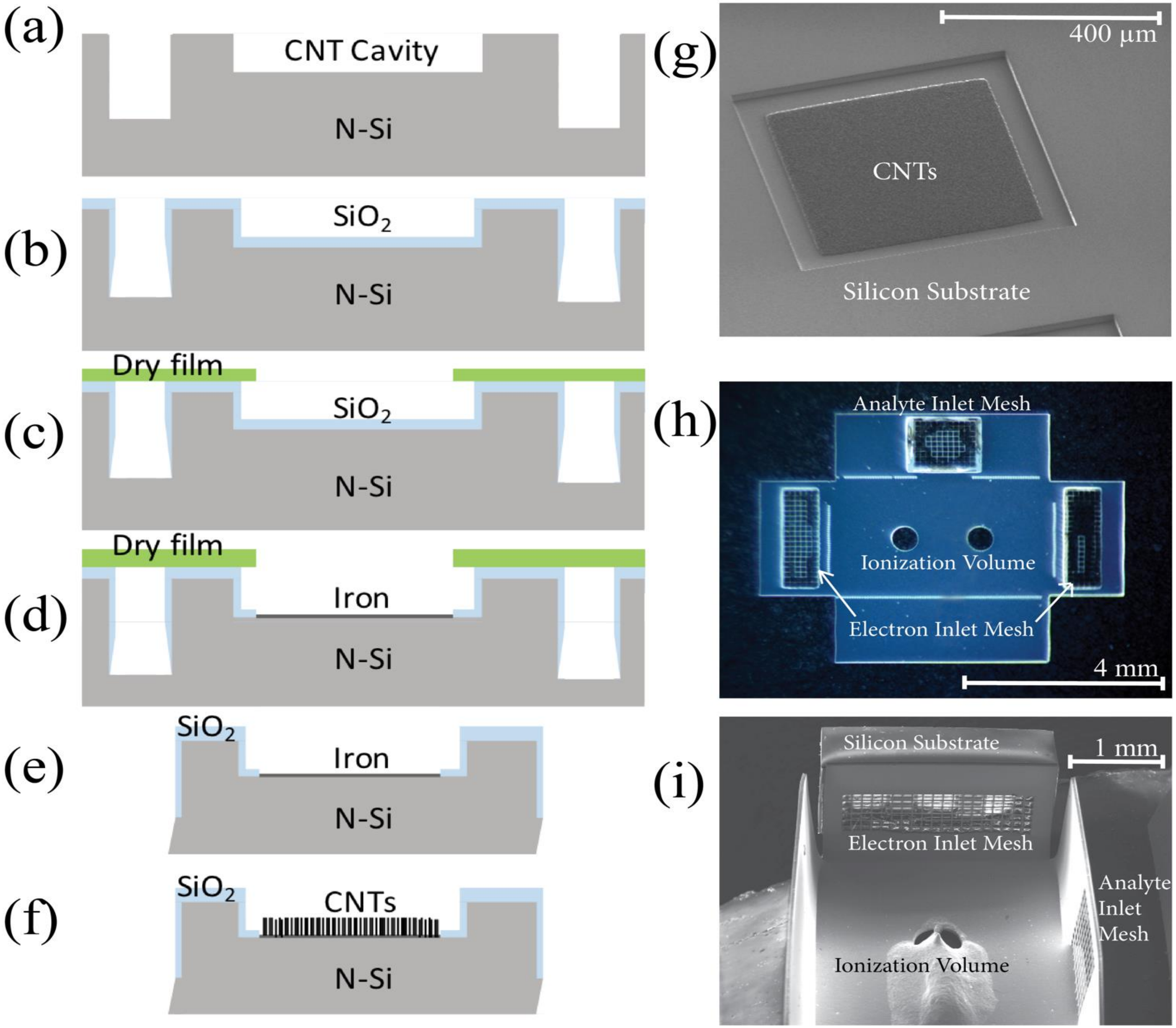
Evans-Nguyen T, Parker CB, Hammock C, Monica AH, Adams E, et al. 2011. Carbon nanotube electron ionization source for portable mass spectrometry. Anal. Chem. 83: 6527-31

Radauscher EJ et al. 2015. Chemical ionization mass spectrometry using carbon nanotube field emission electron sources. J. Am. Soc. Mass Spectr. 26: 1903-10



Vestal, M.L.: Methods of Ion Generation. Chemical Reviews 101, 361-376 (2001)

CNT field emission electron source and ionization volume



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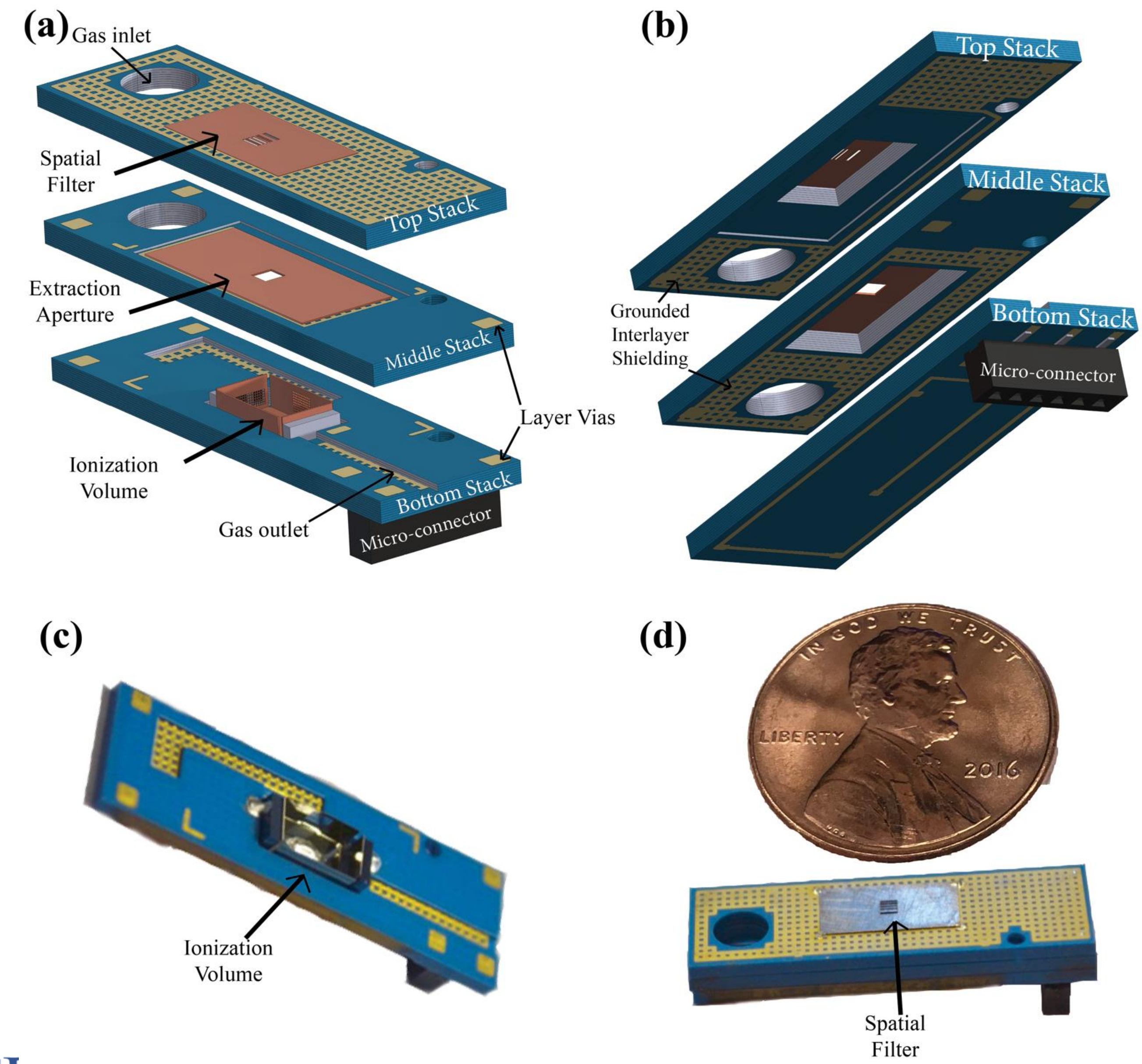

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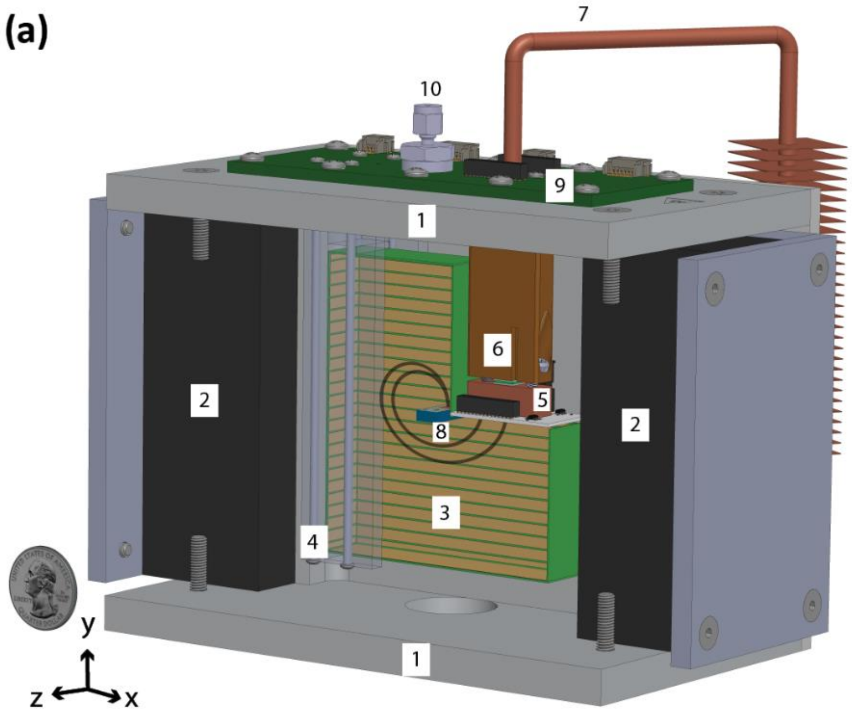
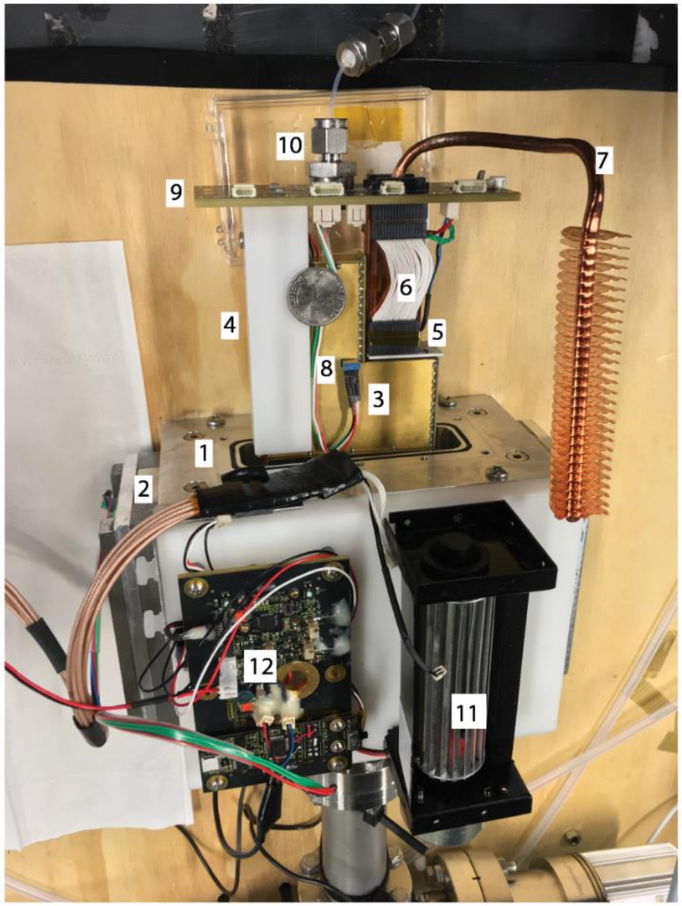


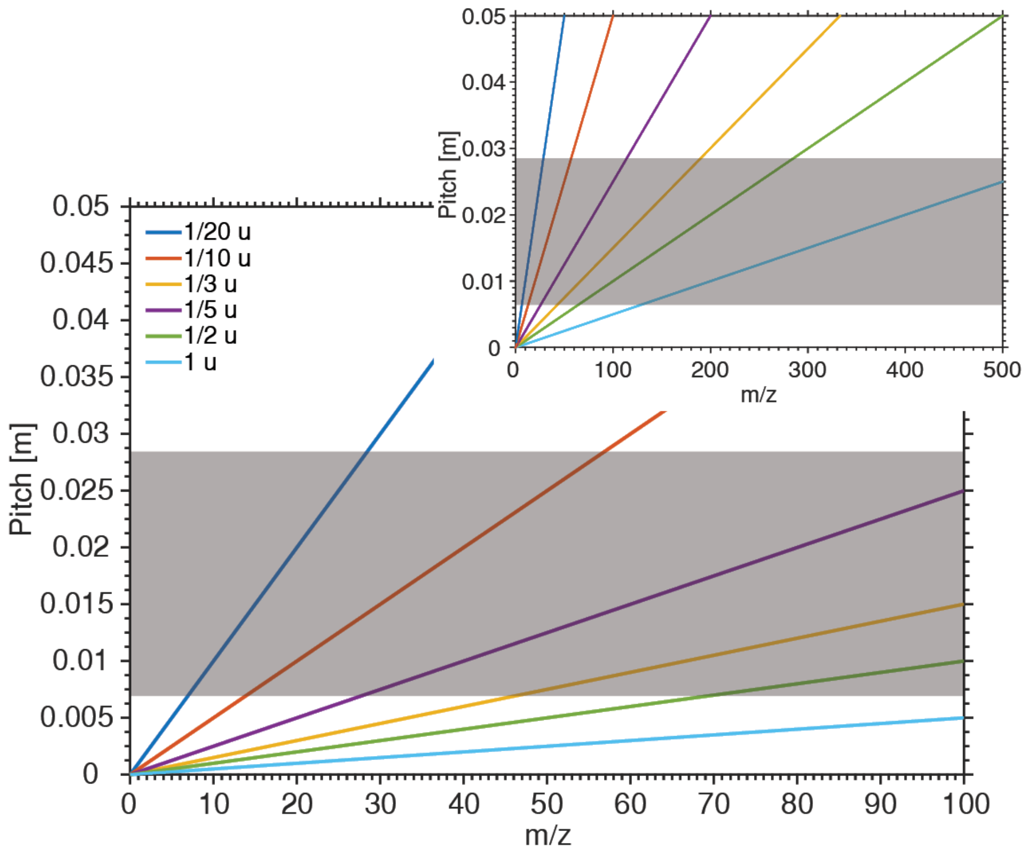
1. Vacuum manifold
2. NiFeB permanent magnet
3. Electric sector
4. Electric sector guide
5. Detector
6. Heat rejection block and thermoelectric device
7. Heat pipe
8. Ion source
9. PC Board vacuum feedthrough

(b)



10. Inlet feedthrough
11. Cross flow fan
12. Thermoelectric device and electric sector control

Mass range and resolution



$$a_i = \frac{m_i}{z} \frac{2\pi E}{B^2}$$

$$L = \frac{B^2 dz}{2\pi E}$$

$$R = \frac{sL}{d} = \frac{szB^2}{2\pi E}$$

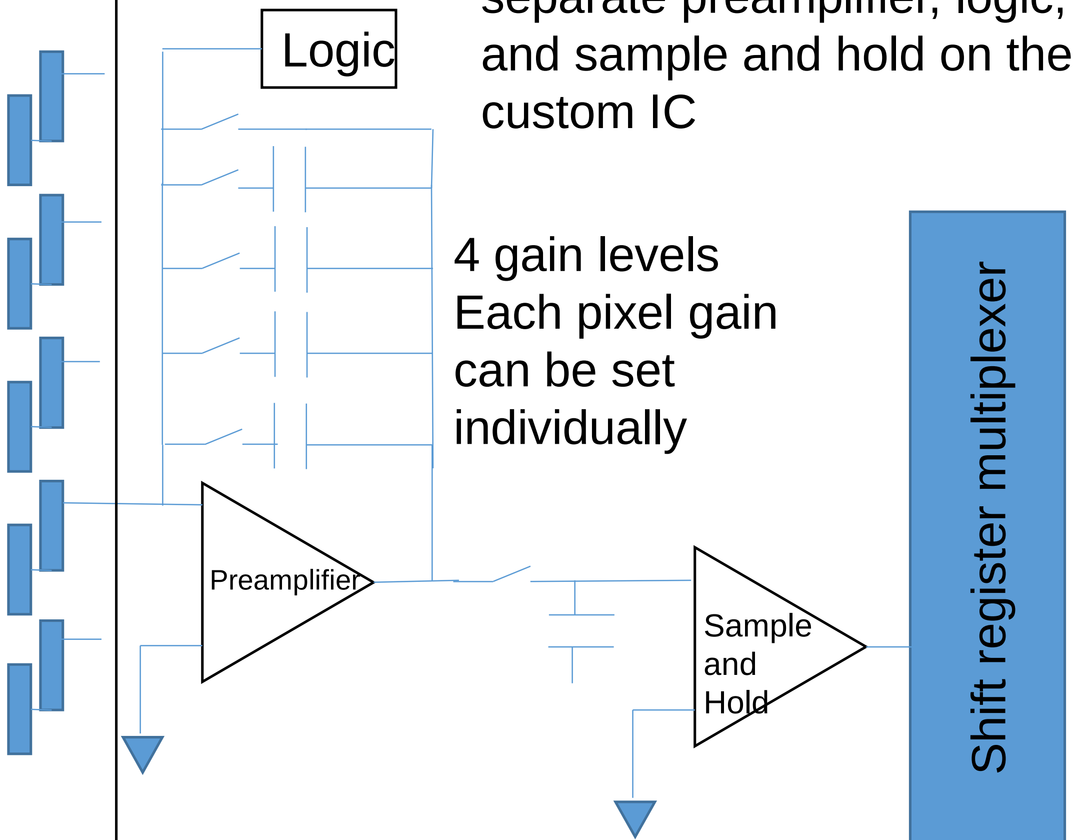
$$a = \frac{ms}{R}$$

- a = pitch
- L = mass range
- R = resolving power
- d = detector length
- s = detector pixel size
- B = magnetic field
- E = Electric field
- m = mass
- z = charge

The mass range and resolving power of CAMMS-ES depends on the electric and magnetic field magnitudes and the width, pixel size, and position of the detector relative to the ion source.

Capacitive transimpedance amplifier detector array

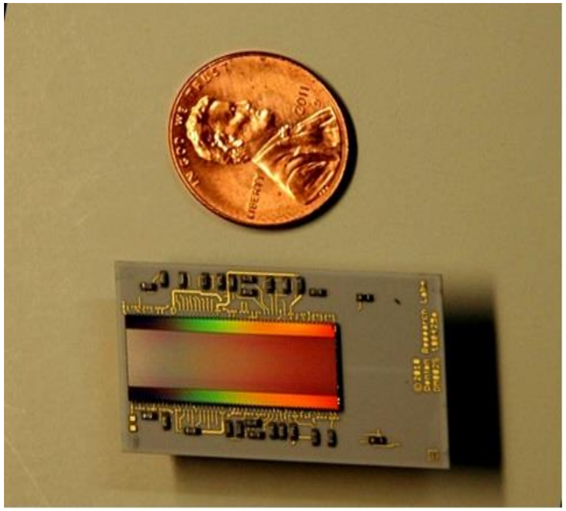
Detector fingers (multiple layers via photolithography for 100% fill factor)



Each detector finger has a separate preamplifier, logic, and sample and hold on the custom IC

4 gain levels
Each pixel gain can be set individually

Custom CMOS integrated circuit
3.3 V, 0.35 µm process

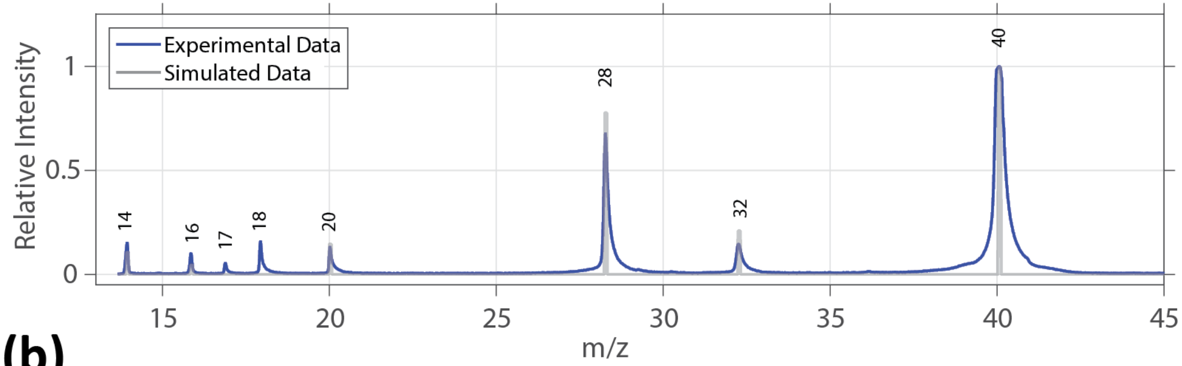


Felton, J. A., G. D. Schilling, S. J. Ray, R. P. Sperline, M. B. Denton, C. J. Barinaga, D. W. Koppenaal and G. M. Hieftje (2011). "Evaluation of a fourth-generation focal plane camera for use in plasma-source mass spectrometry." Journal of Analytical Atomic Spectrometry 26(2): 300-304.

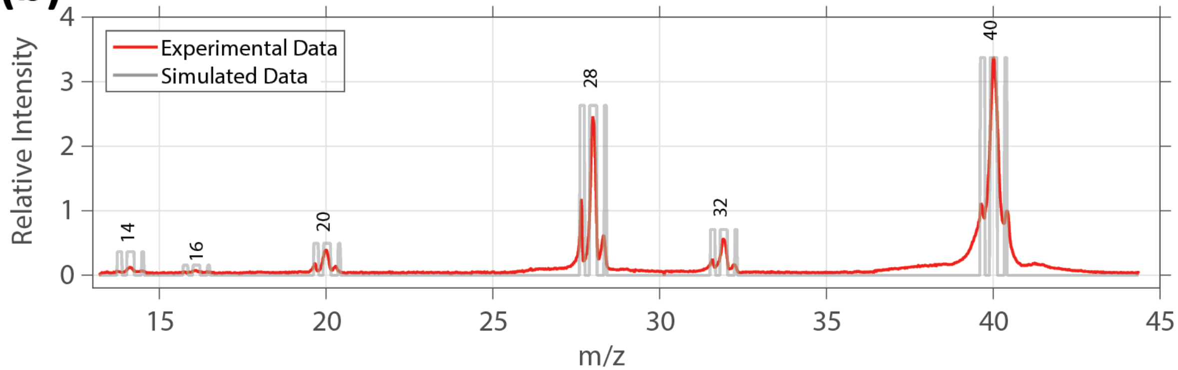
Detection limit ~5 ions, dynamic range 10^{11}: Sensitivity approaching Multichannel plate and dynamic range of a Faraday cup

Solves the sensitivity and dynamic range tradeoff in conventional detectors

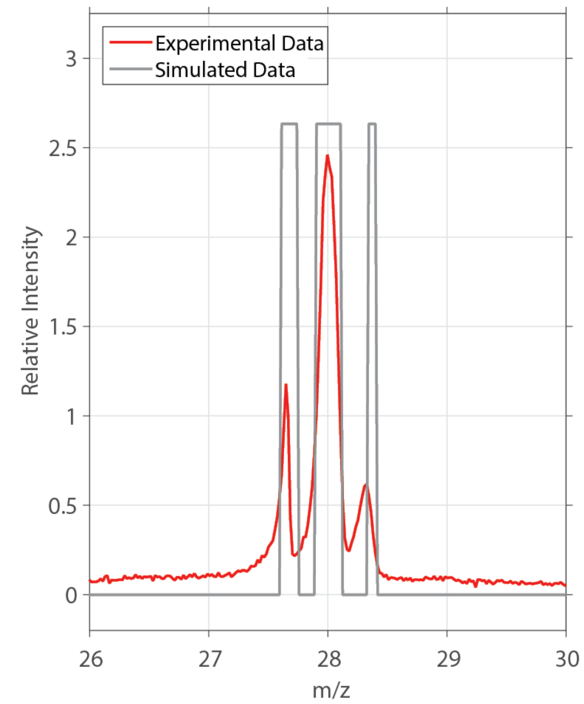
(a) Mass spectrum of a mix of 50% argon and 50% dry air using a 50 µm slit



(b)



(c)



Coded mass spectrum of a mix of 50% pure argon and 50% dry air using a 50 µm element size

Imaging not ideal due to alignment, field uniformity

Simple calibration/reconstruction

- Previously, a sophisticated calibration process was required as field nonuniformity and other system imperfections limited the 'perfect focusing' performance of the instrument
- With the current generation, performance is sufficiently good that we can use a very simple calibration process to validate operation (we ultimately *will* want an advanced approach to maximize performance; but will do that for next prototype)
- Remember that with perfect focusing, the measurement can be written as the convolution of the system response with the input spectrum

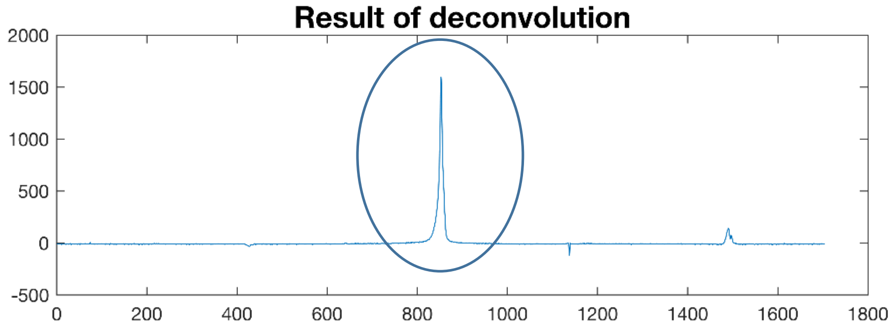
$$\mathbf{m} = \mathbf{r} * \mathbf{s}$$

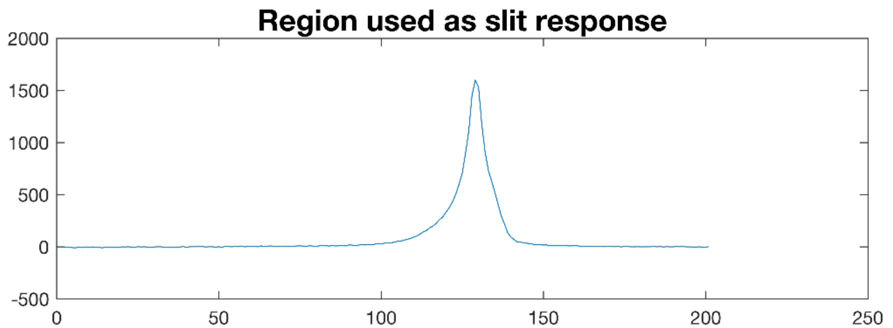
- We can estimate the system response (*calibrate the system*) by deconvolving the true spectrum from the acquired measurements

$$\hat{\mathbf{r}} = \mathcal{F}^{-1}\left[\mathcal{F}\left[\mathbf{m}\right] / \mathcal{F}\left[\mathbf{s}_{\mathrm{NIST}}\right]\right]$$

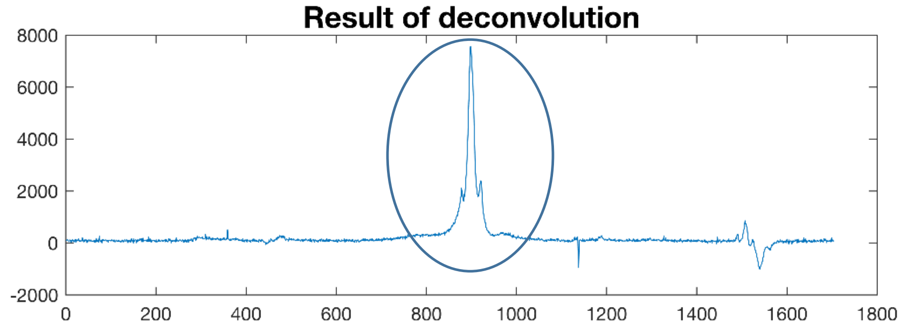
Result of calibration process

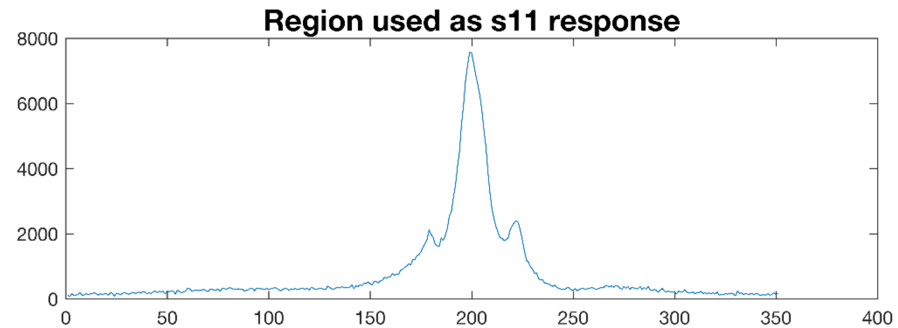
Slit aperture





S11 aperture





- Extract central region (other are artifacts resulting from system imperfections) as estimated system response. Results have expected structure
- Spectral reconstruction then performed by deconvolving acquired measurements by estimate of system response $\hat{\mathbf{s}} = \mathcal{F}^{-1}\left[\mathcal{F}[\mathbf{m}] / \mathcal{F}[\hat{\mathbf{r}}]\right]$

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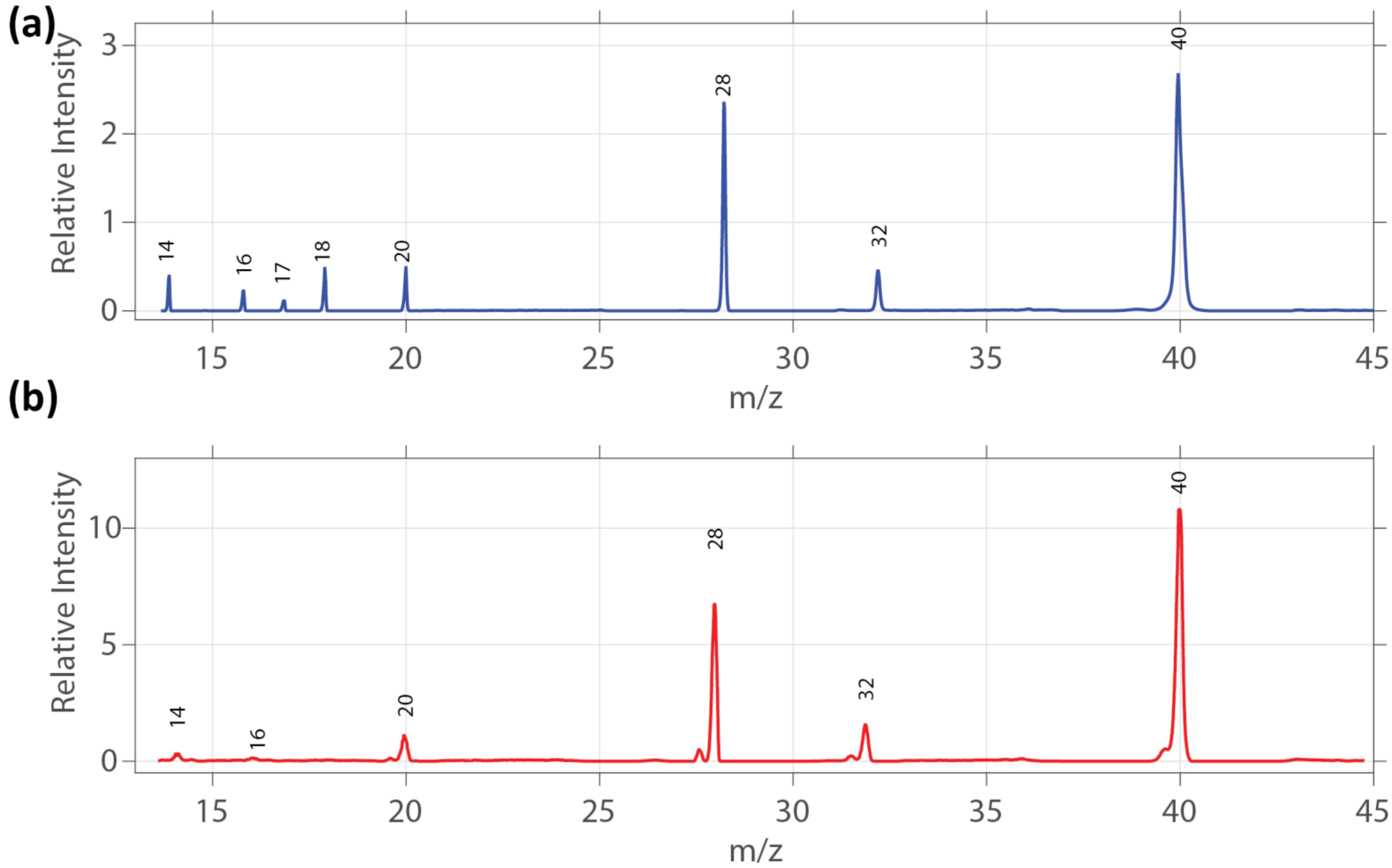
Spectral reconstruction



>10x increase in signal and improved resolution

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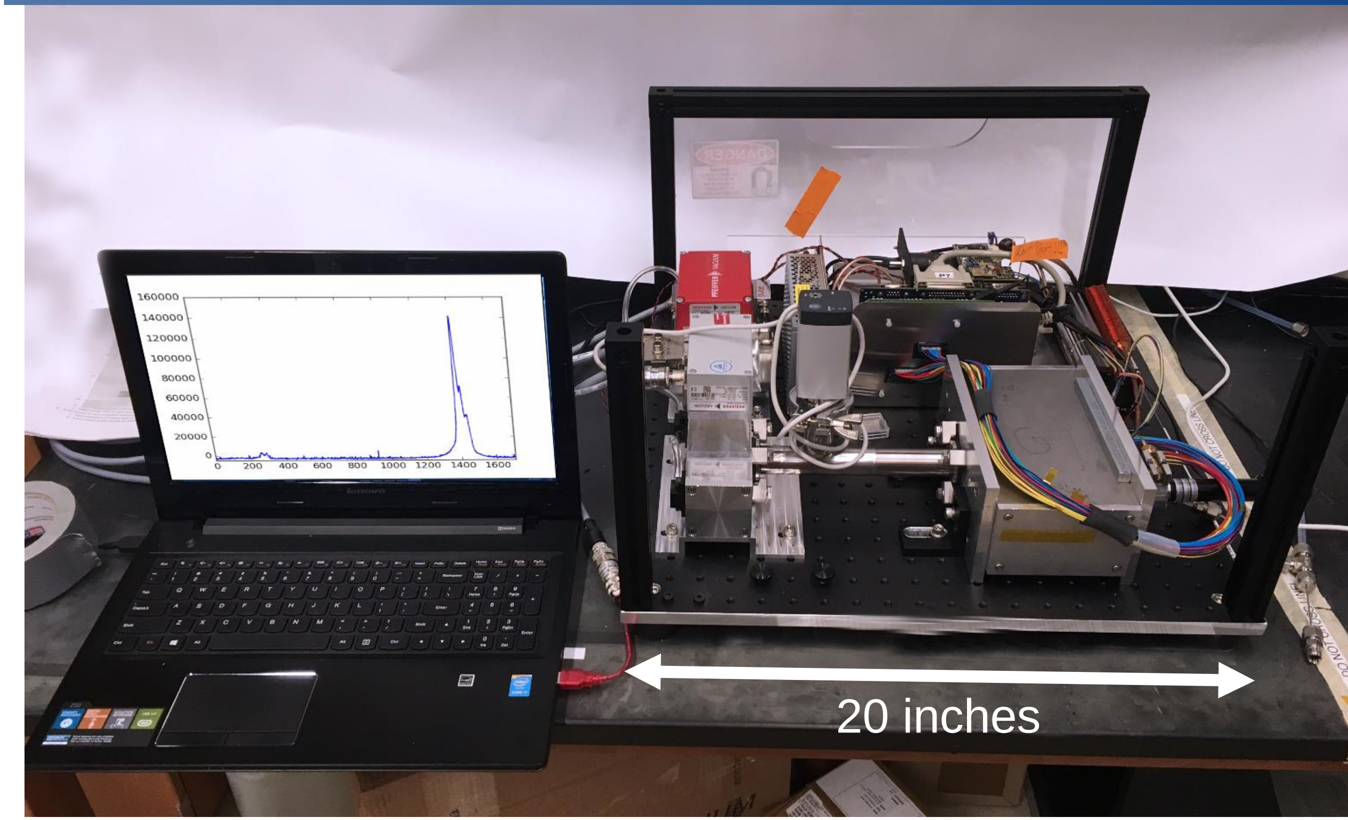
Performance Summary

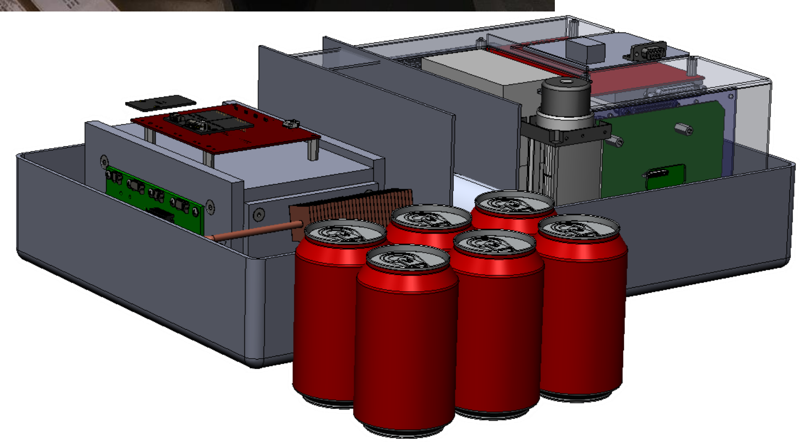
Instrument	Resolving power (FWHM)	Throughput gain
Ideal cycloid with 50 µm slit	0.05 amu	n/a
Lab prototype with 50 µm slit	0.31 amu	1
Lab prototype with Reconstructed 50 µm slit	0.18 amu	1.67
Lab prototype with Reconstructed S-11 coded aperture	0.11 amu	10.4

Mass spectrometer miniaturization at Duke, U of A, and RTI



Current Prototype

Future Prototype



Funded in part by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy, under Award Number DE-AR0000546. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Support from DARPA INVEST Award -1-340-021530652548L

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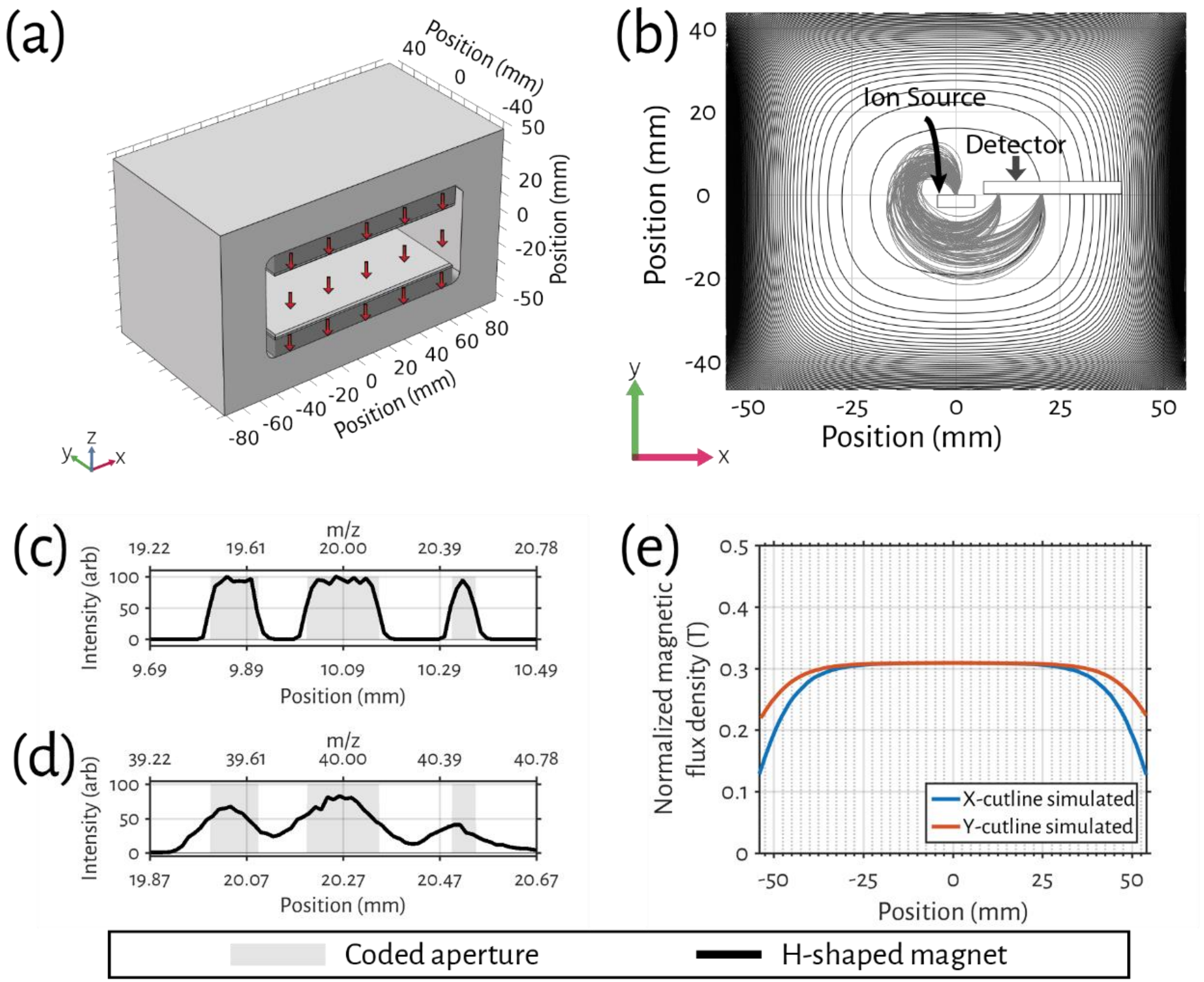
Traditional H-shaped magnet assembly



Field not of sufficient uniformity for coded aperture imaging

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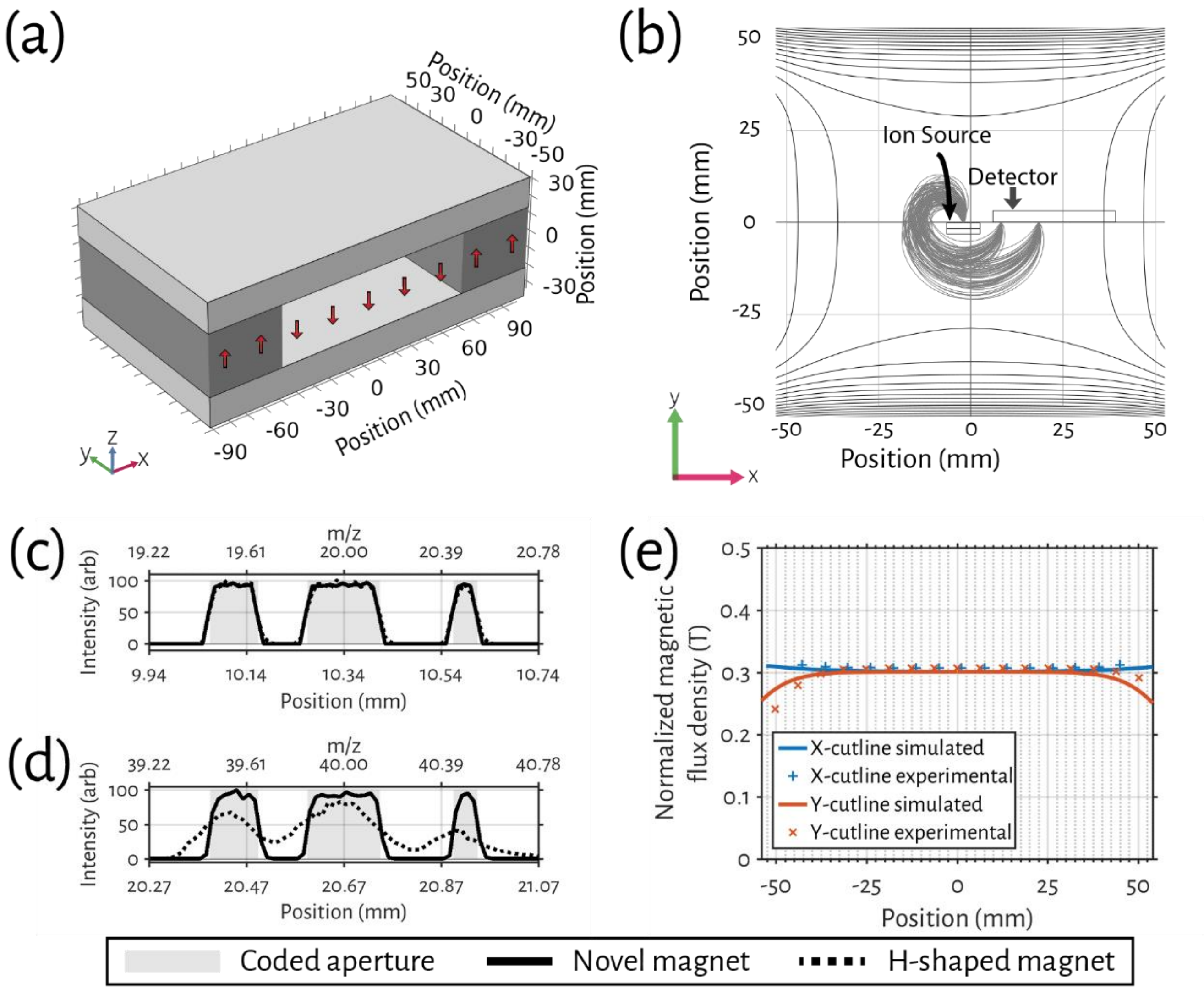
Our new magnet assembly



Field varies by <1% along the ion trajectories = good aperture imaging

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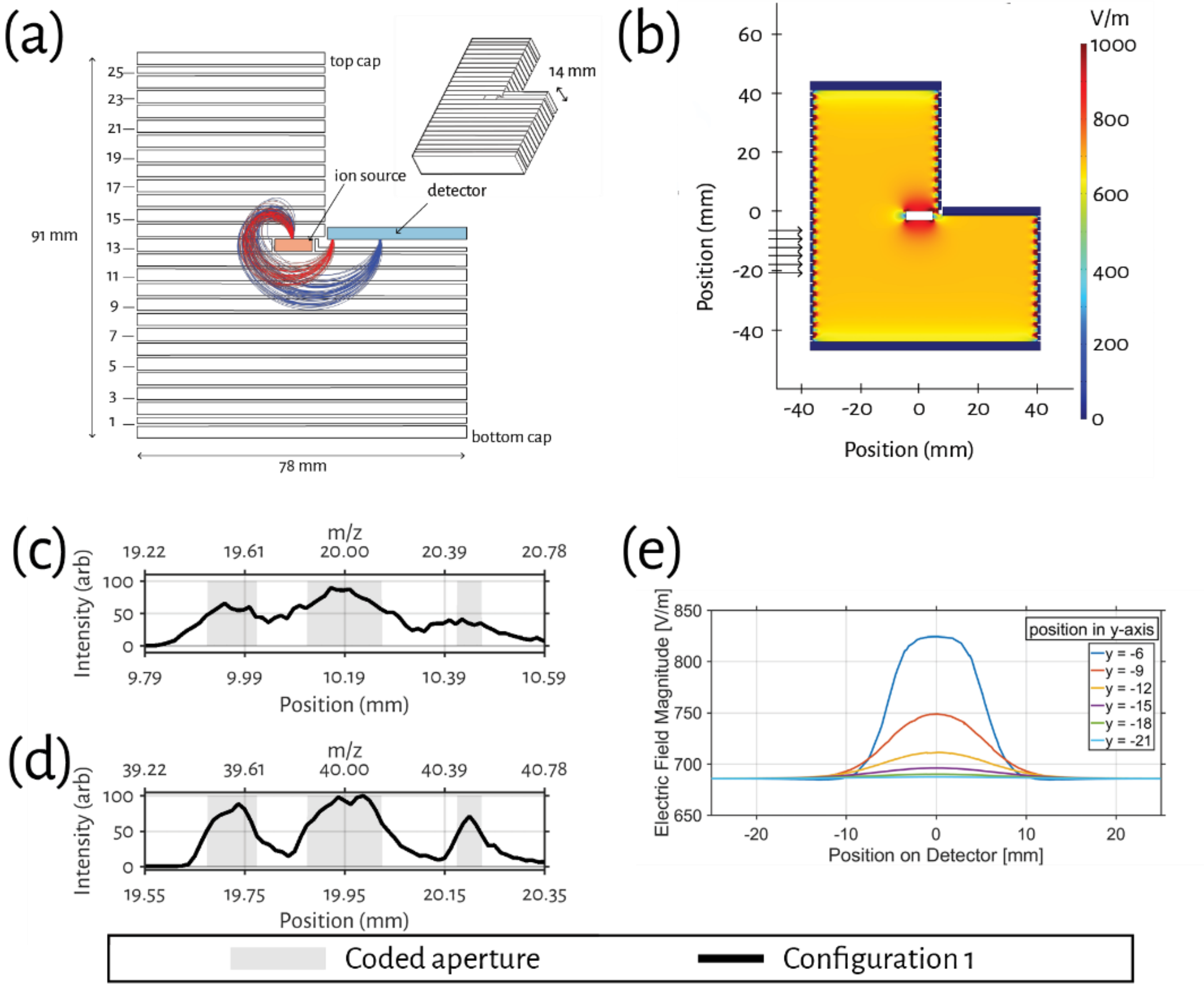

Relatively poor imaging quality due to field non uniformity around the ion source

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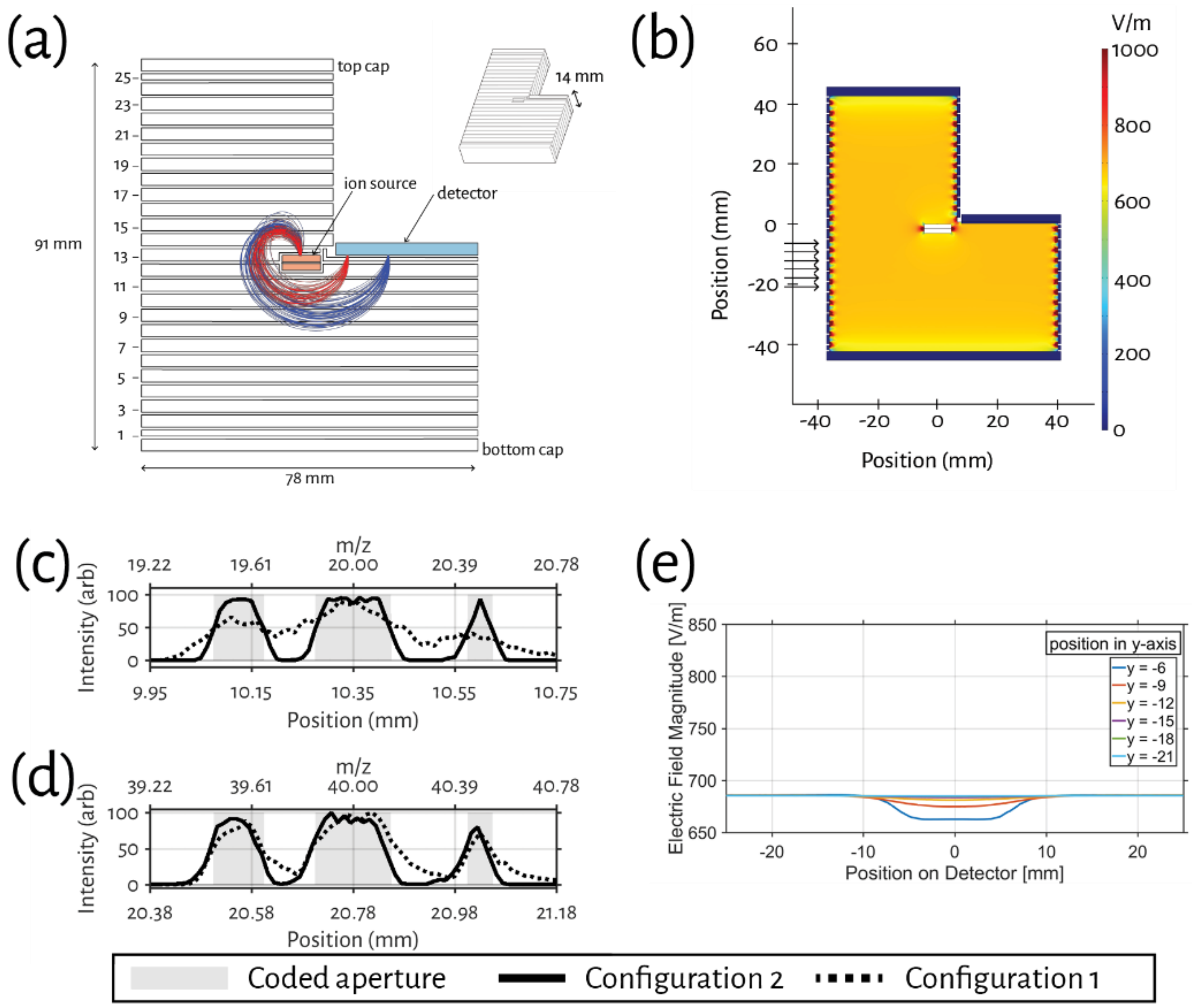
Improved electric sector configuration



Placing the ion source between adjacent electrodes and making the top and bottom half different potentials improves field uniformity and aperture imaging

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