Use of computational sensing techniques to improve the performance of mass spectrometers in harsh environments

13th Workshop on Harsh-Environment Mass Spectrometry

September 16–19, 2019, Myrtle Beach, South Carolina

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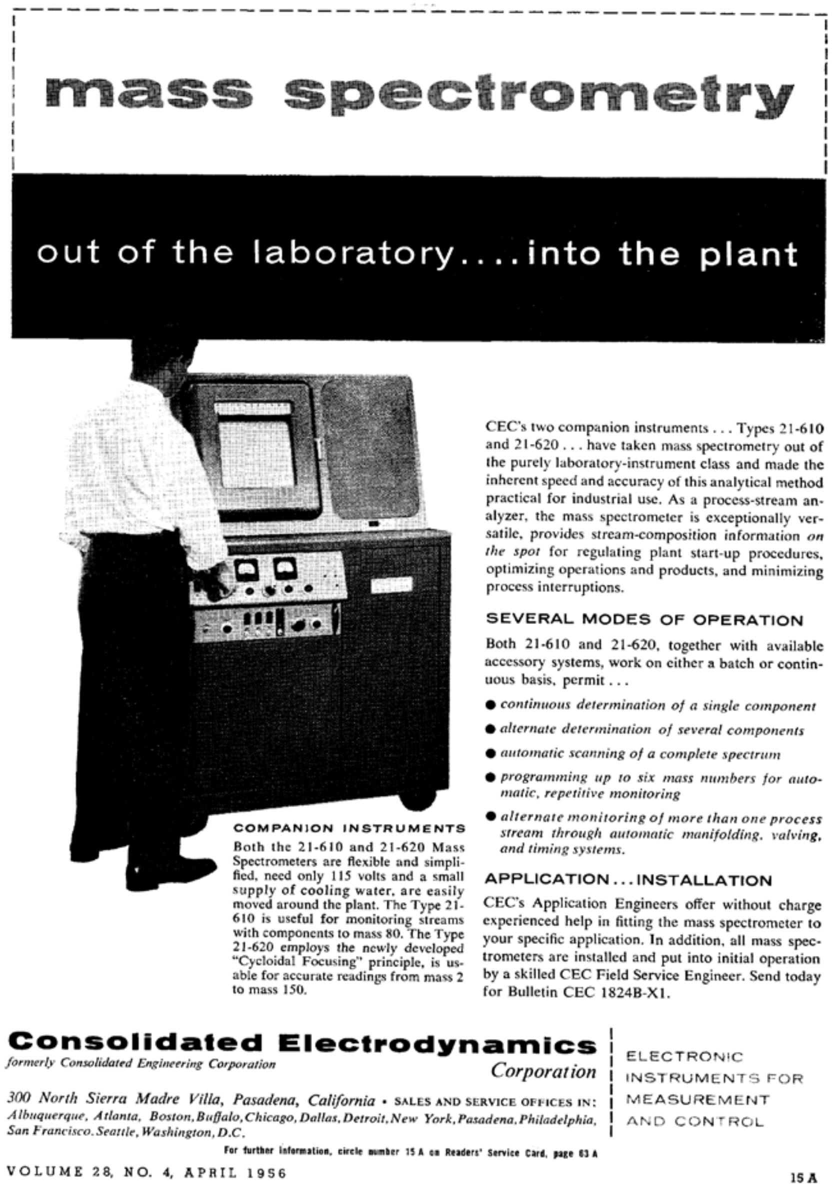
Mass Spectrometer Miniaturization



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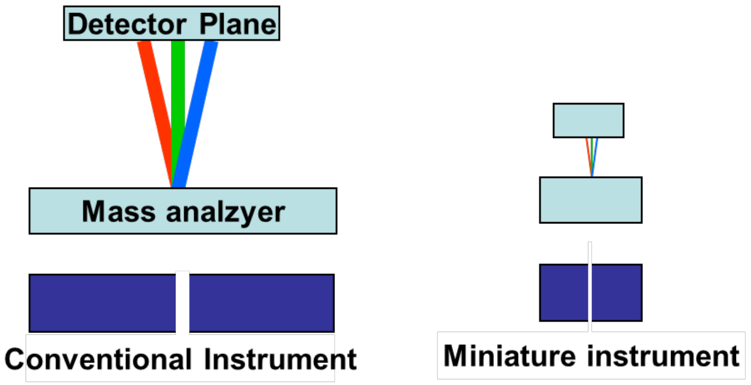
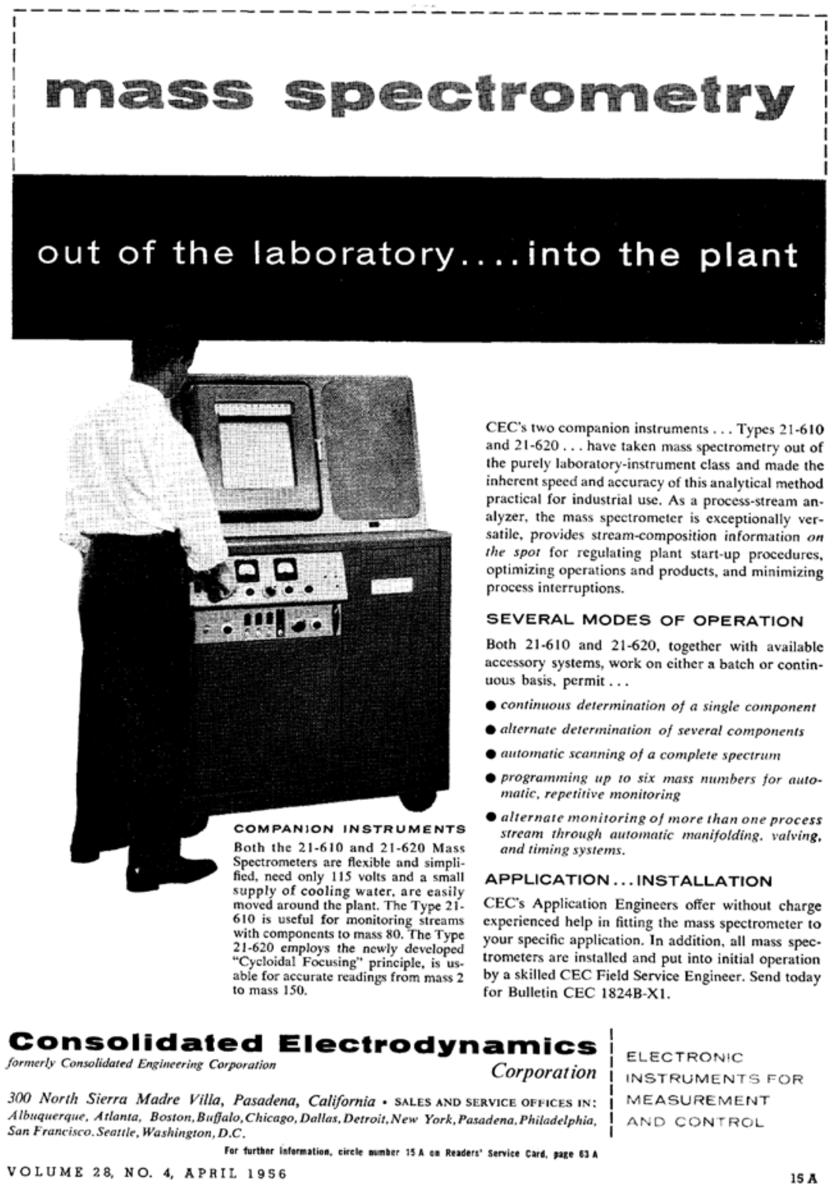
- People have been trying to make high performance small mass spectrometers for over 60 years!
- Limited success because:
  1. Throughput vs. resolution tradeoff during miniaturization
  2. High power requirements
  3. Limited detector technologies



Reduced throughput for same resolution

Mass Spectrometer Miniaturization



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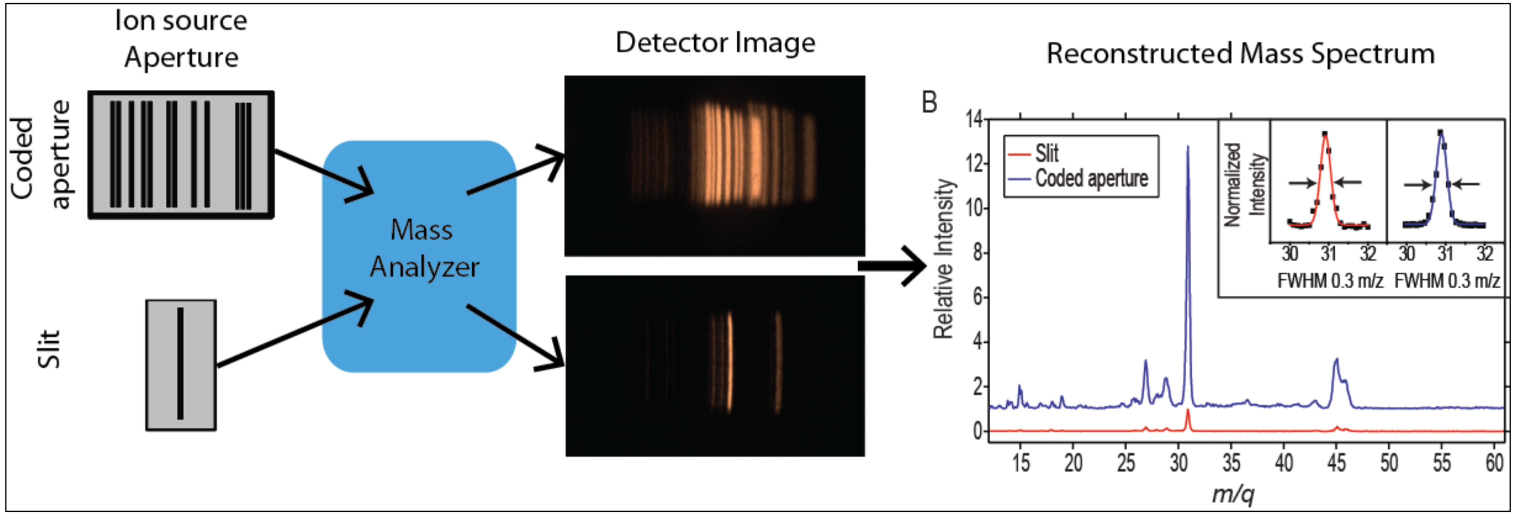
- ***Computational sensing combined with microfabrication can lead to high performance miniature instruments***

"Bring MS out of the laboratory and into the field"

Four Miniaturization Enabling Technologies

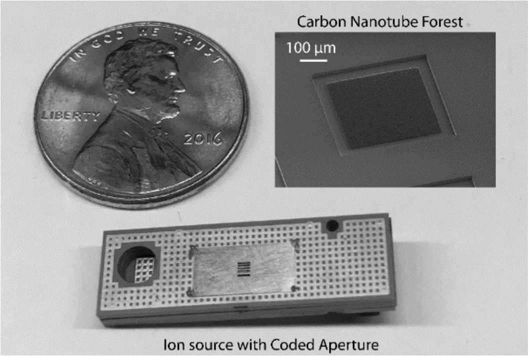
1) Aperture Coding: increased throughput, no loss in resolution

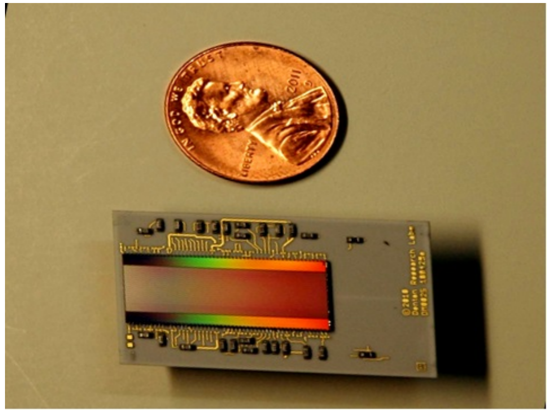


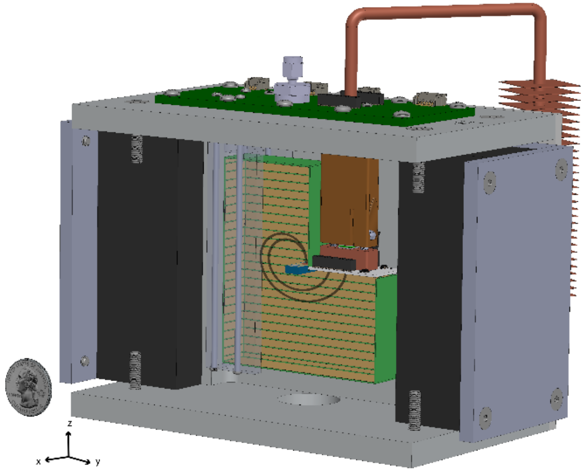
2) Microfabricated CNT field emission ion source

3) Focal plane array detector

4) Cycloidal mass analyzer







See poster by Raul Vyas
For more info on CNTs

Outline

- What is computational sensing and aperture coding?
- Why use a cycloidal mass analyzer with aperture coding?
- What is the performance of CAMMS-ES (Coded aperture miniature mass spectrometer for environmental sensing)?

What is Computational Sensing?

- Measurements are a convolution of the actual spectrum and the system response

$$m = r * s$$

Conventional Sensor

- Make design choices so that the instrument response = δ

$$m \approx \delta * s$$

$$m \approx s$$

Computational Sensor

- Design the system response to maximize parameters of interest

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

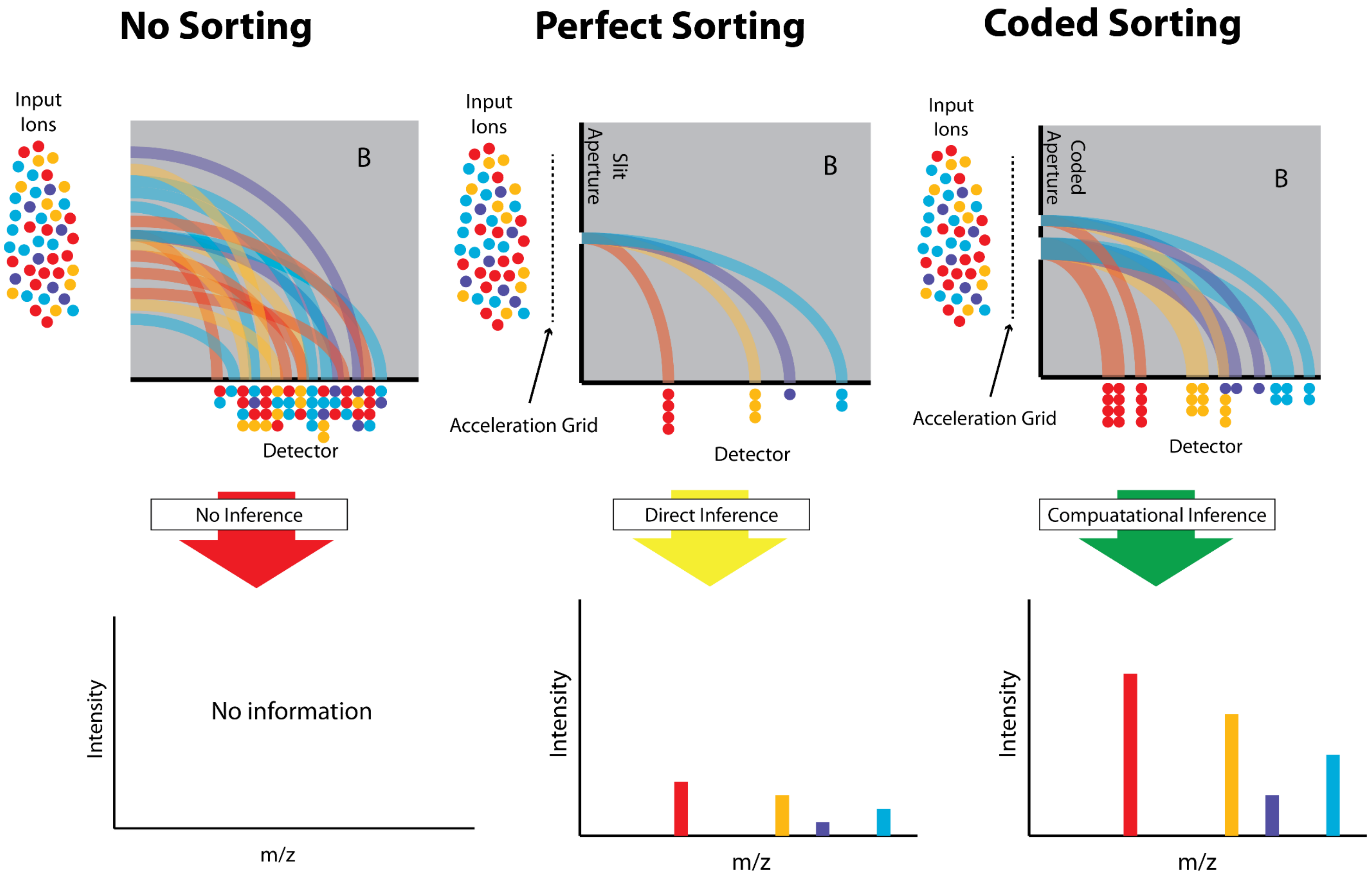
- Deconvolve the system response from the measurements to estimate the spectrum

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

Design choices in conventional instruments actually limit system performance

Availability of cheap fast computing power enables improved system performance (and miniaturization)

Computational Sensing and aperture coding



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)

Outline

- What is computational sensing and aperture coding?
- Why use a cycloidal mass analyzer with aperture coding?
- What is the performance of CAMMS-ES?

Cycloidal mass analyzer and perfect focusing

APRIL 1, 1938 PHYSICAL REVIEW VOLUME 53

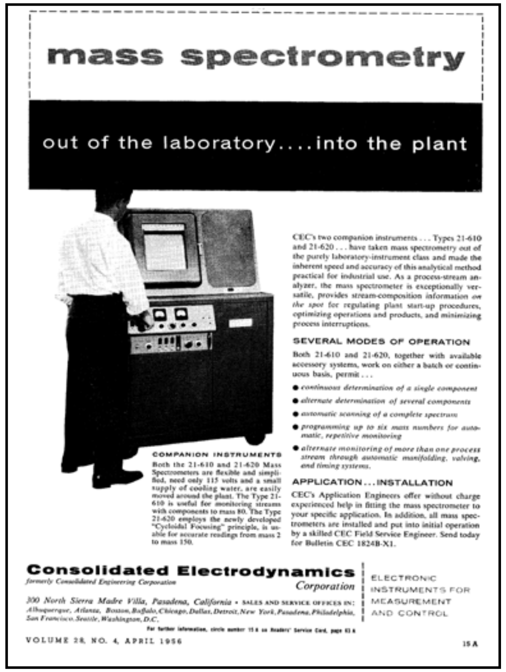
A New Mass Spectrometer with Improved Focusing Properties

WALKER BLEAKNEY AND JOHN A. HIPPLE, JR.
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey

(Received February 7, 1938)

The use of crossed electric and magnetic fields for a mass spectrometer is discussed. It is shown that this arrangement has perfect focusing properties; the focusing depends only on the m/e of the ion selected, and not on the velocity or direction of the charged particles entering the analyzer. The projection of the path in the plane perpendicular to the magnetic field is a trochoid. The theory necessary for the design of the apparatus is developed in some detail. A method of drawing the trochoids is described as well as a chart which is a great help in rapidly correlating the many variables. It is shown that there are two types of path to be considered, the curtate and the prolate. The former was employed in the first model constructed and gave encouraging results in spite of some structural difficulties encountered. The second apparatus was the prolate type and worked exceptionally well. Some typical mass spectra are shown. It was found that a distribution in energy amounting to 50 percent of the potential accelerating the ions had no effect on the resolution.

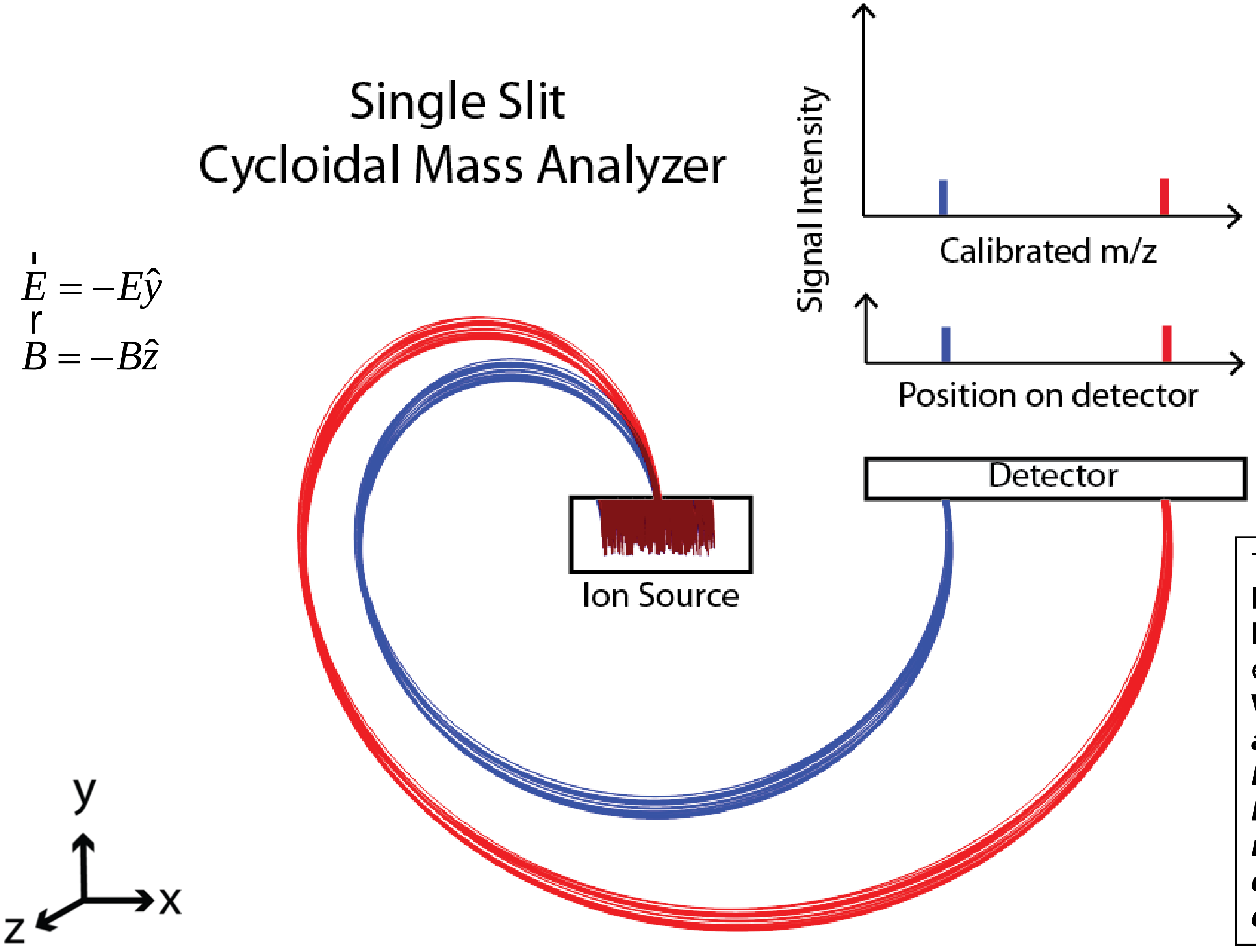
- "…this arrangement has perfect focusing properties."
- Cycloidal mass analyzers were utilized in the 1950's and 1960's
- Need array detector to fully realize the potential of the cycloidal mass analyzer



Single Slit Cycloidal Mass Analyzer

$\vec{E} = -E\hat{y}$

$\vec{B} = -B\hat{z}$

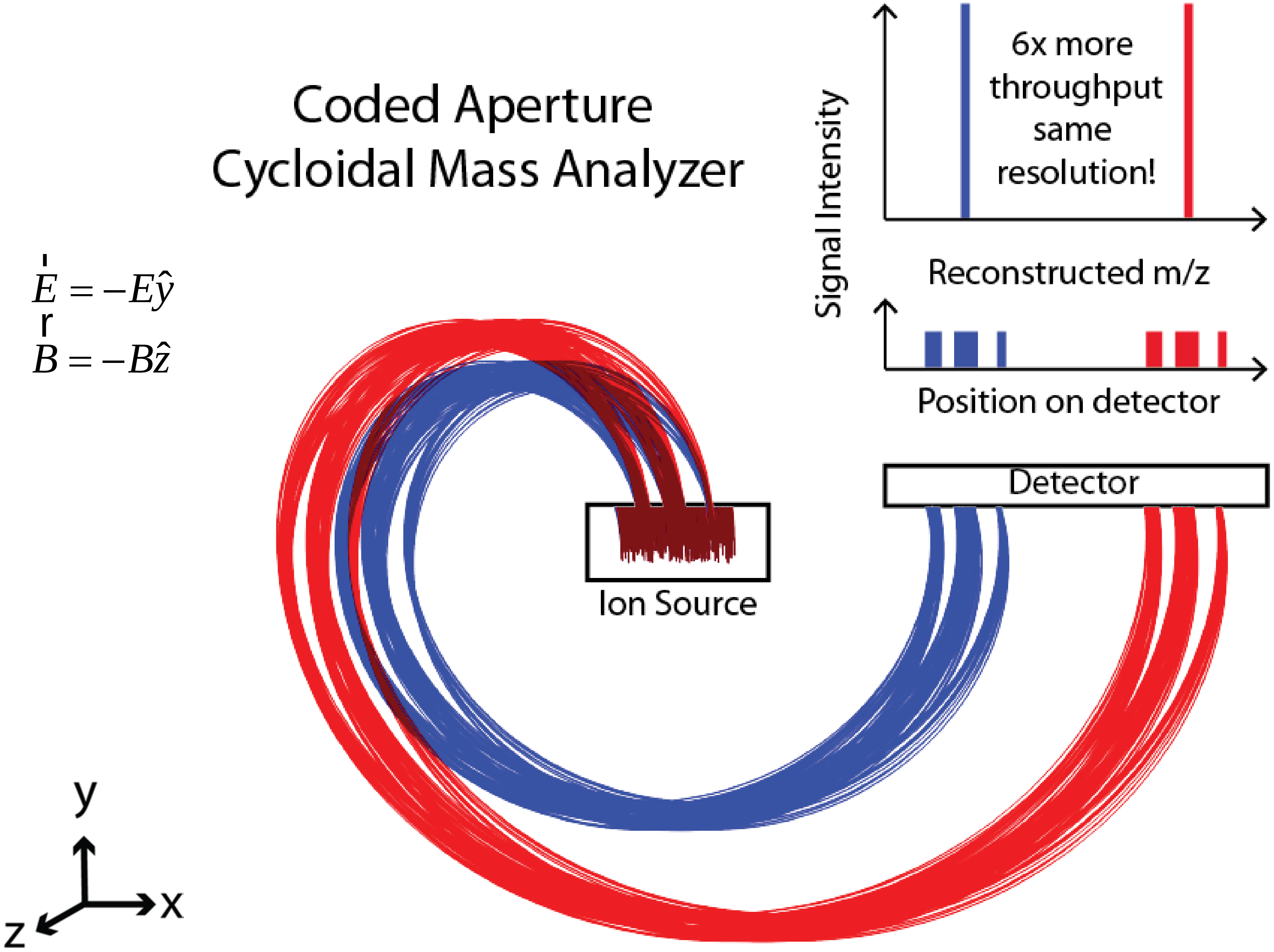


$$a_i = \frac{m_i}{z}\frac{2\pi E}{B^2}$$

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

Where:

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*



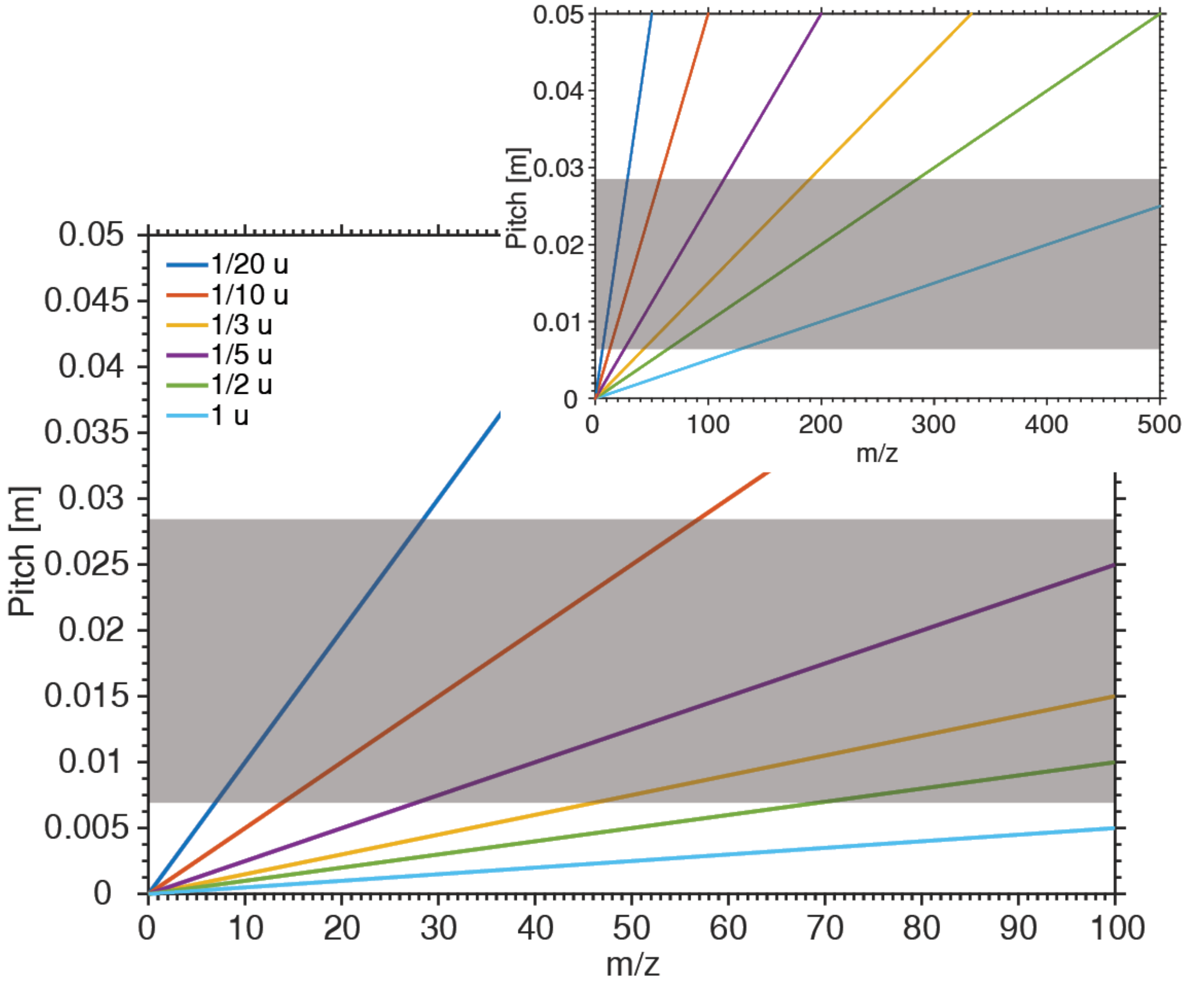
$$\vec{E} = -E\hat{y}$$
$$\vec{B} = -B\hat{z}$$

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

Requirements for a Cycloidal coded aperture mass spectrometer

1. Electric and magnetic field uniformity
2. Requires small ion source
3. Requires an array detector that functions in a magnetic field

Expected mass range and resolution



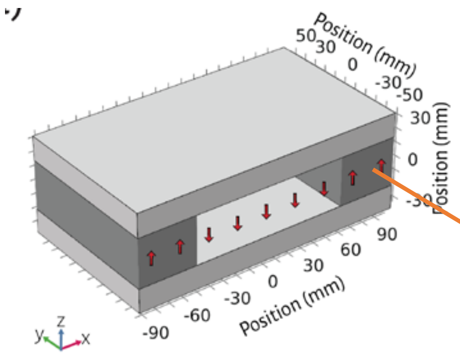
CAMMS-ES
0.3 T magnetic field
10-45 amu
25-120 amu
For methane and BTEX detection

See Kat Horvath's talk for
Work on increasing mass range

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

CAMMS-ES mass analyzer section view

Opposed dipole magnet



CAMMS-ES
0.3 T magnetic field
10-45 amu
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For methane and BTEX detection

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Sample inlet

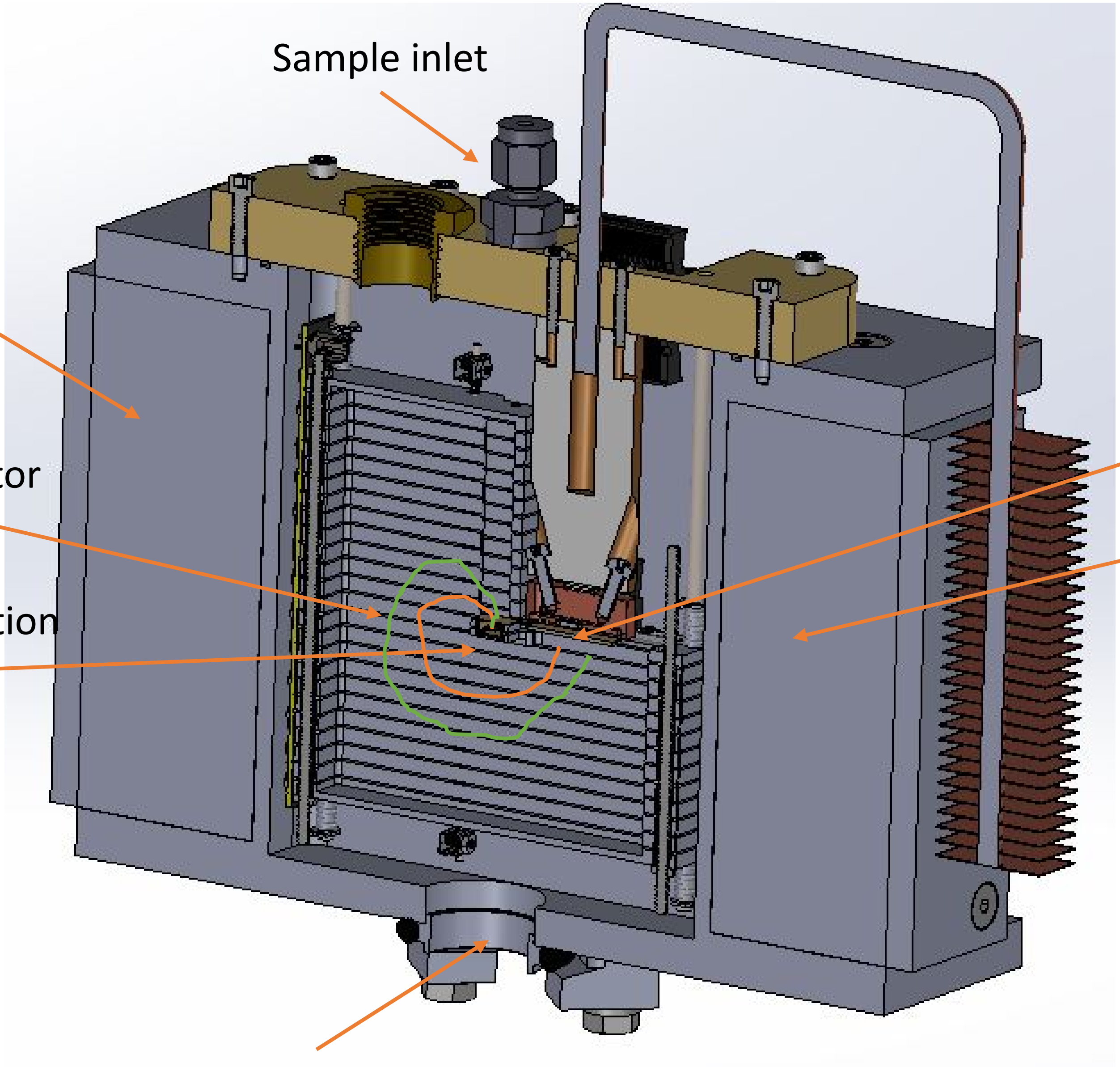
Electric sector

Electron Ionization source

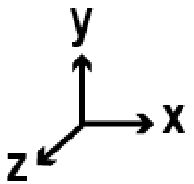
Detector

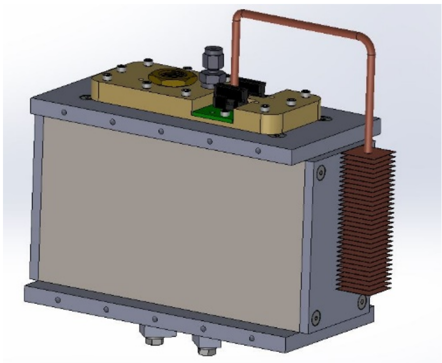
Magnet

Vacuum connection

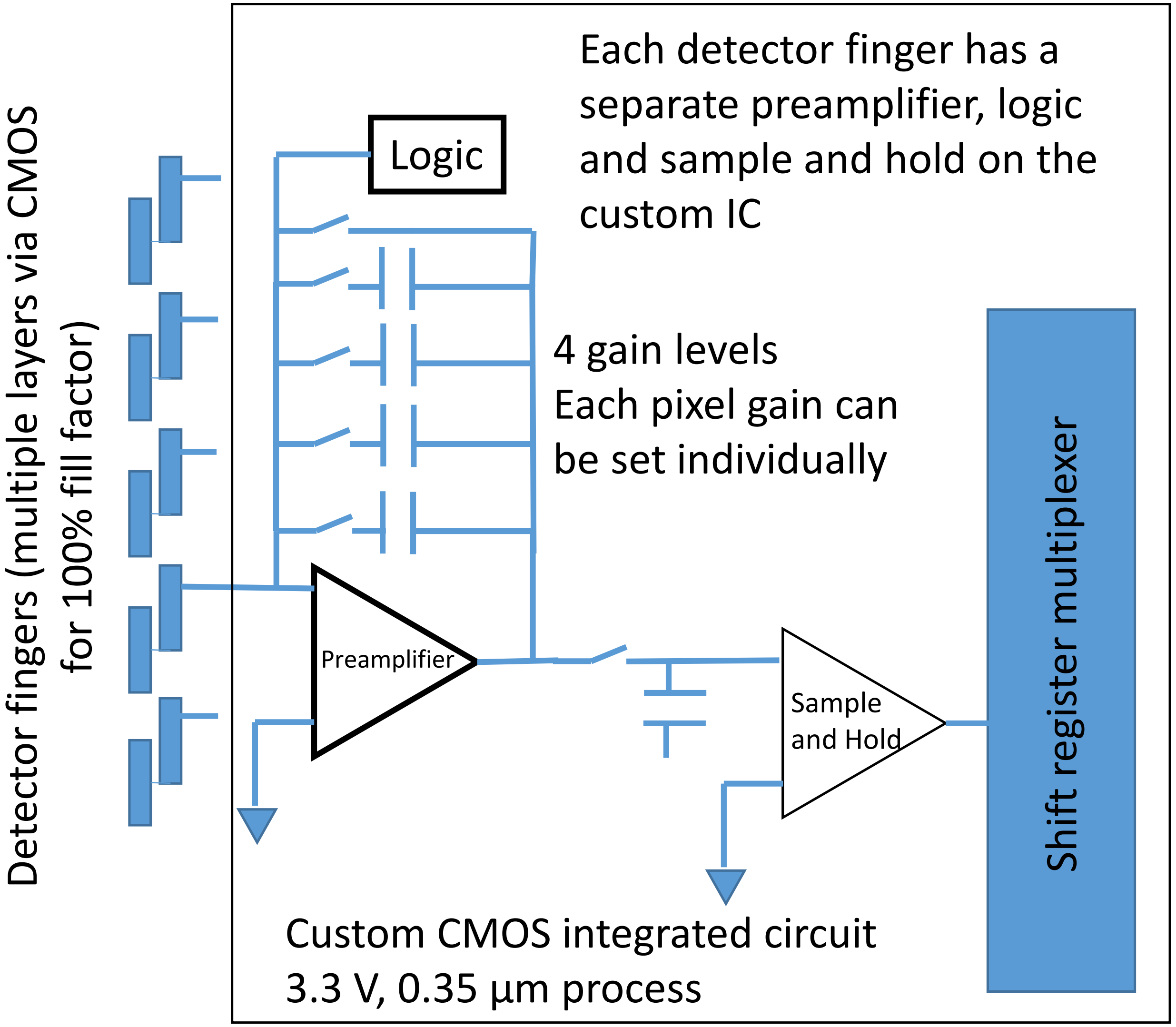


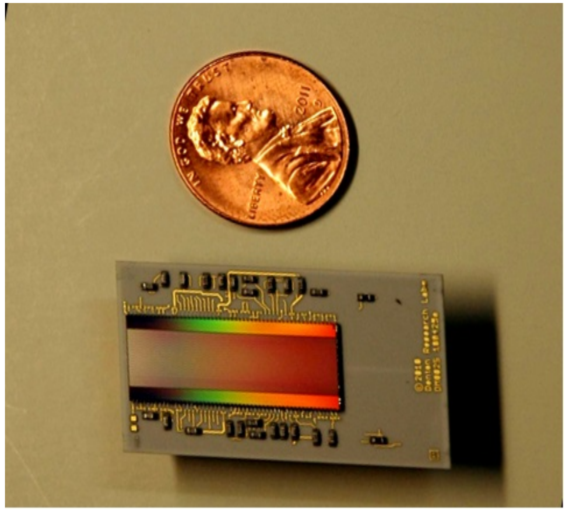
$$\vec{E} = -E\hat{y}$$
$$\vec{B} = -B\hat{z}$$





Capacitive transimpedance amplifier detector array

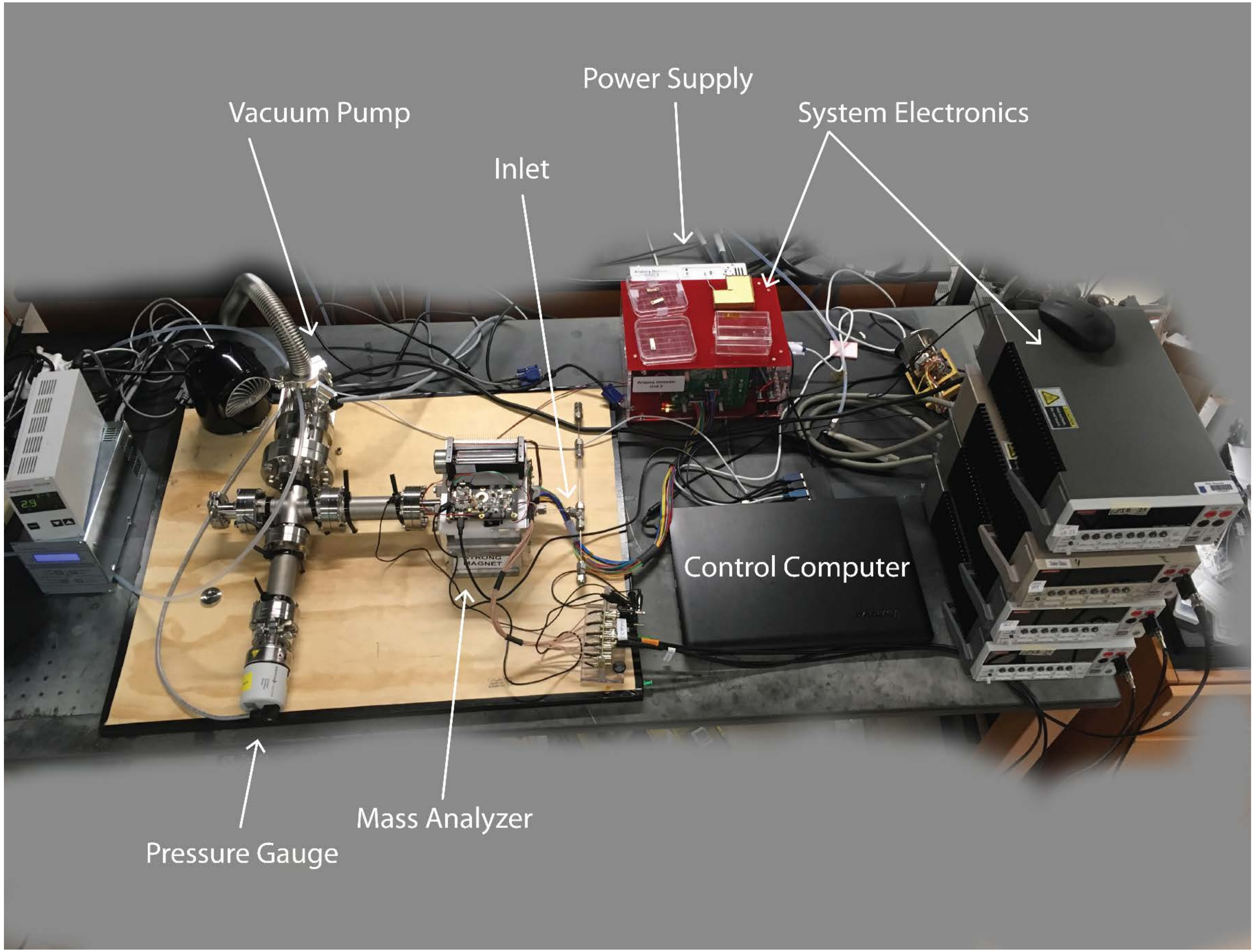




- 15 µV/e⁻ at high gain
- Dynamic range 10^{11} using the 4 gain stages
- Limited cross-talk
- Nondestructive readout

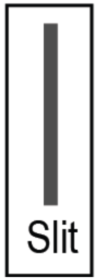
Felton, J. A., G. D. Schilling, S. J. Ray, R. P. Sperline, M. B. Denton, C. J. Barinaga, D. W. Koppenaal and G. M. Hieftje (2011). "Evaluation of a fourth-generation focal plane camera for use in plasma-source mass spectrometry." Journal of Analytical Atomic Spectrometry **26**(2): 300-304.

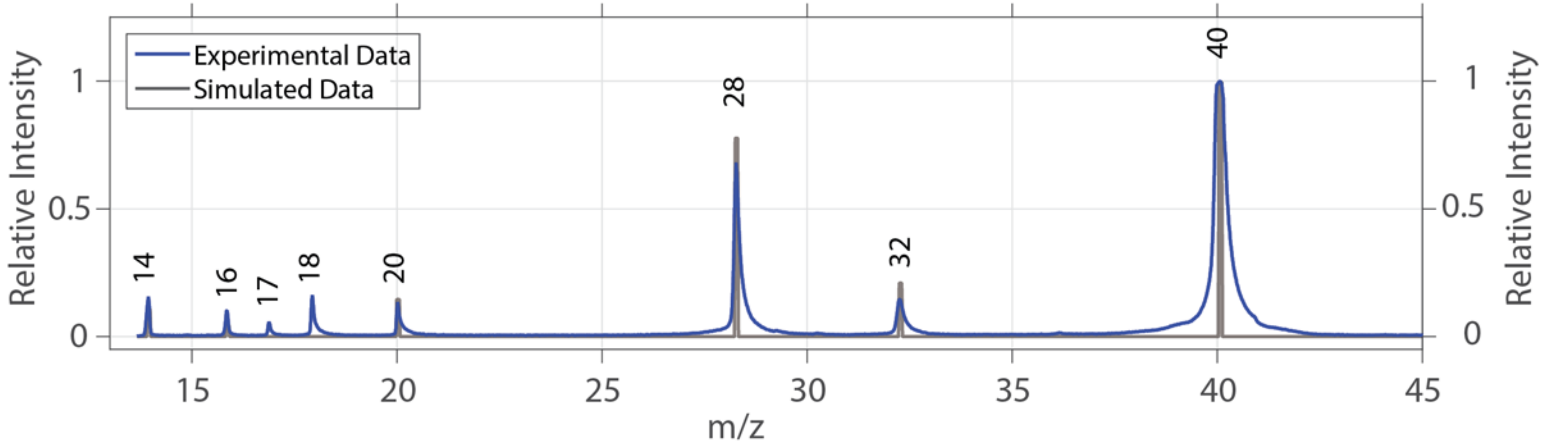
CAMMS-ES Laboratory prototype proof of concept



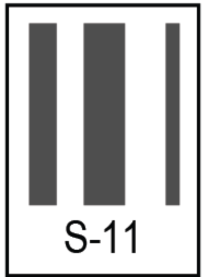
- What is computational sensing and aperture coding?
- Why use a cycloidal mass analyzer with aperture coding?
- What is the performance of CAMMS-ES?
  - Does aperture coding actually work?
  - What is the sensitivity for toluene in air?

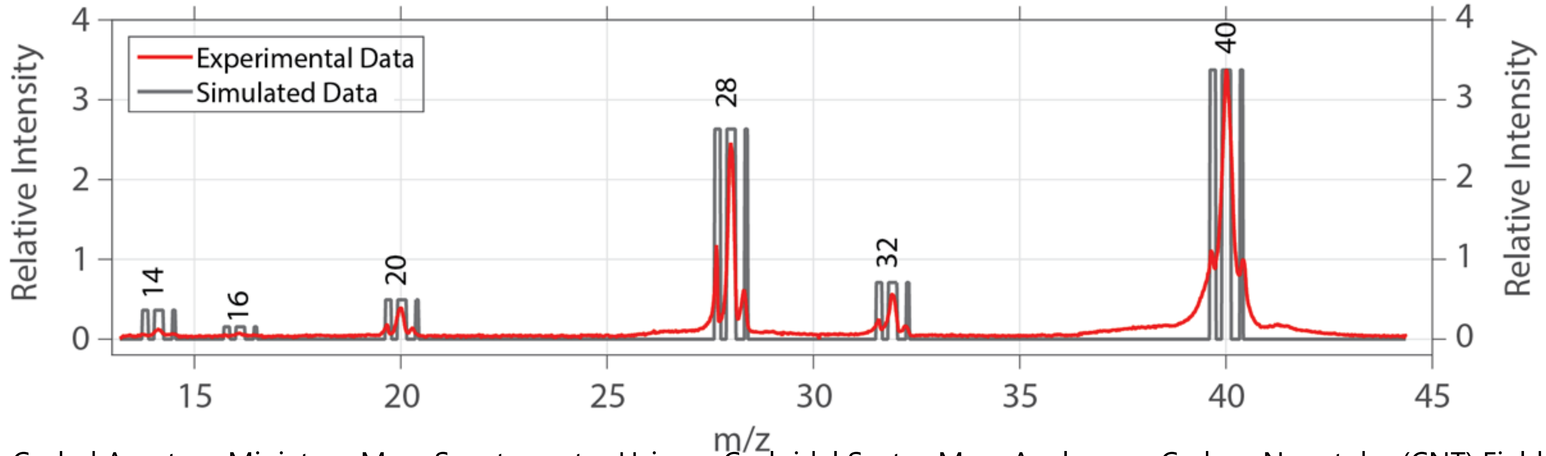
50 µm Slit



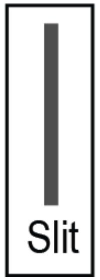


S-11 Coded apertrure with 50 µm minimum feature size

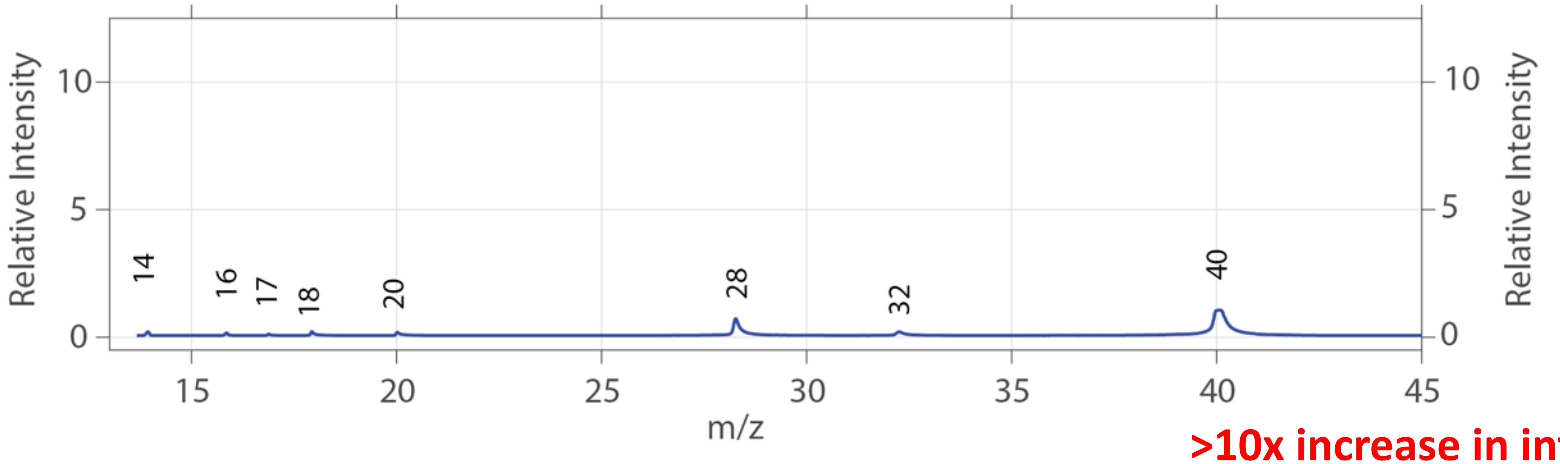




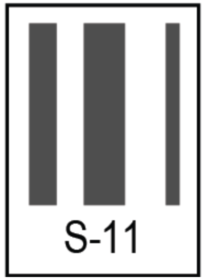
"Proof of Concept Coded Aperture Miniature Mass Spectrometer Using a Cycloidal Sector Mass Analyzer, a Carbon Nanotube (CNT) Field Emission Electron Ionization Source, and an Array Detector," J. J. Amsden, P. J. Herr, D. M. W. Landry, W. Kim, R. Vyas, C. B. Parker, M. P. Kirley, A. D. Keil, K. H. Gilchrist, E. J. Radauscher, S. D. Hall, J. B. Carlson, N. Baldasaro, D. Stokes, S. T. Di Dona, Z. E. Russell, S. Grego, S. J. Edwards, R. P. Sperline, M. B. Denton, B. R. Stoner, M. E. Gehm, and J. T. Glass. J Am Soc Mass Spectrom 29, 360-372. (2018) 10.1007/s13361-017-1820-y



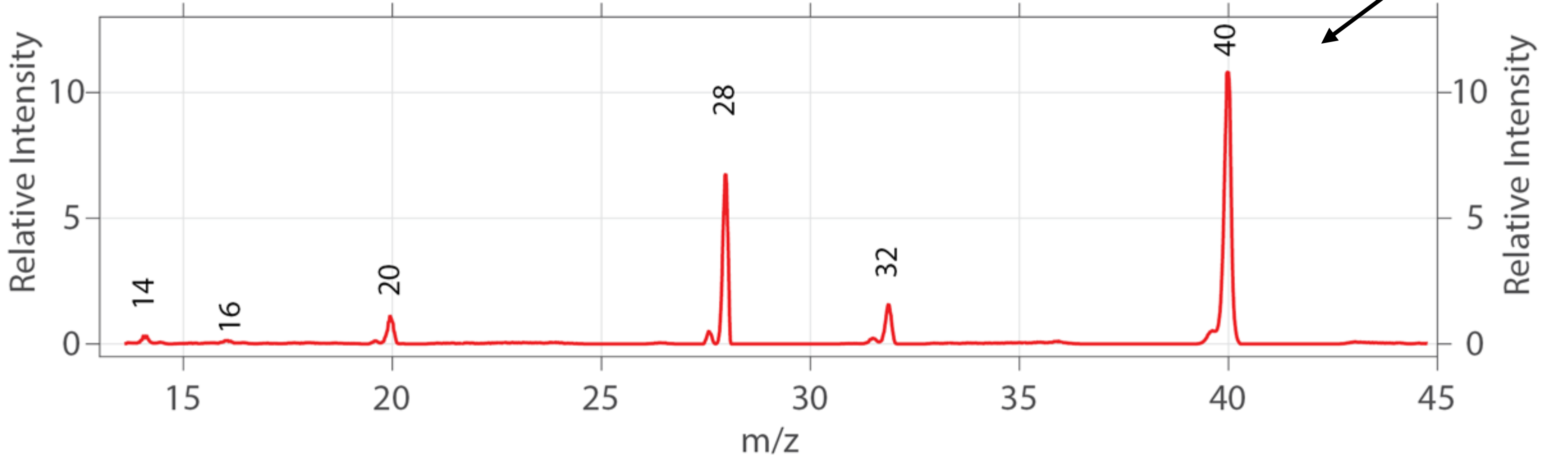
50 µm Slit Experimental Data



>10x increase in intensity!



S-11 Coded apertrure with 50 µm minimum feature size Reconstruction



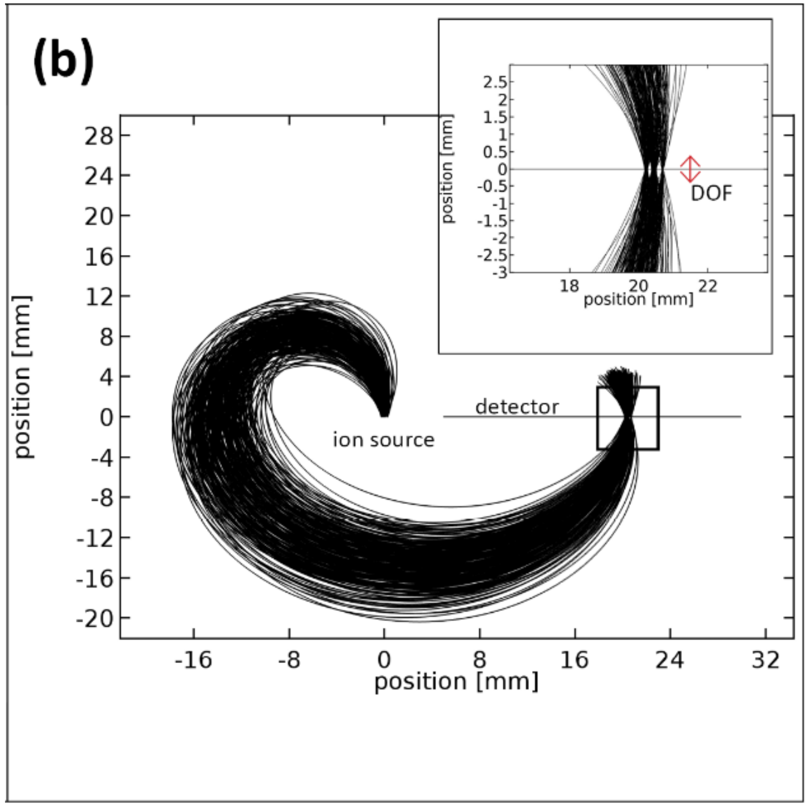
>10x increase in signal and improved resolution

However, reconstruction exhibits artifacts as the system response is not uniform across the detector due to alignment

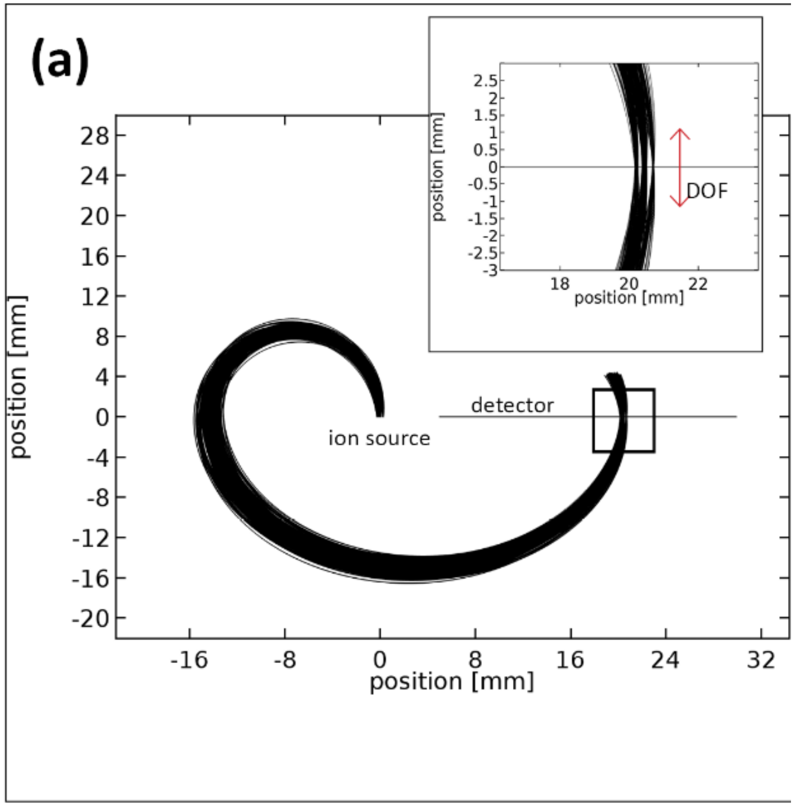
Why are there artifacts in the reconstruction?

- Electric and magnetic field non-uniformities
- Depth of focus and Alignment of detector with mass analyzer focal plane

Depth of focus for ion source with large dispersion

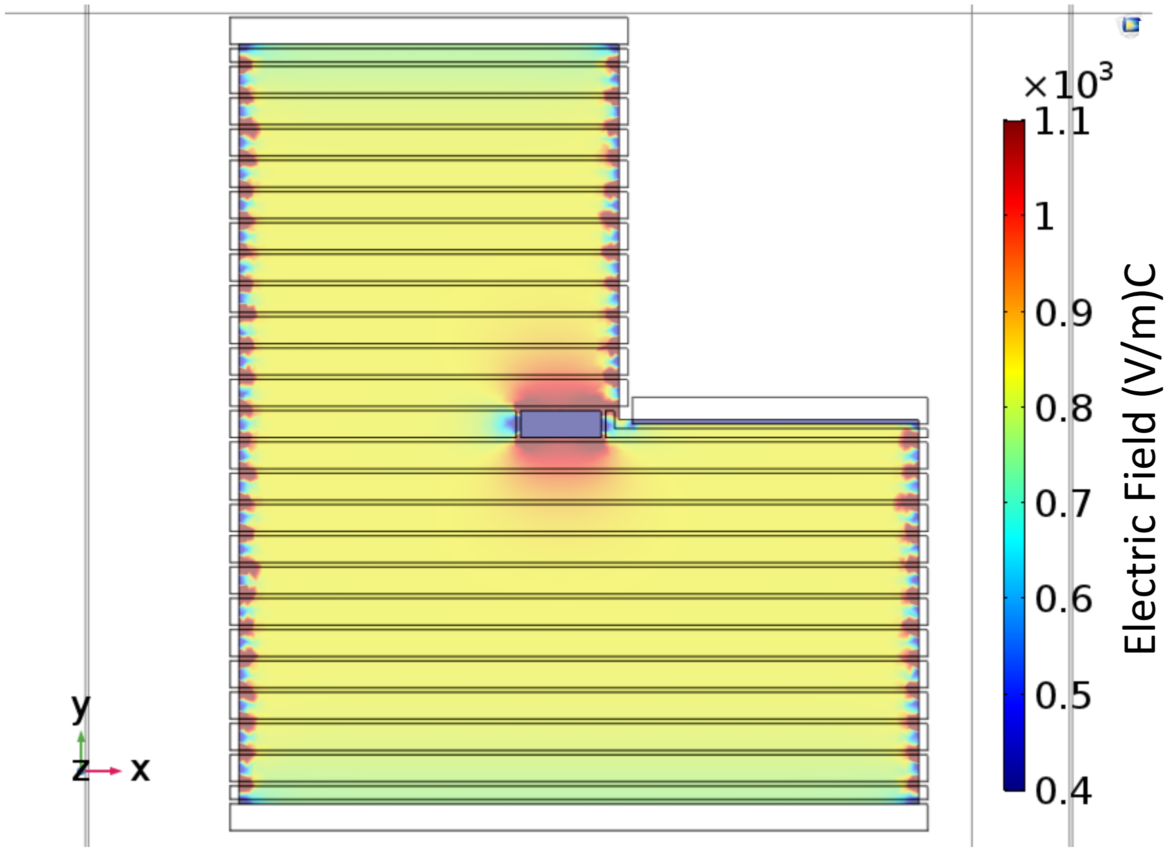


Depth of focus for ion source with small dispersion

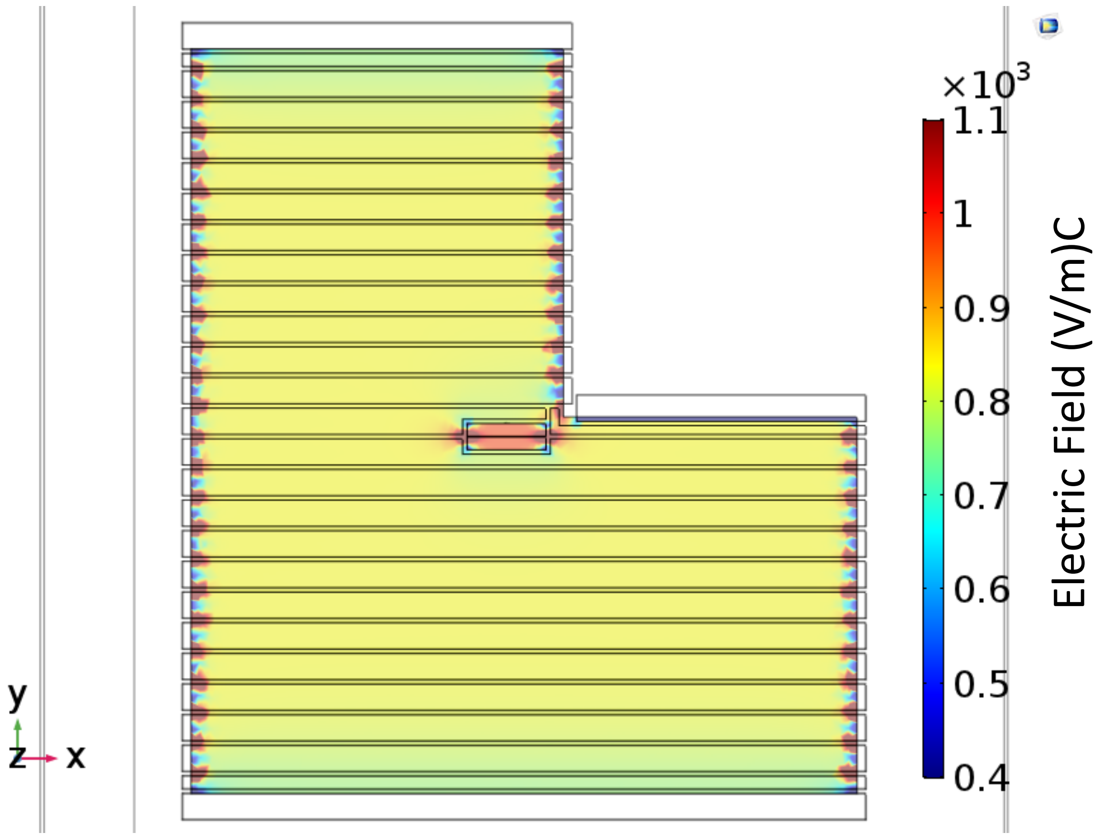


Improving field uniformity by repositioning the ion source

Original Electric sector



Improved electric sector

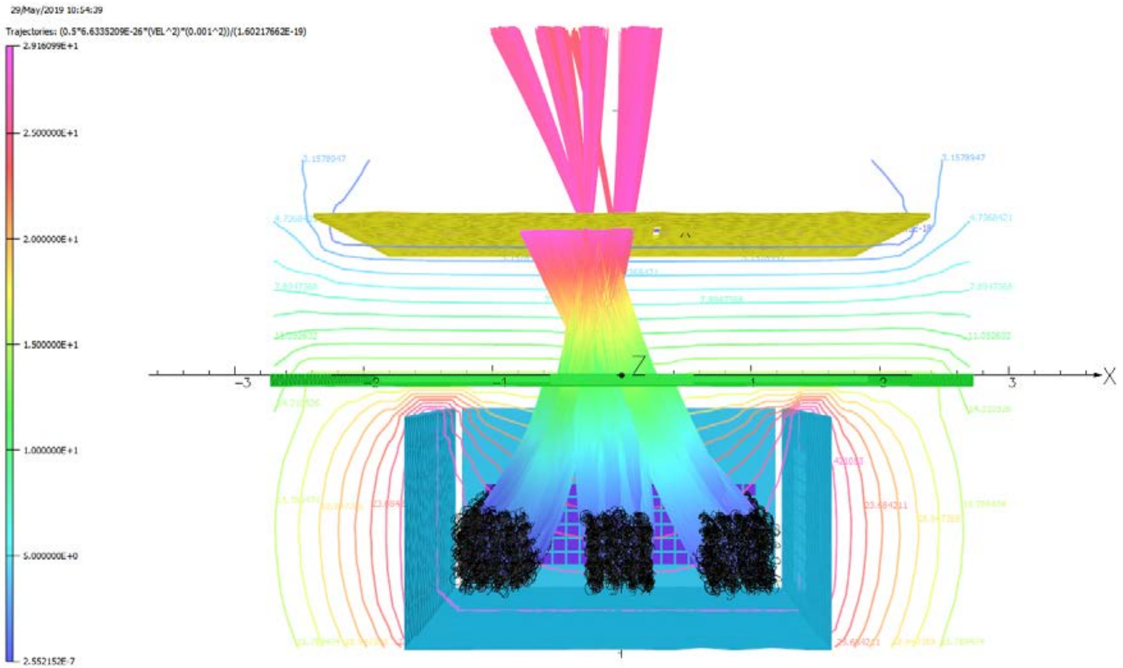


"Effects of Magnetic and Electric Field Uniformity on Coded Aperture Imaging Quality in a Cycloidal Mass Analyzer," D. M. W. Landry, W. Kim, J. J. Amsden, S. T. Di Dona, H. Choi, L. Haley, Z. E. Russell, C. B. Parker, J. T. Glass, and M. E. Gehm. J Am Soc Mass Spectrom 29, 352-359. (2018) 10.1007/s13361-017-1827-4

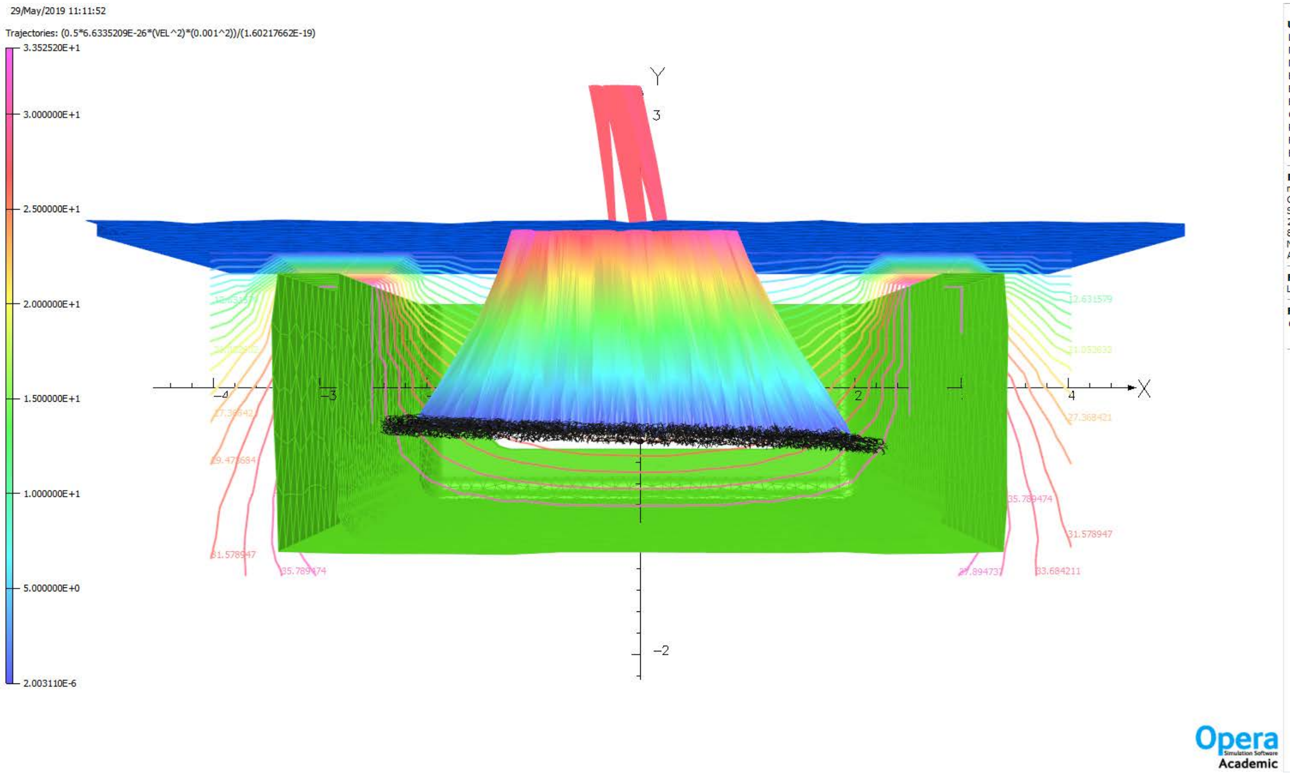
To improve field uniformity, place the ion source between electric sector electrodes

Reduce source dispersion and increase depth of focus

Original ion source configuration with CNTs



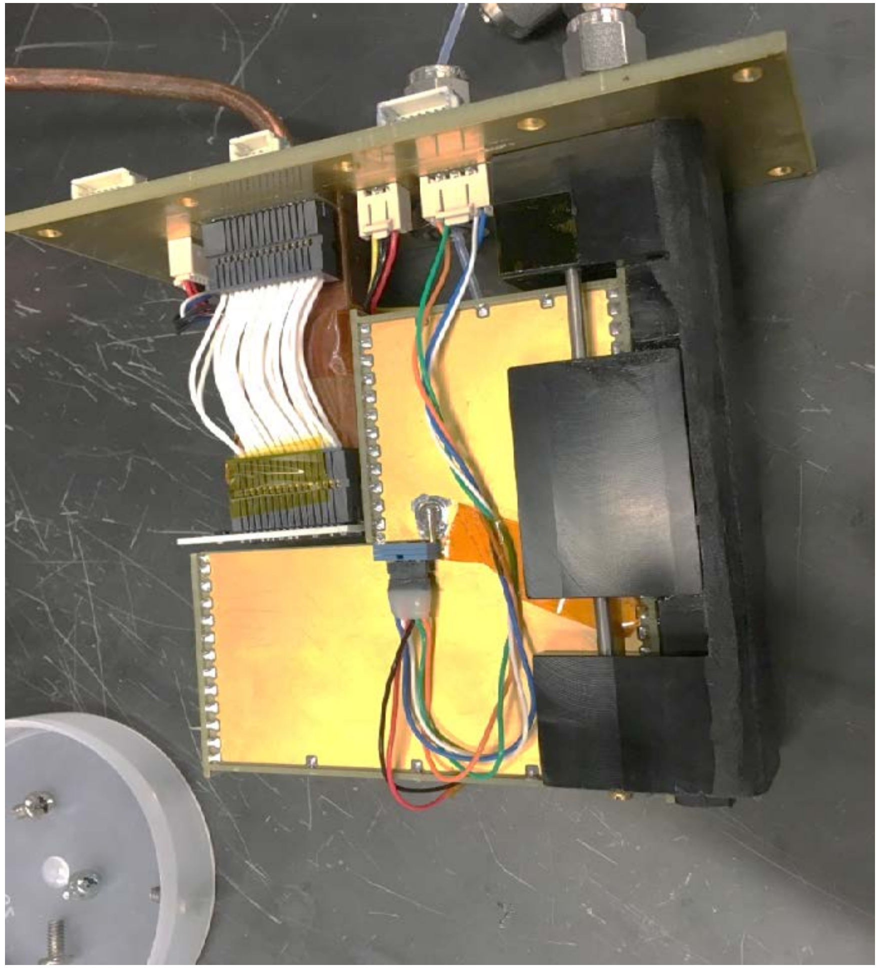
Current ion source configuration with filament



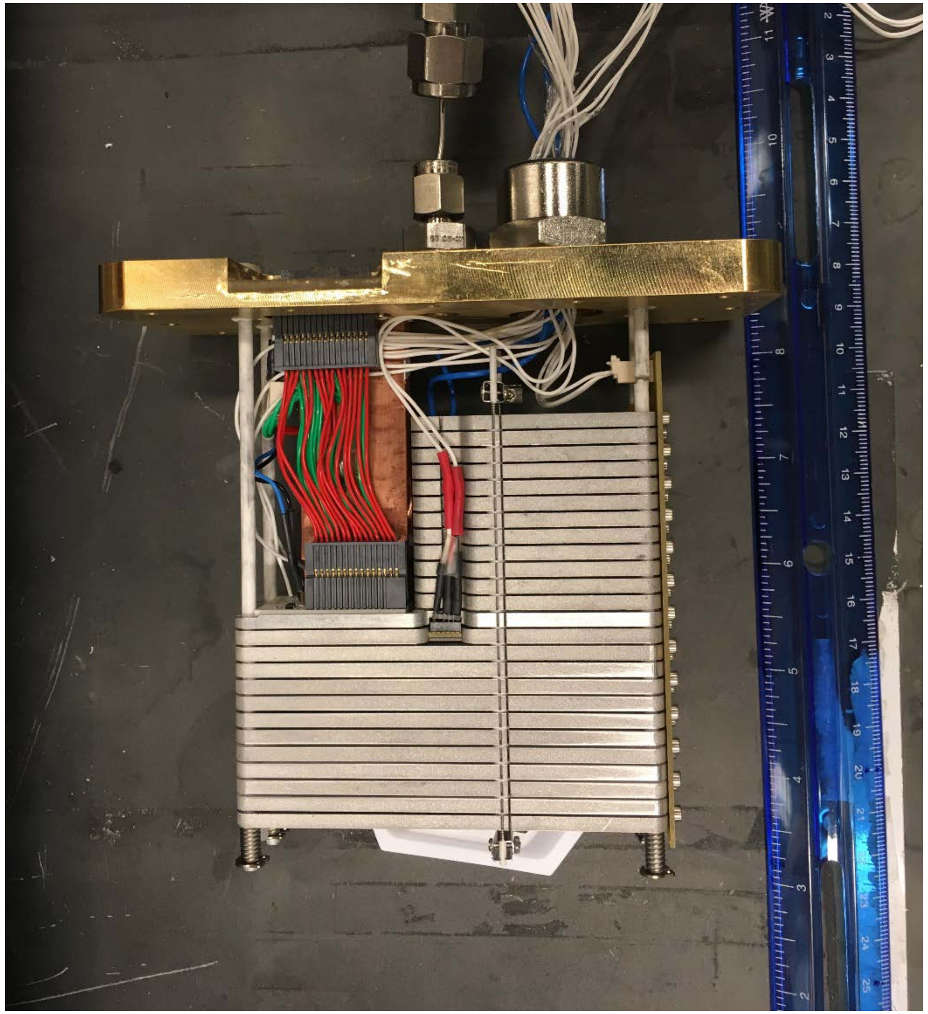
Ions generated over a smaller potential gradient -> less dispersion -> larger depth of focus

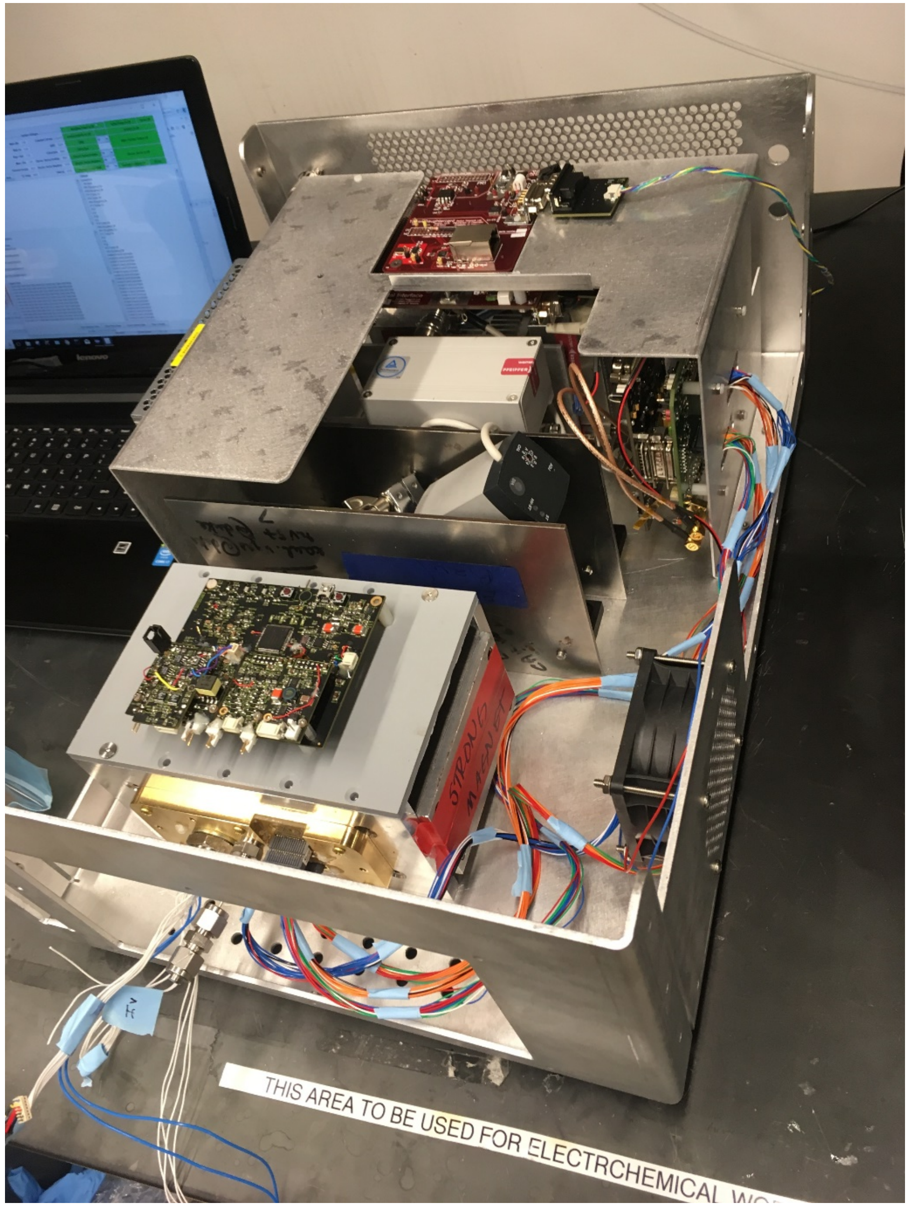
Improve alignment by redesign of the electric sector

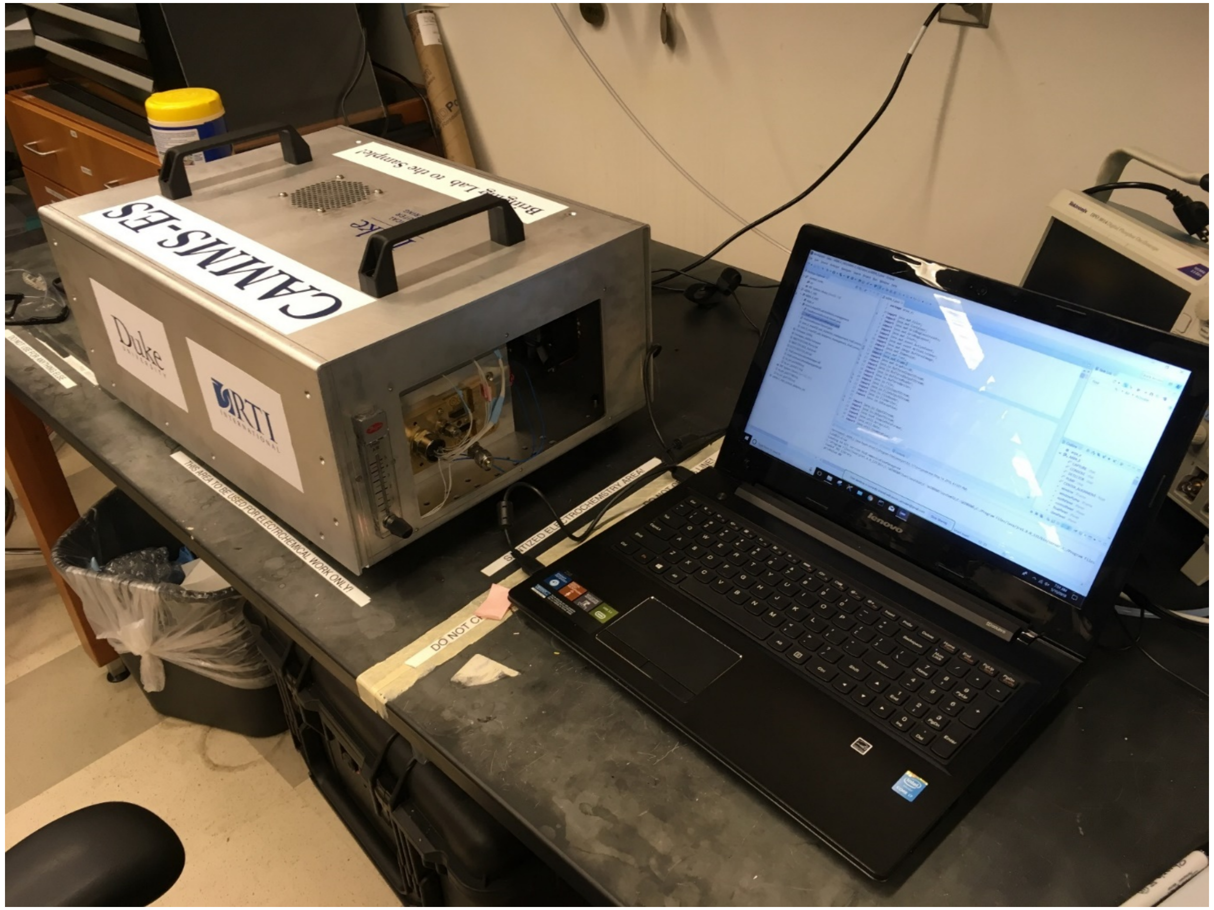
Old Analyzer



New Improved Analyzer



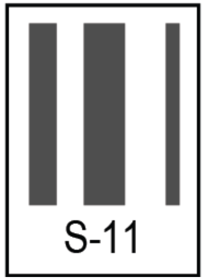


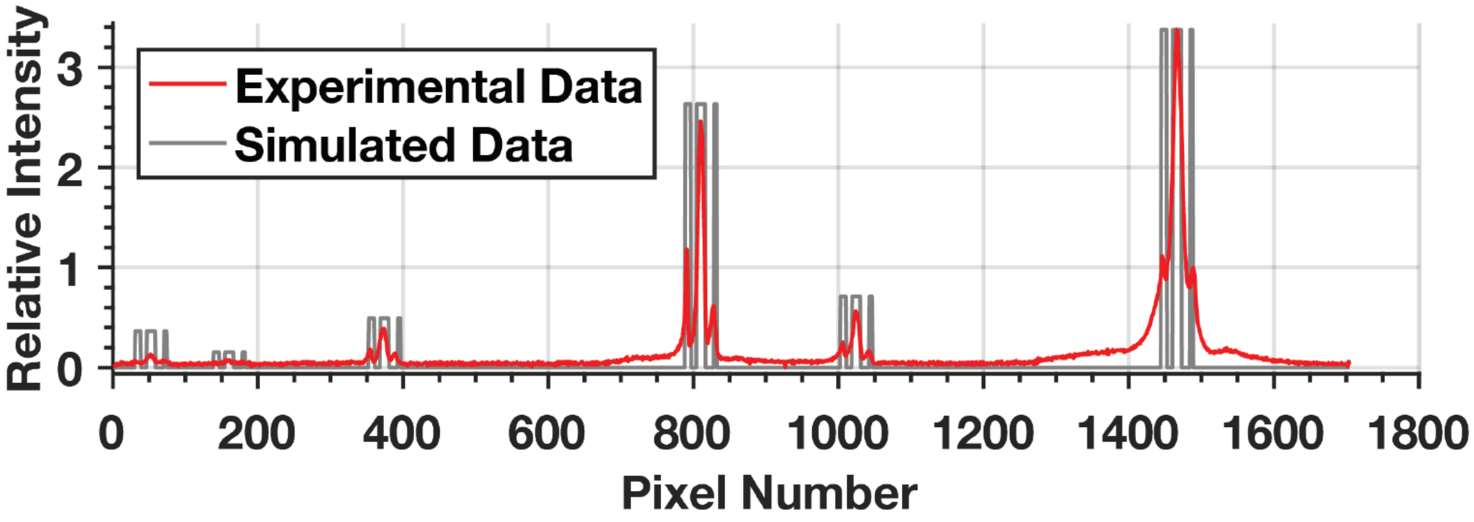


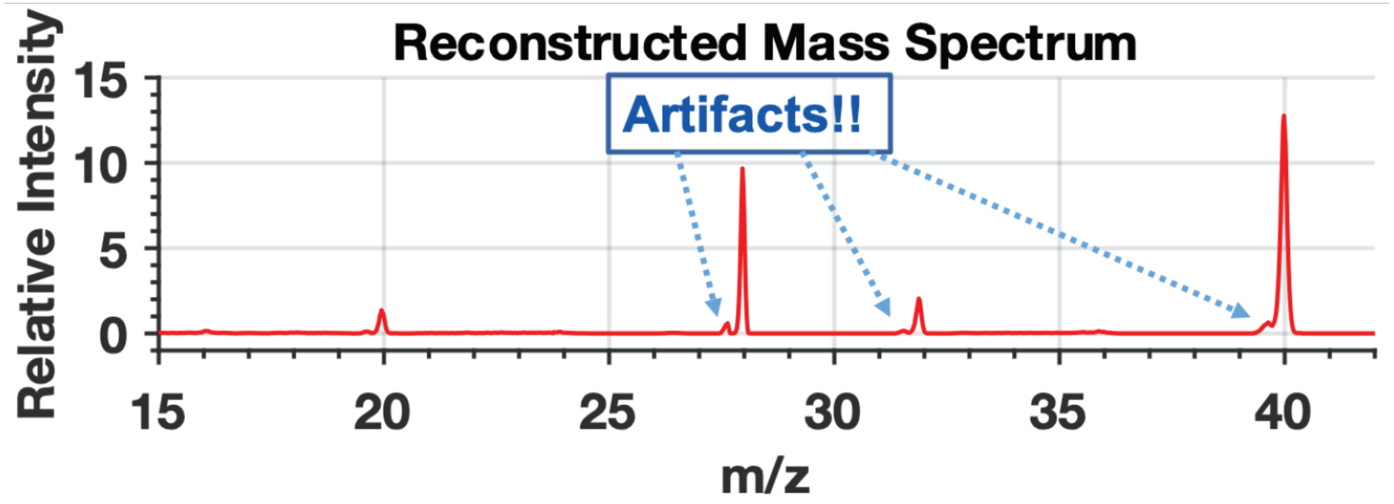
CAMMS-ES

- ***40 lbs, 40 W***
- ***Mass range 10-120 amu***
- ***Membrane inlet***
- ***Goal 1 ppb detection limit for toluene in "real time"***

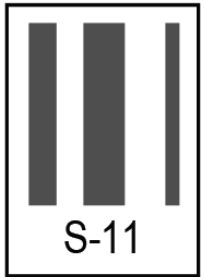
Laboratory prototype data

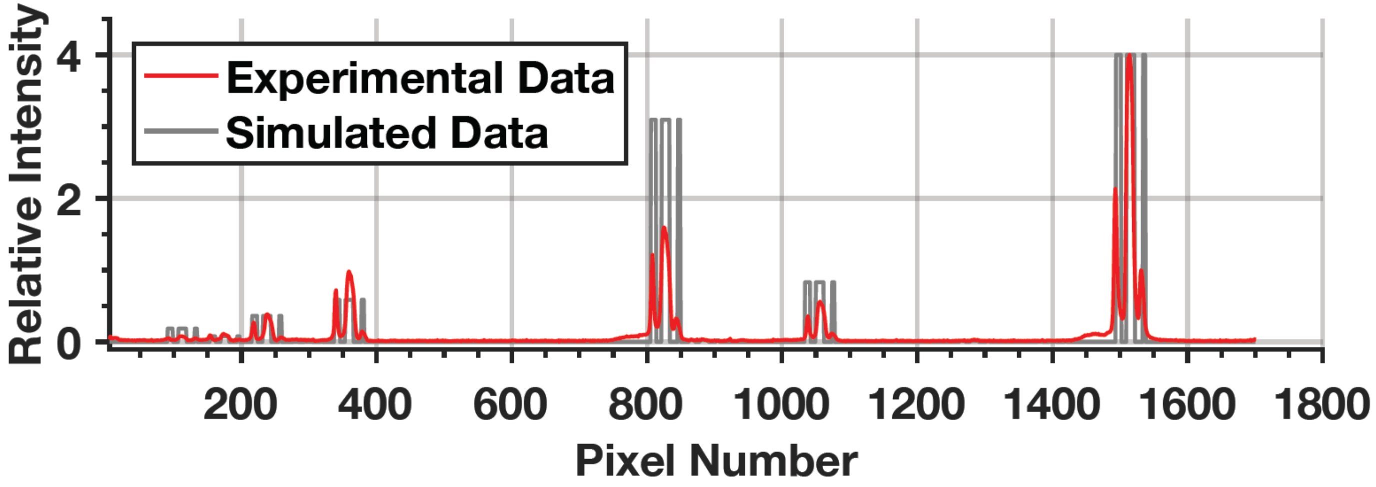


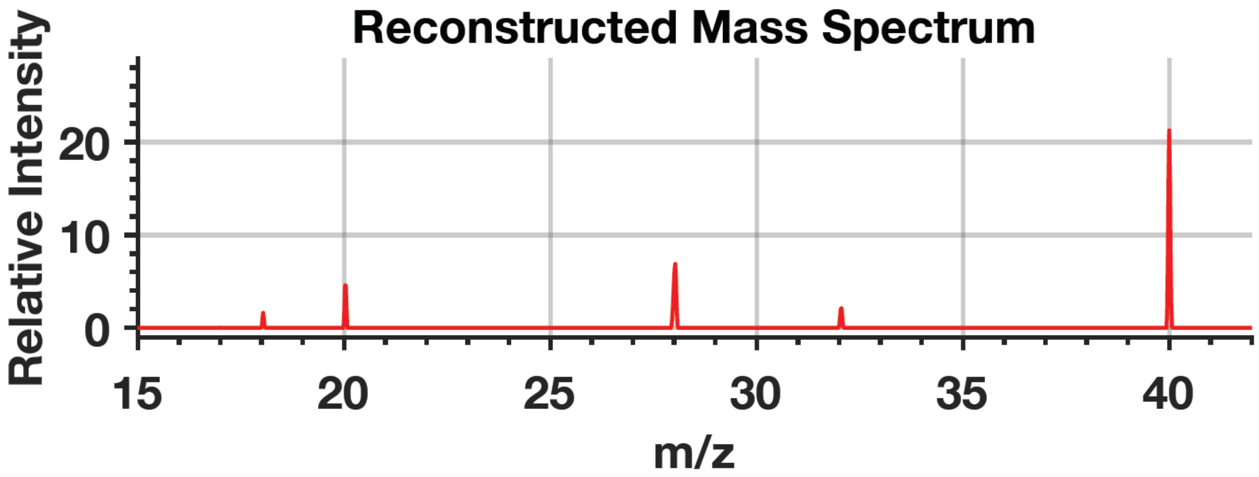




New improved prototype data

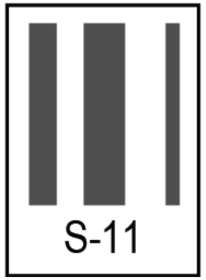


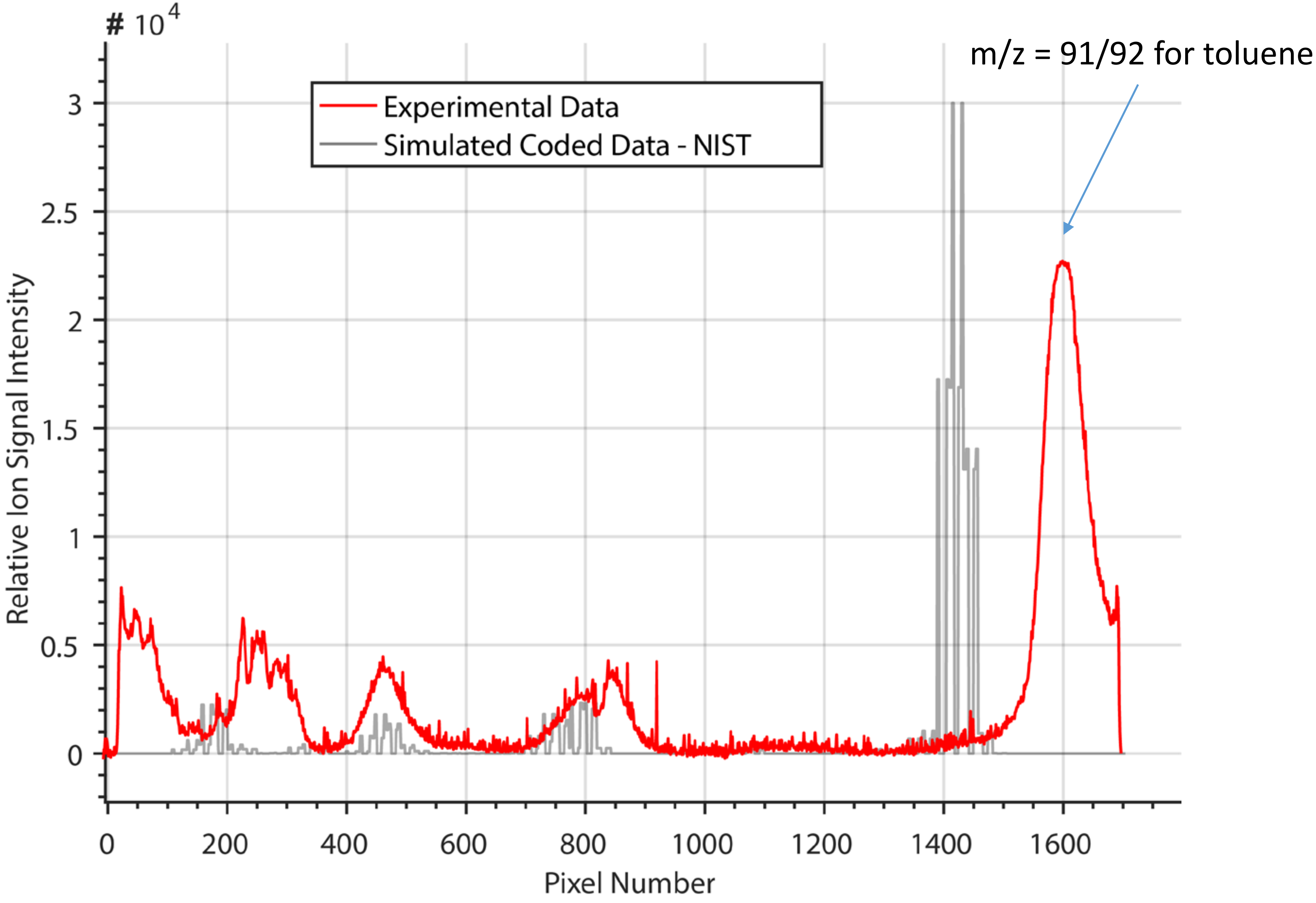




No artifacts present

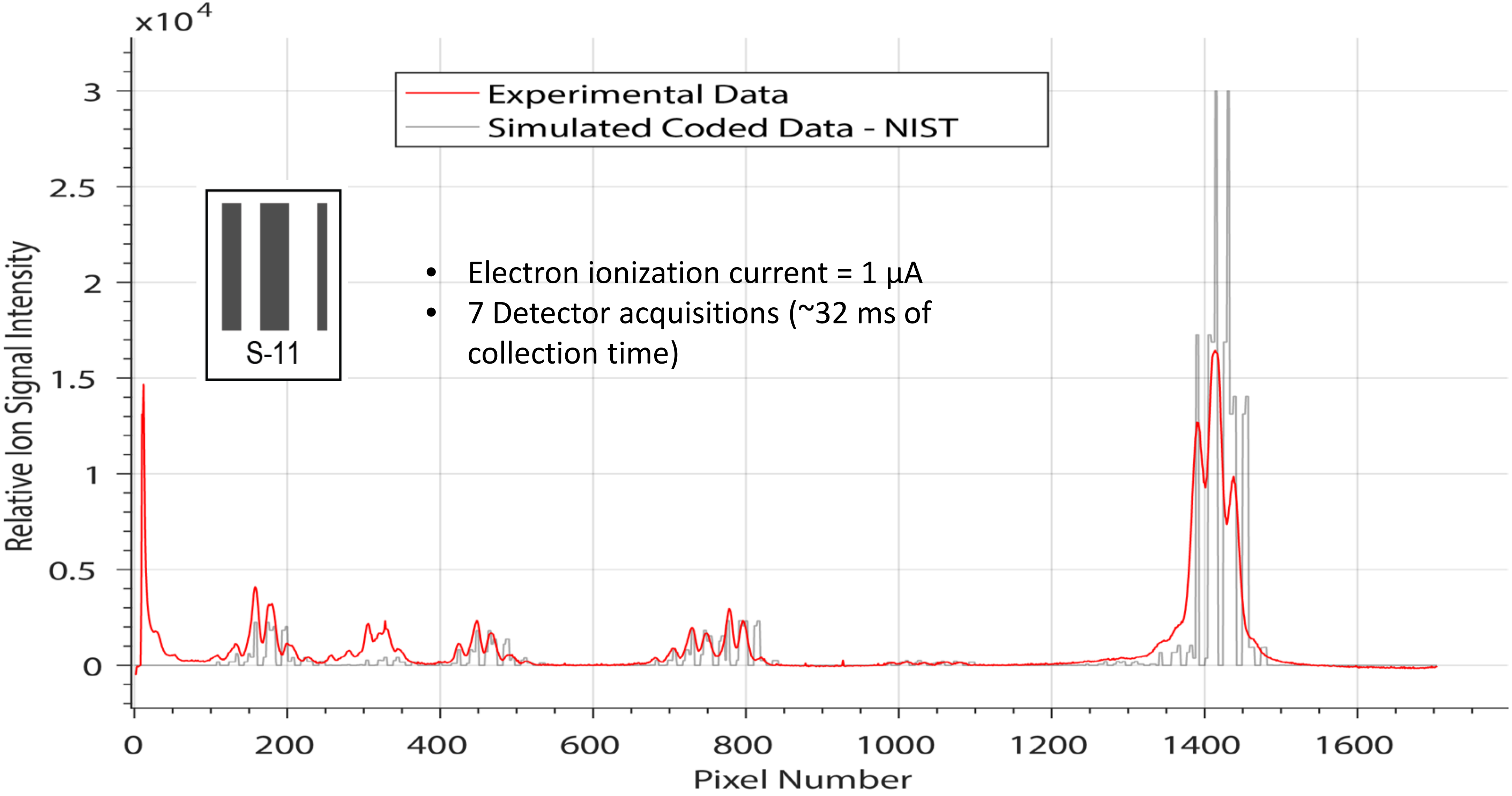
Coded toluene mass spectrum





See Tanouir Aloui's talk for how we solved this problem

Coded Toluene (100 ppm in dry air) after fixing charging issue

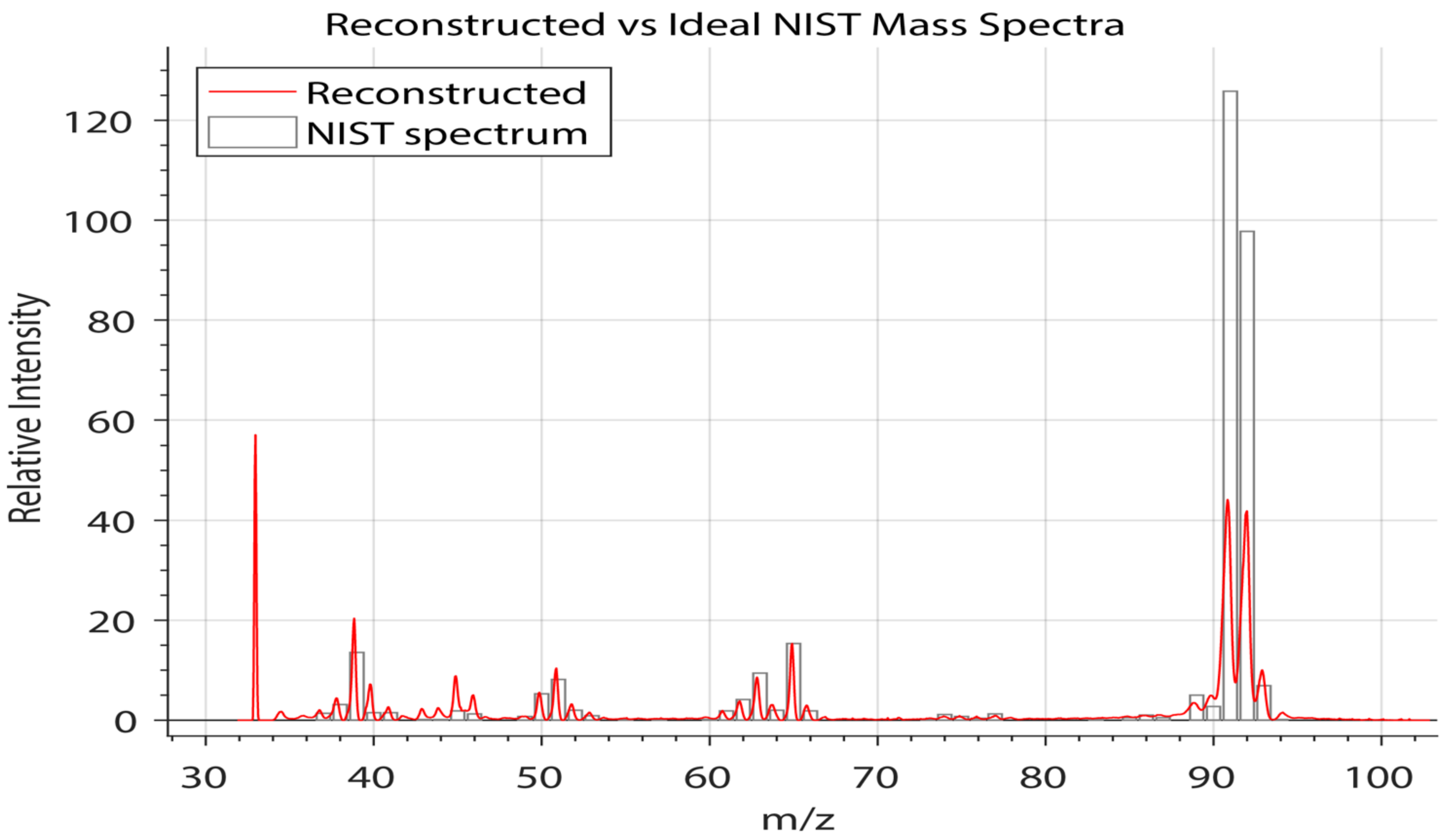


- Electron ionization current = 1 μA
- 7 Detector acquisitions (~32 ms of collection time)

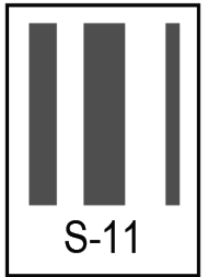
Loss in intensity at higher m/z – due to out of plane velocity components due to thermal energy of ions

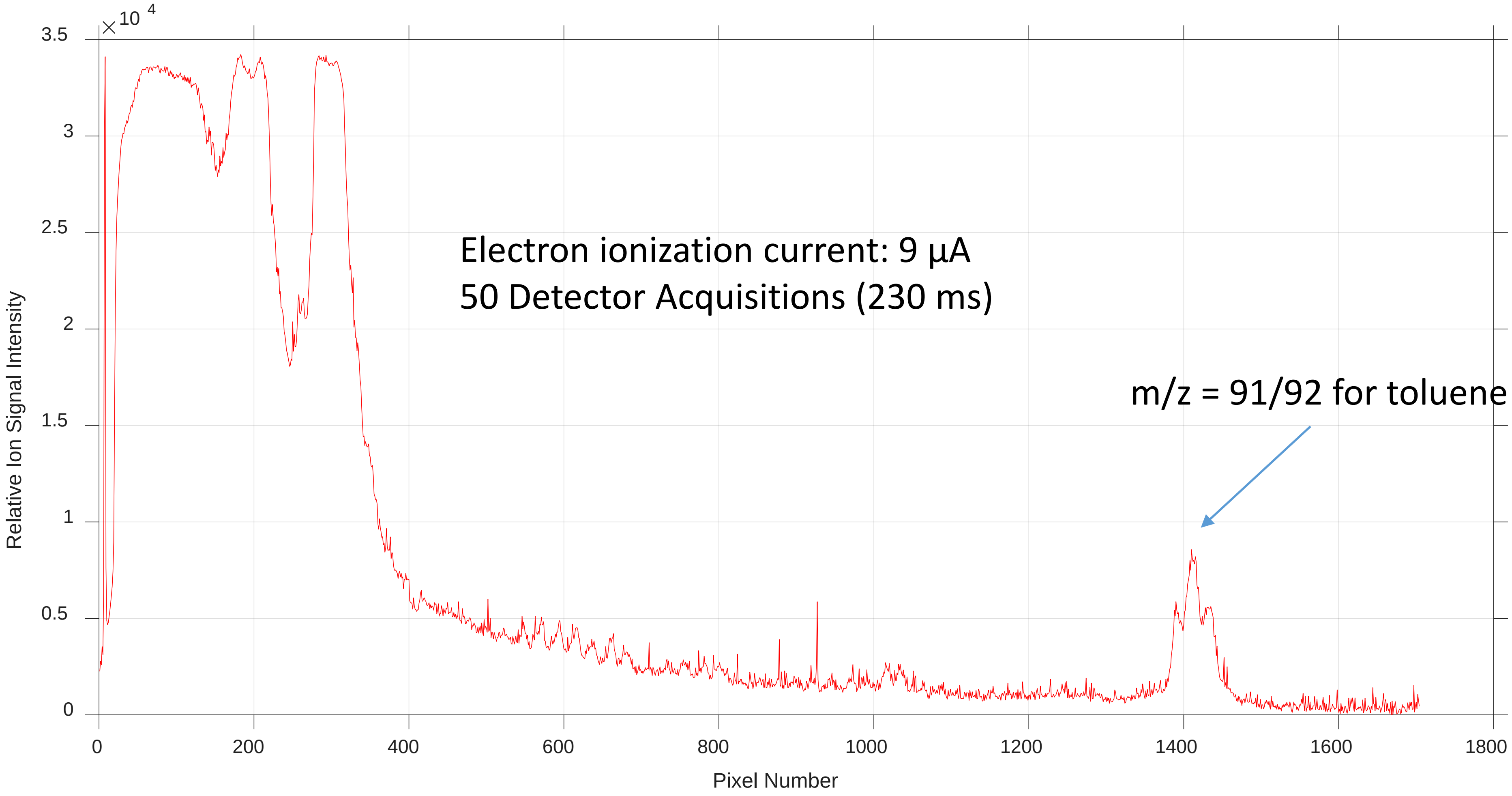
50 micron slit in S-11 aperture not fully illuminated

100 ppm Toluene spectrum after reconstruction



Coded toluene spectrum at ~100 ppb





Signal to background ~20:1 -> 5 ppb or better detection limit

Summary and future work

- Computational sensing can help with the throughput vs resolution tradeoff encountered in miniaturization
- CAMMS-ES
  - 40 lbs, 40 W
  - Mass range 10-120 amu
  - Toluene detection limit: ~5 ppb (goal 1 ppb)

- ***What is next?***
- Portable stable isotope ratio analysis of CHNS
- Single particle analysis
- Increase mass range and further improve resolution
- Further miniaturization

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