Designing a Coded Aperture Cycloidal Mass Analyzer to Detect Perfluorocarbon Tracers

Harsh Environment Mass Spectrometry

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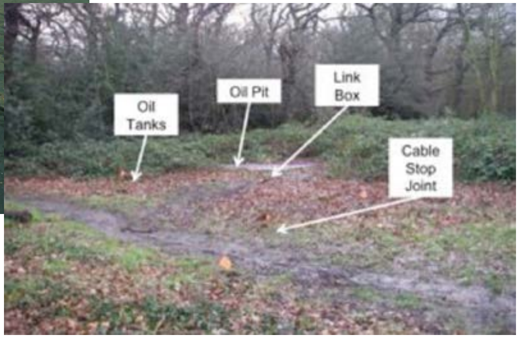
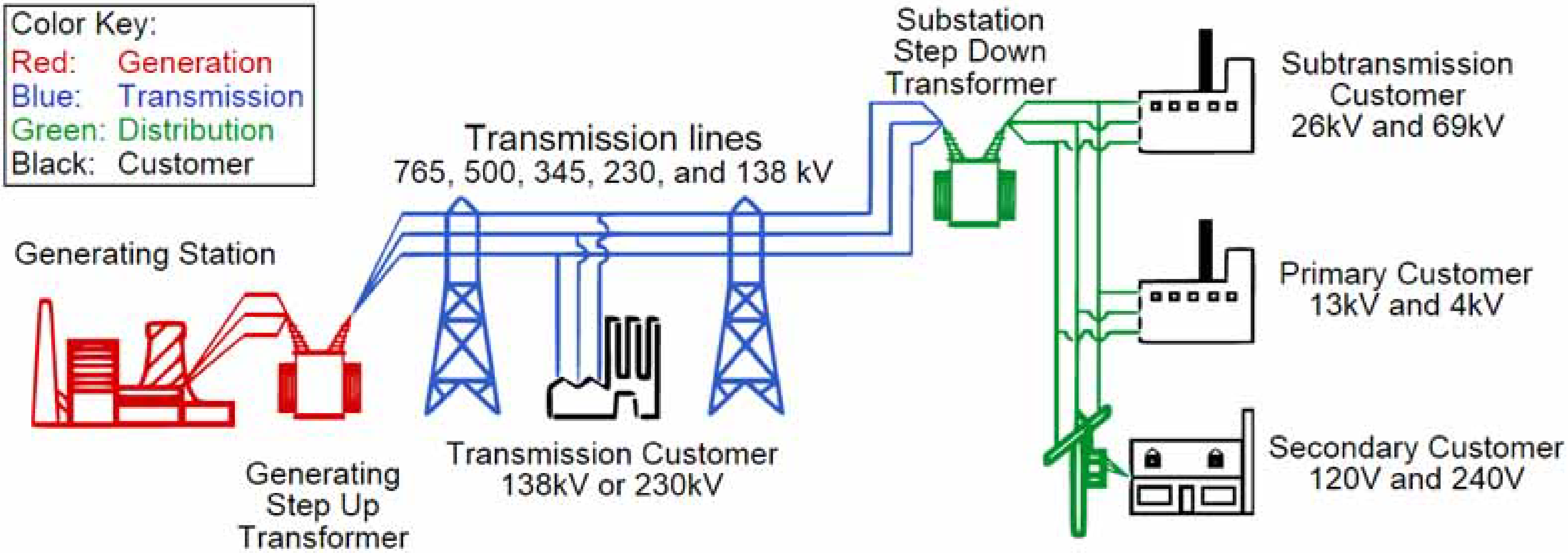
Outline



- Introduce the urban harsh environment problem
- Our portable mass spectrometer solution
- Process for designing the mass analyzer
- Plans for field use

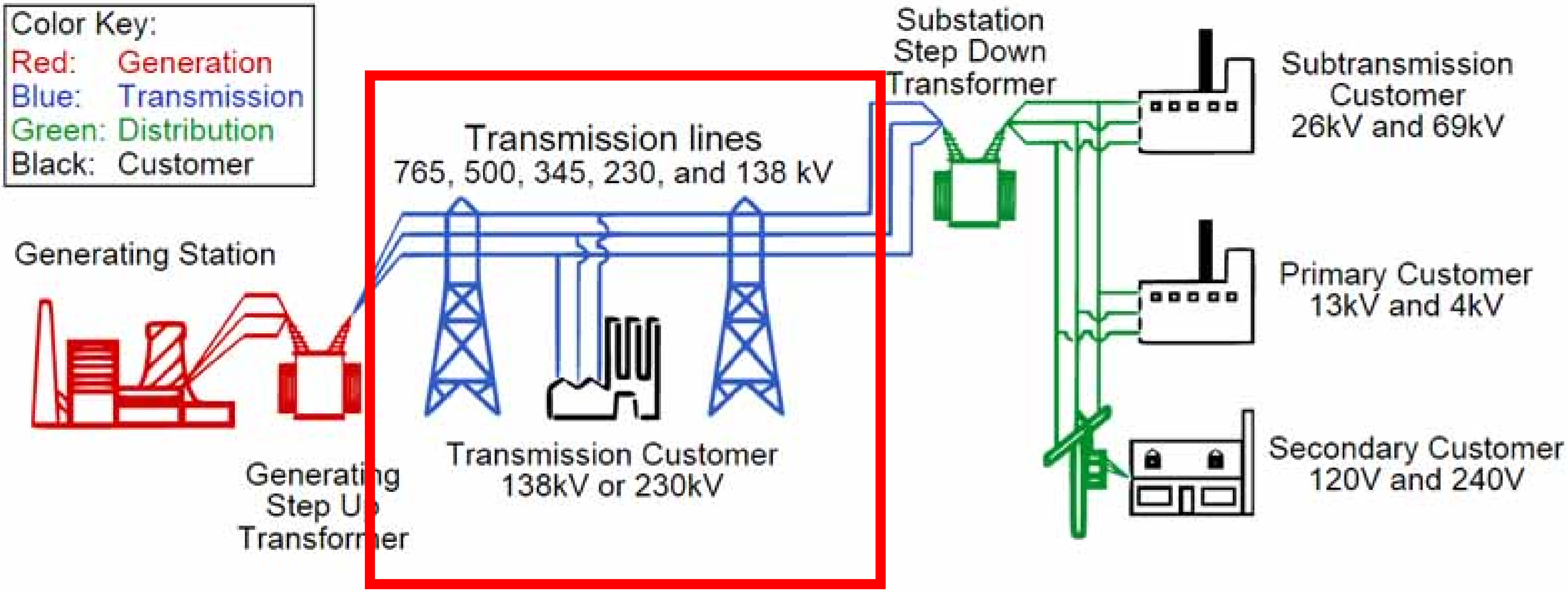
Basics of the Electrical Utility Grid



https://www.emersonautomationexperts.com/2015/industry/power/ultra-high-voltage-transmission-uhv-a-new-way-to-move-power/

1. Generate electricity at power plant typically far away from the end user
2. Step up the electricity to a higher voltage which will minimize power losses over long distances
3. Step the electricity back down to lower voltages so that it can be consumed by the end user

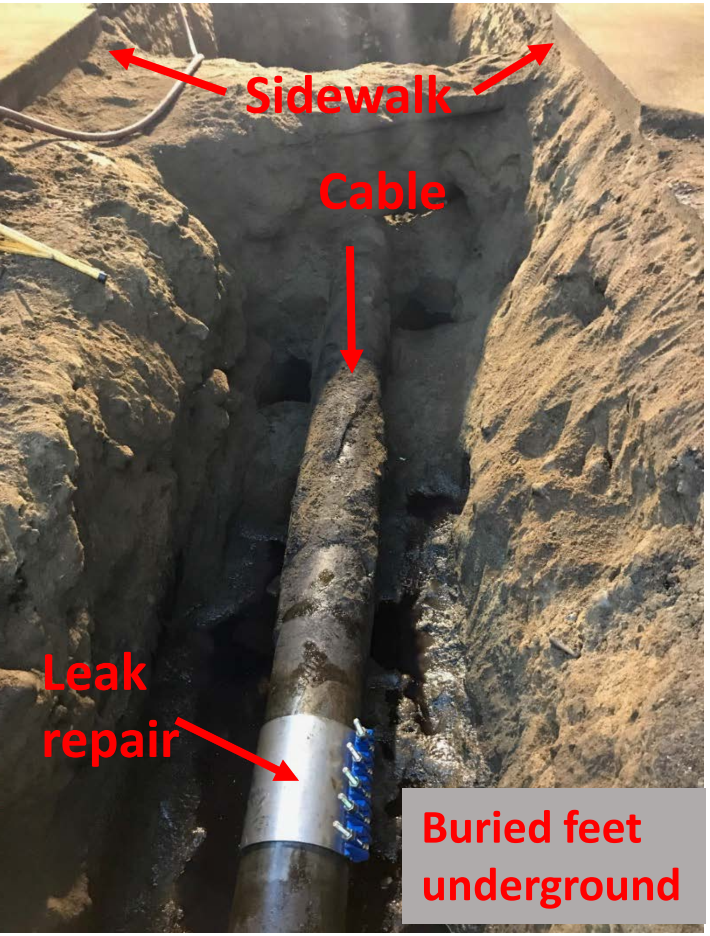
Basics of the Electrical Utility Grid



https://www.emersonautomationexperts.com/2015/industry/power/ultra-high-voltage-transmission-uhv-a-new-way-to-move-power/

The mass spectrometer will be used to improve the performance of high voltage transmission cables (HVTCs)

Problem: Leaking High Voltage Transmission Cables



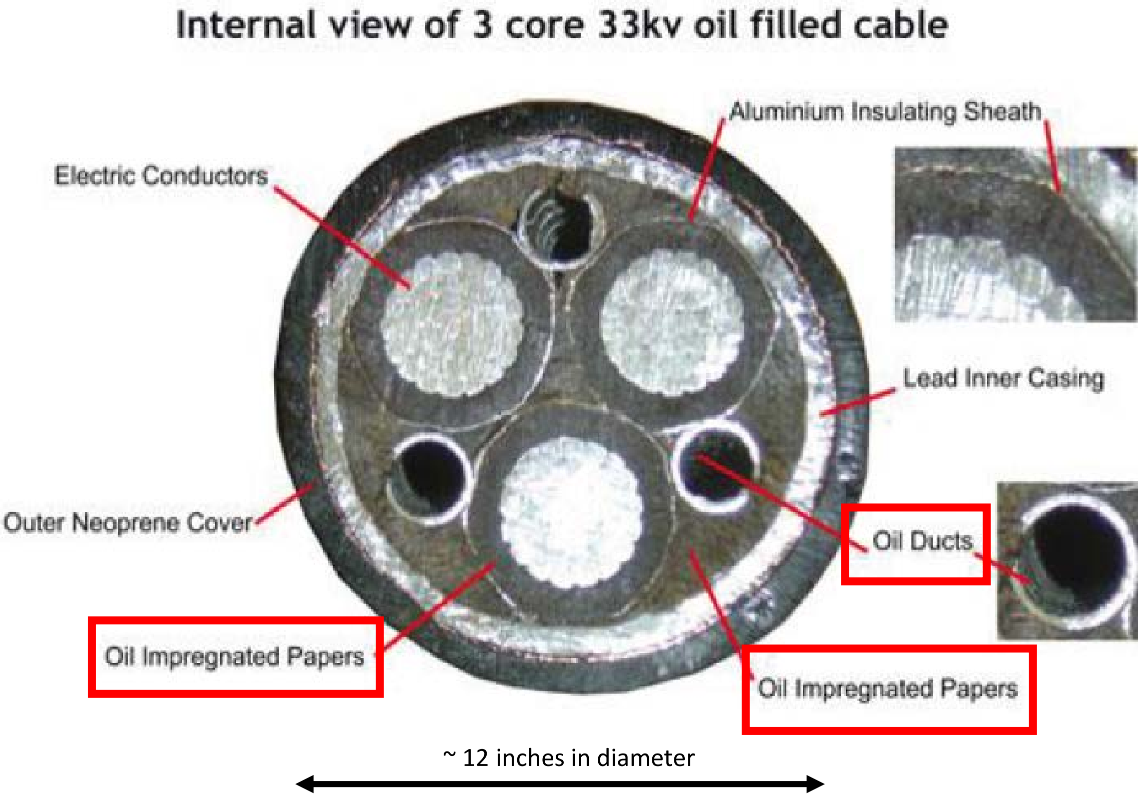


Photo curtesy of Pat Keelan – PFT Technology Limited, A. C. The Hydrogel Purging System. http://aescables.co.uk/power_line_cleaning.htm (09/12/2018),

As the high voltage transmission cables age they degrade and leak the petroleum-based dielectric fluid

Problem: Leaking High Voltage Transmission Cables

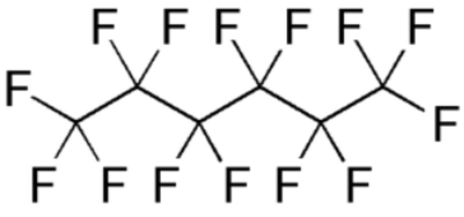
Photo curtesy of Pat Keelan – PFT Technology

Environmental, Safety, and Economic Problem!

Leak location detection is challenging, time consuming, and expensive.

How to Locate a Leak in a High Voltage Transmission Cable

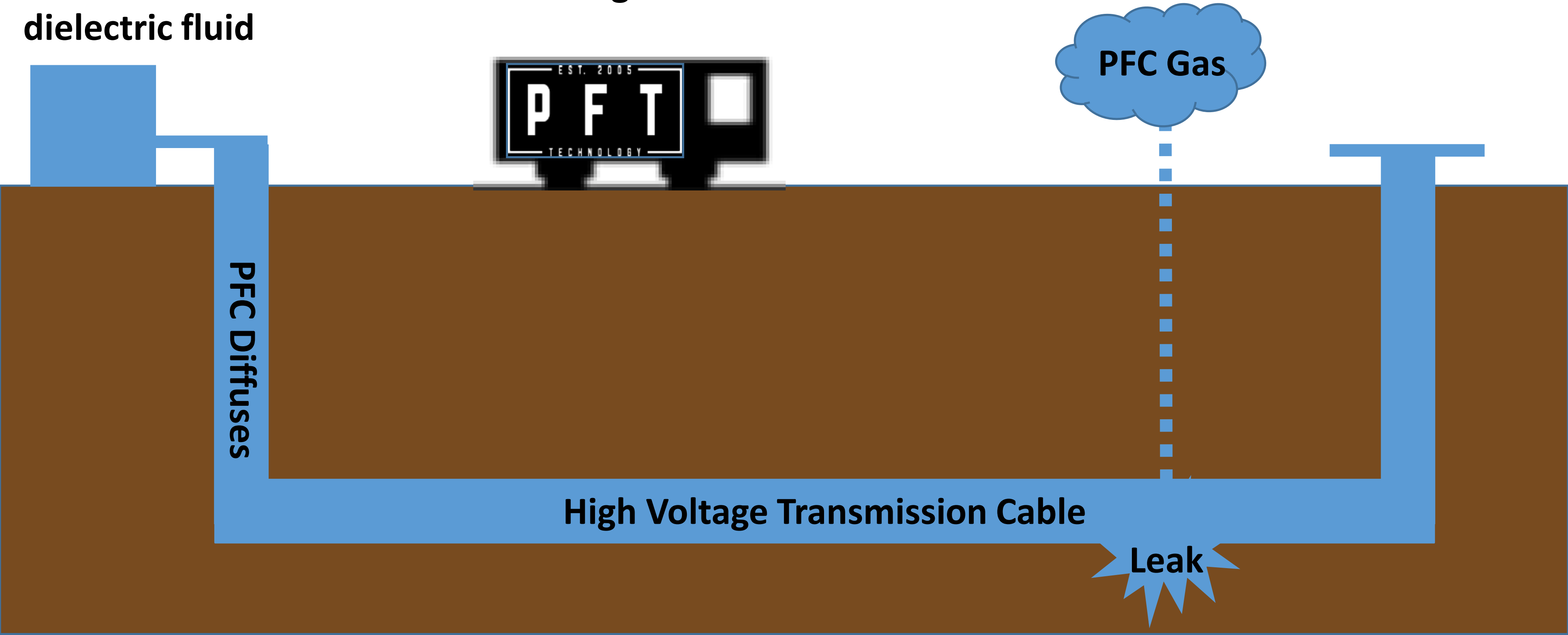
Perfluorocarbons (PFCs) are a tracer molecules that is easily detectable and unique unlike hydrocarbons



Chemical Structure of a PerFluorocarbon

Inject PFC into dielectric fluid

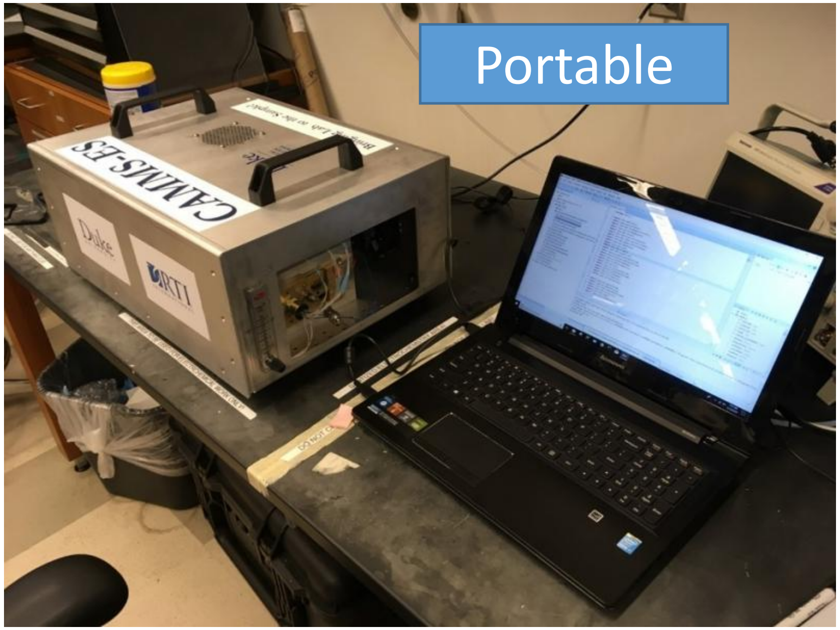
Drive along cable collecting air samples searching for PFC



Gas Chromatograph → Mass Spectrometer

Our portable mass spectrometer will be less expensive and more portable than PFT Tech's GC

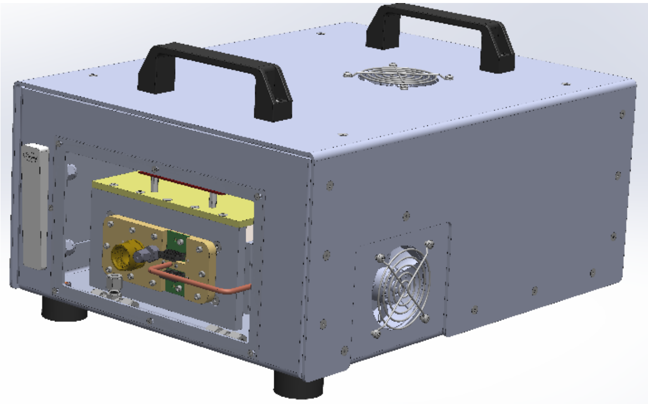
Example Wasson Gas Chromatograph like what PFT Technology Uses



Current Coded Aperture Miniature Mass Spectrometer – Environmental Sensing (CAMMS-ES) Prototype developed under a different project

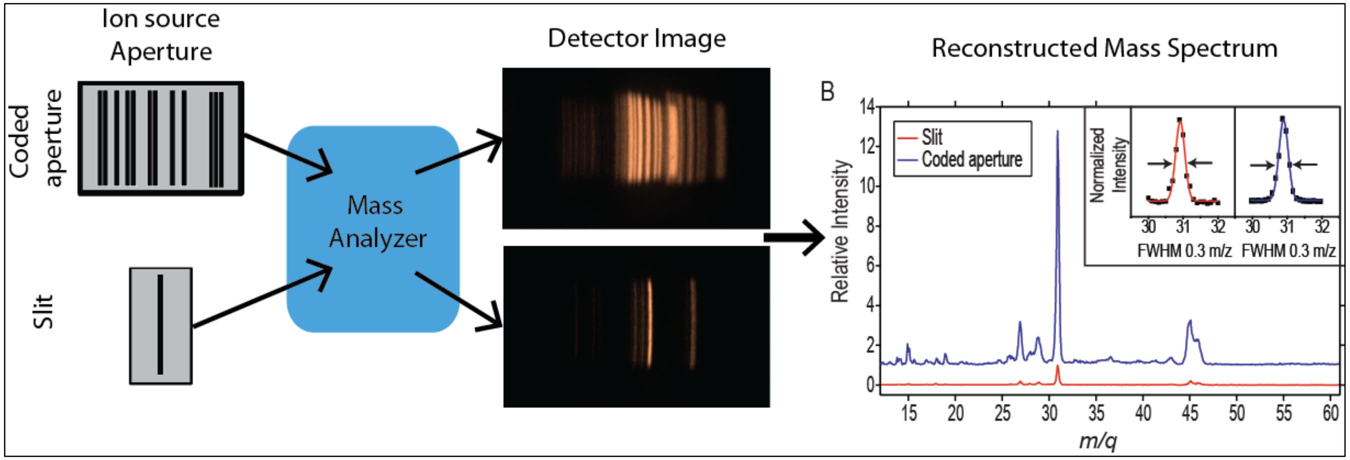
Duke's Mass Spec Core Technologies

Current Mass Spectrometer Prototype



Aperture coding allows for an increase in analyte throughput without sacrificing resolution. This improves our limit of detection.

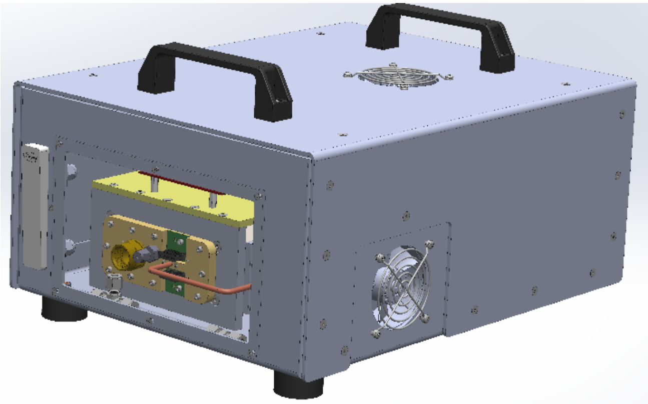
1) Aperture Coding



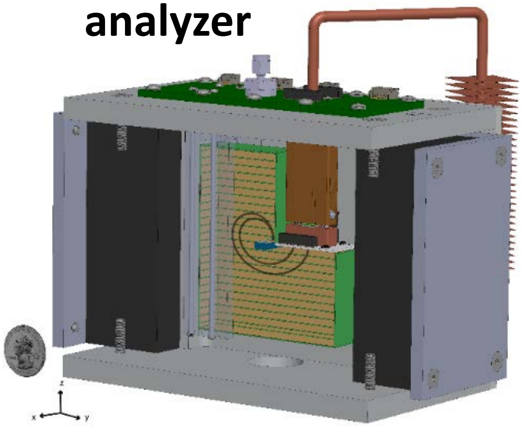
Amsden, Jason. J, et al. *J. Am. Soc. Mass Spectr.* **2018,** 29, (2), 360-372.

Duke's Mass Spec Core Technologies

Current Mass Spectrometer Prototype

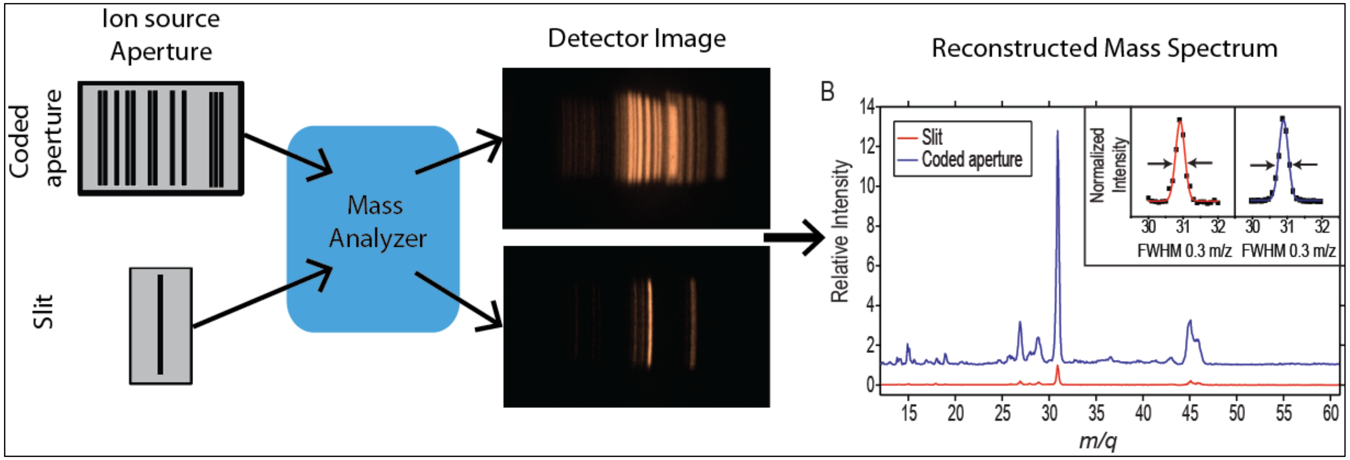


2) Cycloidal mass analyzer



Perpendicular electric and magnetic fields cause the ions to move in a cycloidal motion. Ions become separated by m/z as they travel from the ion source to the detector.

1) Aperture Coding



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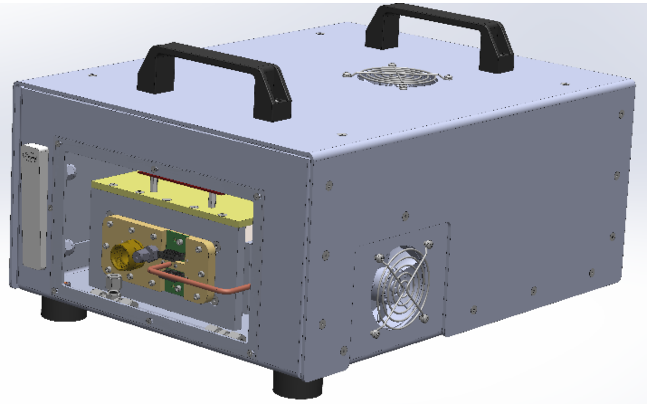
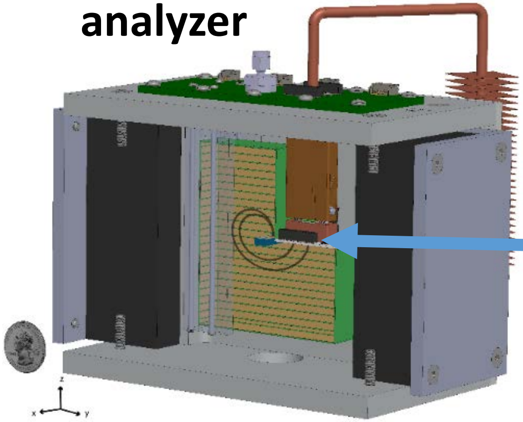
Duke's Mass Spec Core Technologies

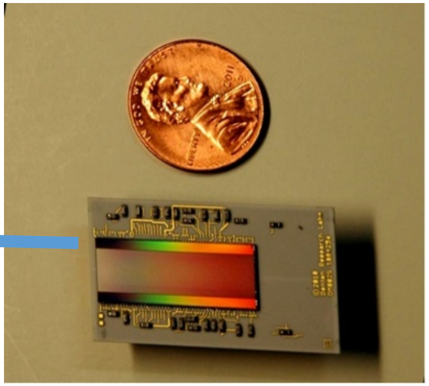
Current Mass Spectrometer Prototype



2) Cycloidal mass analyzer

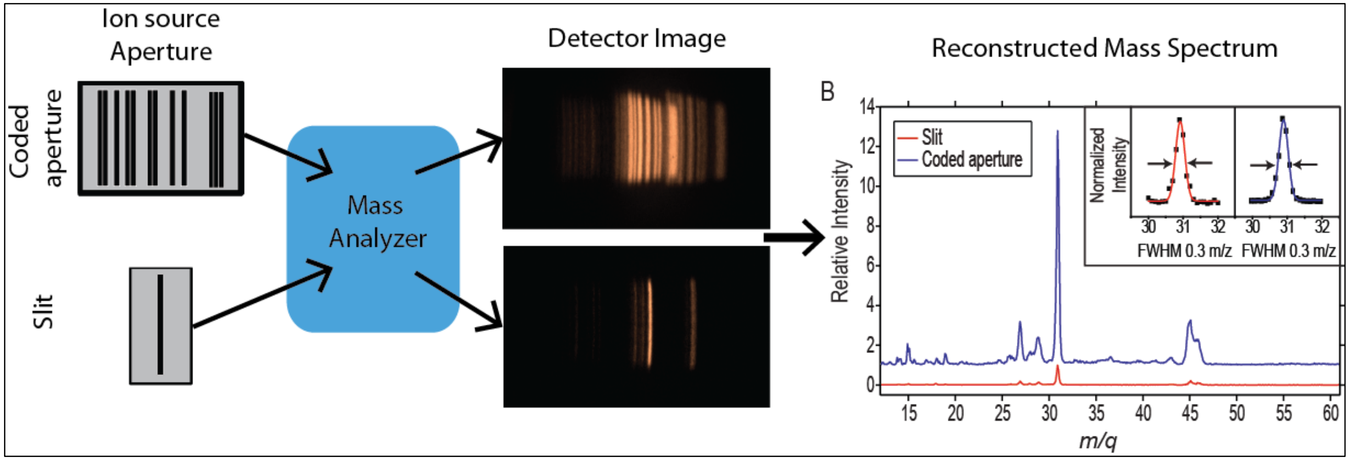


3) Focal plane array detector



M. Bonner Denton, et. al., *Analytical Letters*, 2011, 44: 6, 1050-1057

1) Aperture Coding



Faraday cup that allows for <u>simultaneous detection</u> of multiple chemical species with <u>high sensitivity</u>

Amsden, Jason. J, et al. *J. Am. Soc. Mass Spectr.* **2018,** 29, (2), 360-372.

Ionizing Perfluorocarbon Molecules

We have discussed:

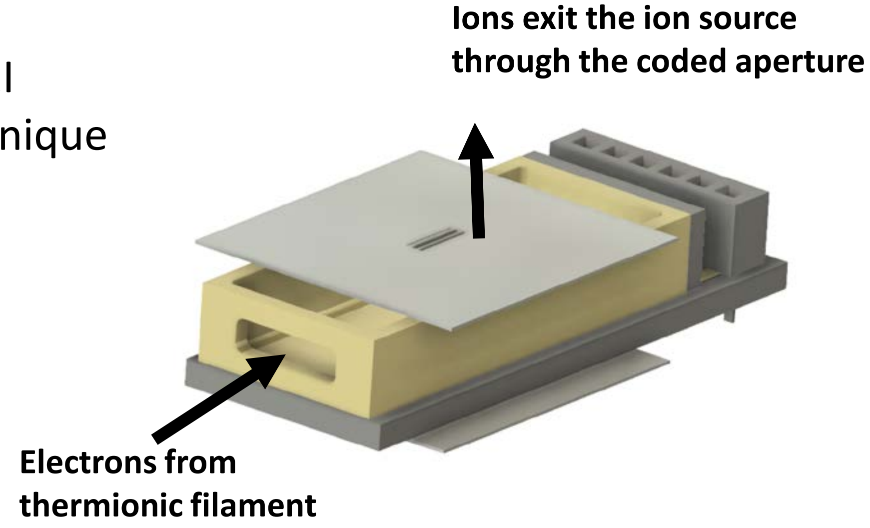
- The problem of leaking HVTC
- The leak detection solution of adding PFC tracers
- The need for a portable mass spectrometer to detect PFCs

Now, begin discussing the design process for a new instrument

The CAMMS instrument utilizes electron impact ionization (EI)

$$\mathrm{M} + \mathrm{e}^- \longrightarrow \mathrm{M}^{+\bullet} + 2\,\mathrm{e}^-$$

We needed to first make sure that we could use EI to ionize PFC and that the peak fragments were unique

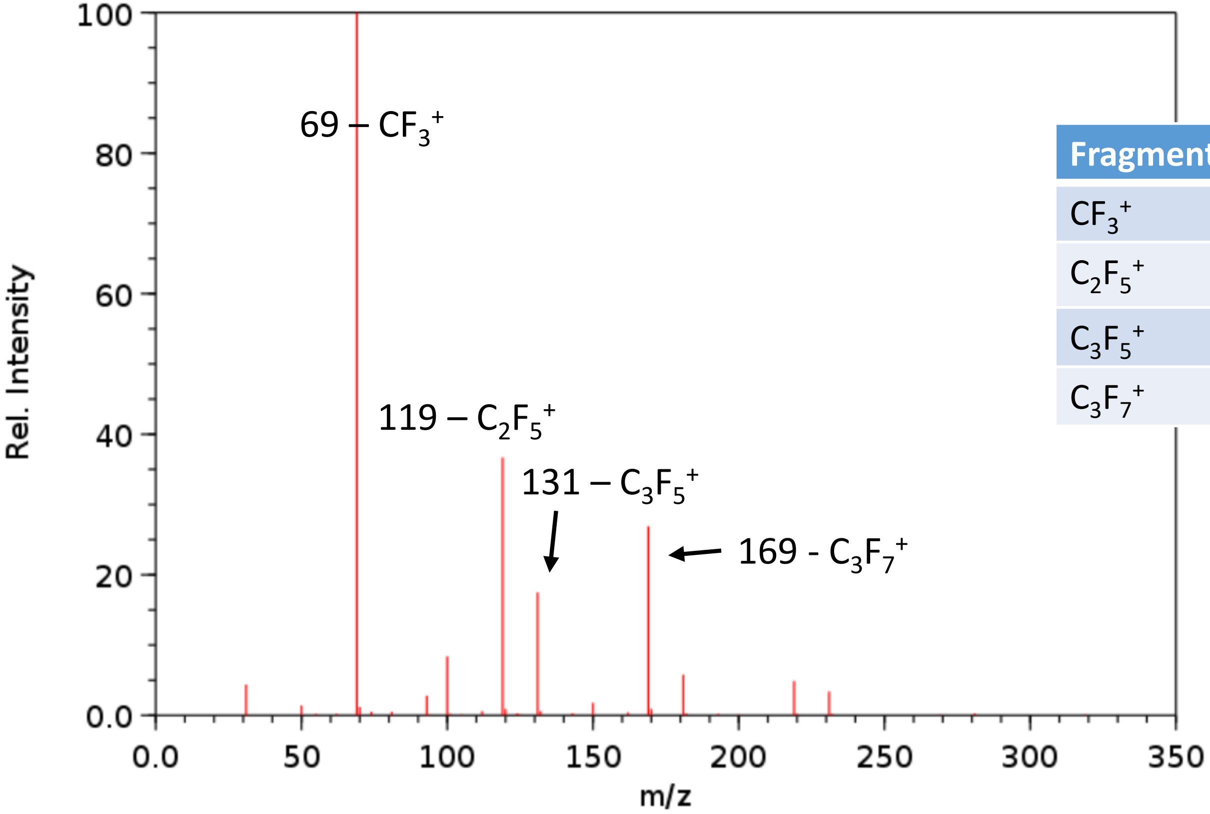


Perfluorocarbon Fragments

We studied the NIST EI spectrum of $\mathbf{C_6F_{14}}$, the molecule that PFT Tech uses and other PFCs

The PFC high intensity peaks are shown and a literature reviews showed that no other molecules shared a similar peak signature to PFC.

NIST Mass Spectrum of C_6F_{14}



https://webbook.nist.gov/cgi/cbook.cgi?ID=C355420&Mask=200#Mass-Spec

Fragment	m/z	Relative Intensity %
CF_3^+	68.9952	100
$C_2F_5^+$	118.9920	38
$C_3F_5^+$	130.9920	16
$C_3F_7^+$	168.9888	28

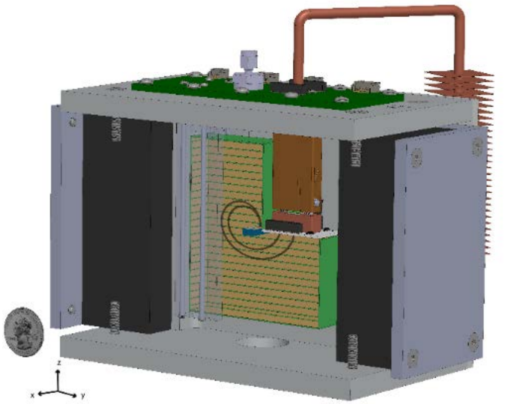
Decided to redesign the CAMMS instrument to detect PFCs using these fragment peaks

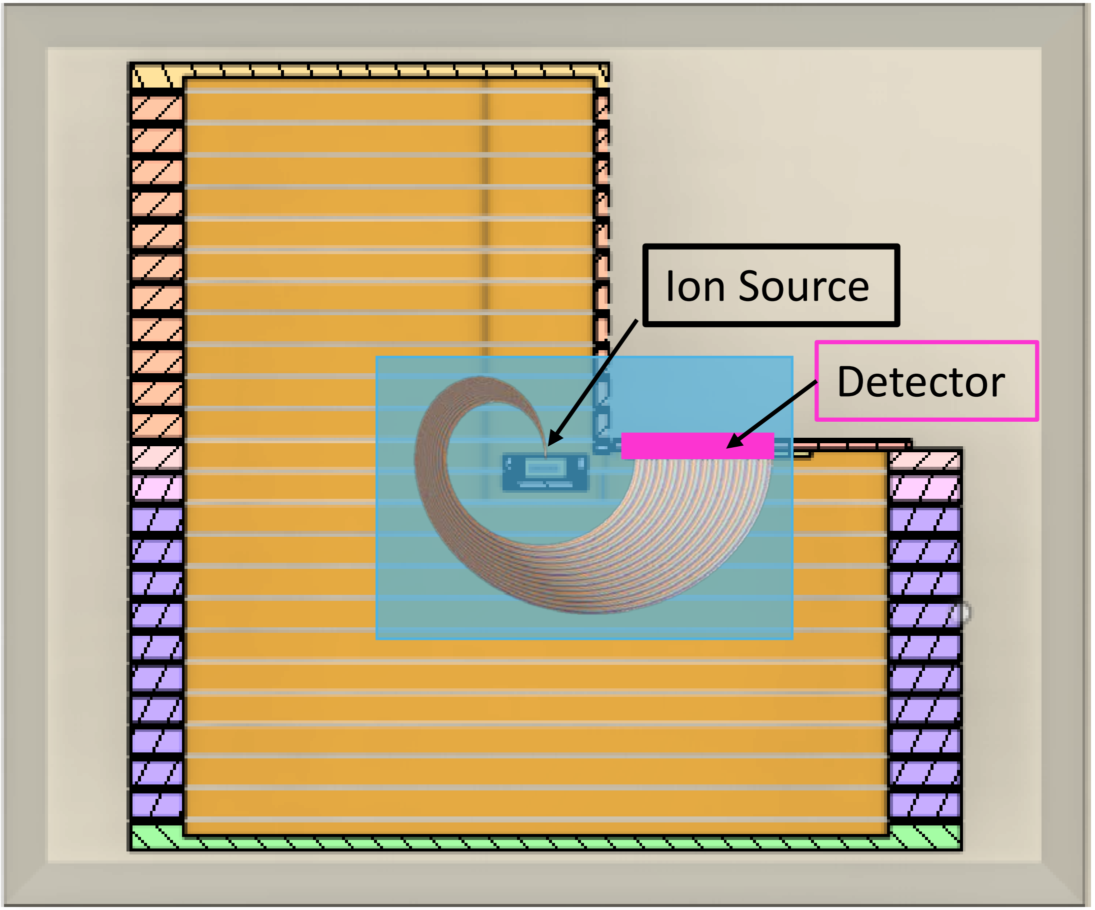
Design Criteria

Limit of detection target: 10 parts per billion

Resolution: 0.5 amu – only looking for PFC presence

Minimize weight and size for portability





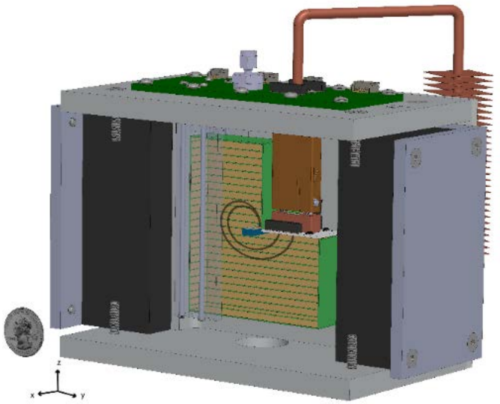
⊗ B-field direction

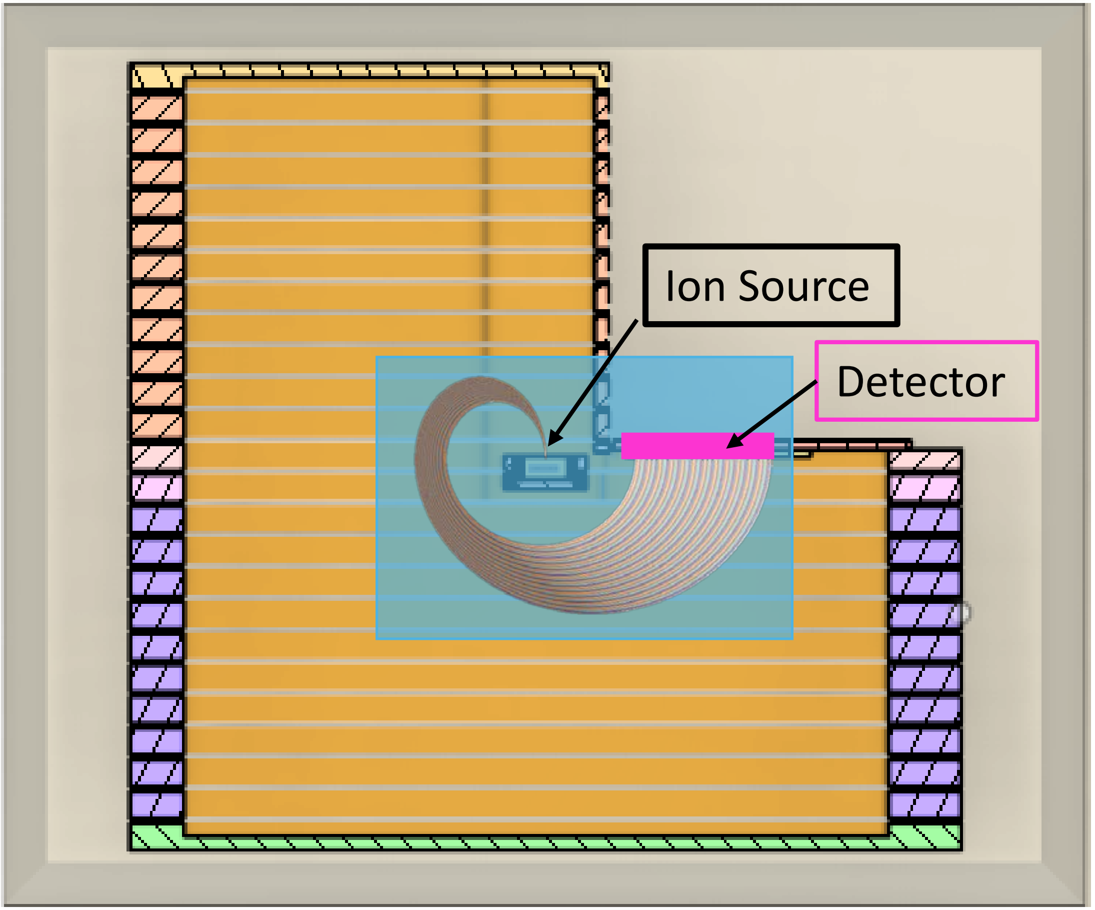
↓ E-field direction

Top-down view of electric sector and ion simulated ion trajectories

Design Criteria

Uniformity of the electric and magnetic fields are the most important design goals





Top-down view of electric sector and ion simulated ion trajectories

⊗ B-field direction

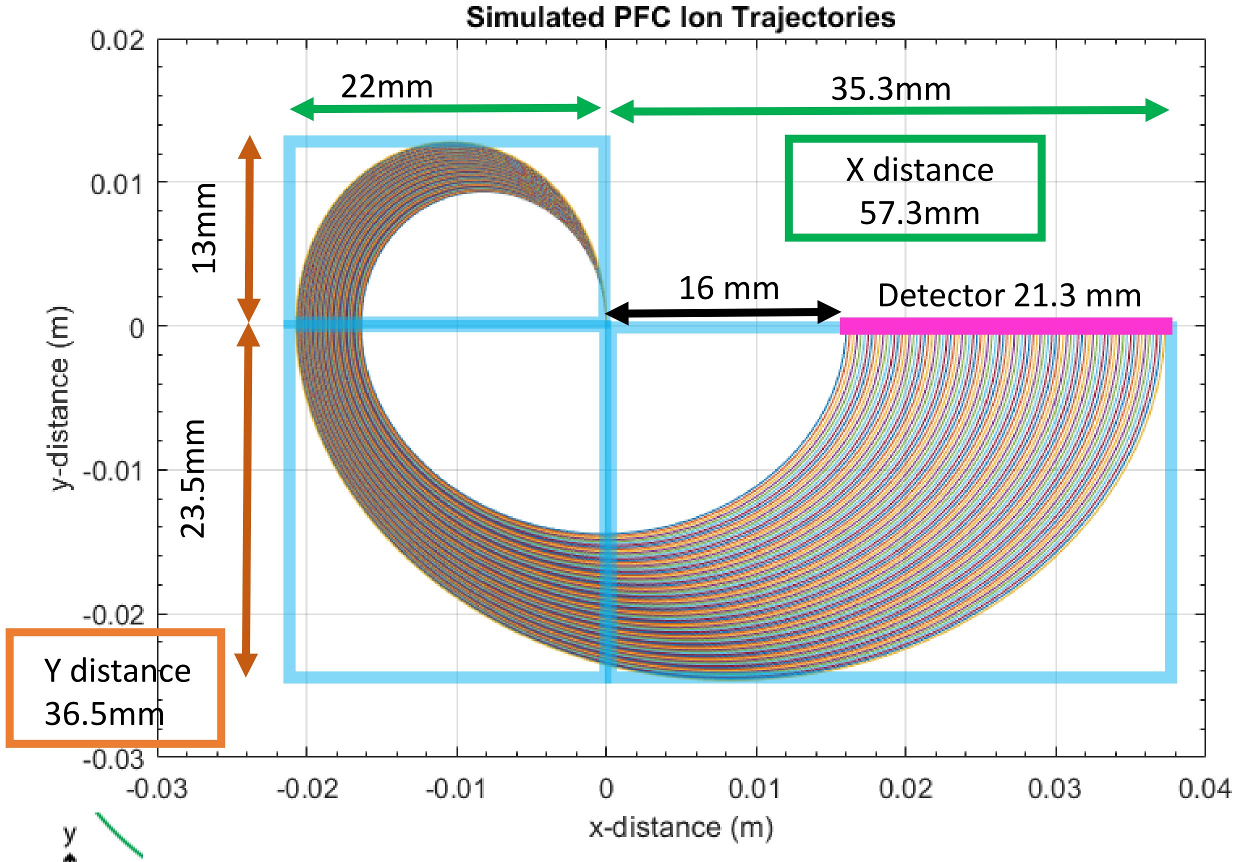
↓ E-field direction

Blue box signifies the necessary region of E-field and B-field uniformity

Uniformity must be < 1% across the region where the ions travel to ensure reproducible results

Redesigning the Mass Analyzer for PFC

The calculations of the PFC ion trajectories motivate the size and design of the mass analyzer. Magnetic sector is designed first (since it is solid state) and then the electric sector (since the potential is varied).



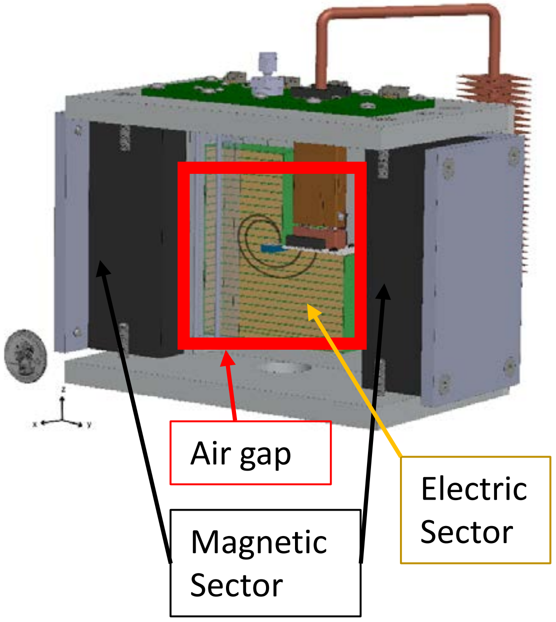
B = 0.7 T, **E** = 1881 V/m, **Ion Energy** = 50 eV, **Resolution** = 0.5 amu, **Mass range** = 59 – 170 amu

Classical Equation of Charged Particles

$$\left(\frac{m}{q}\right)a = E + v \times B$$

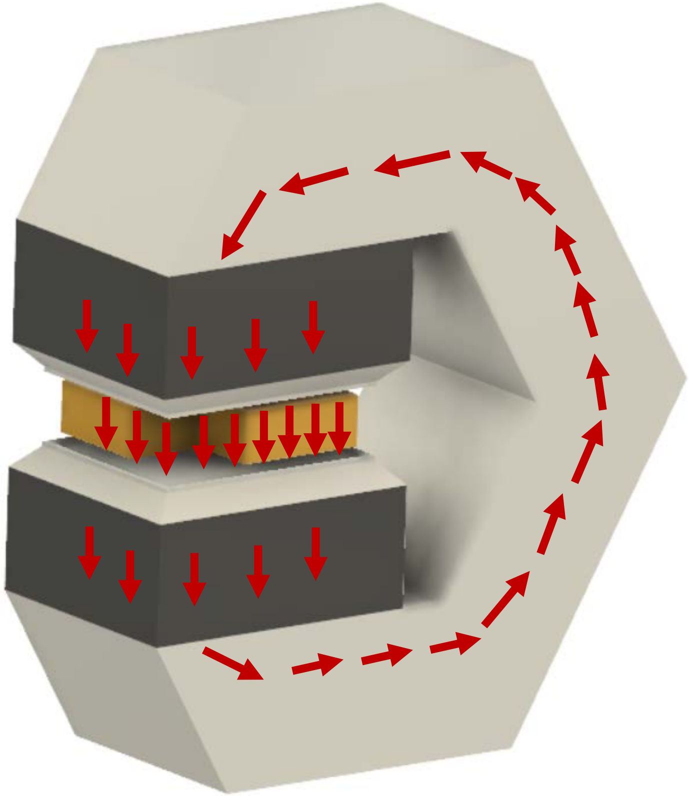
Pitch Distance

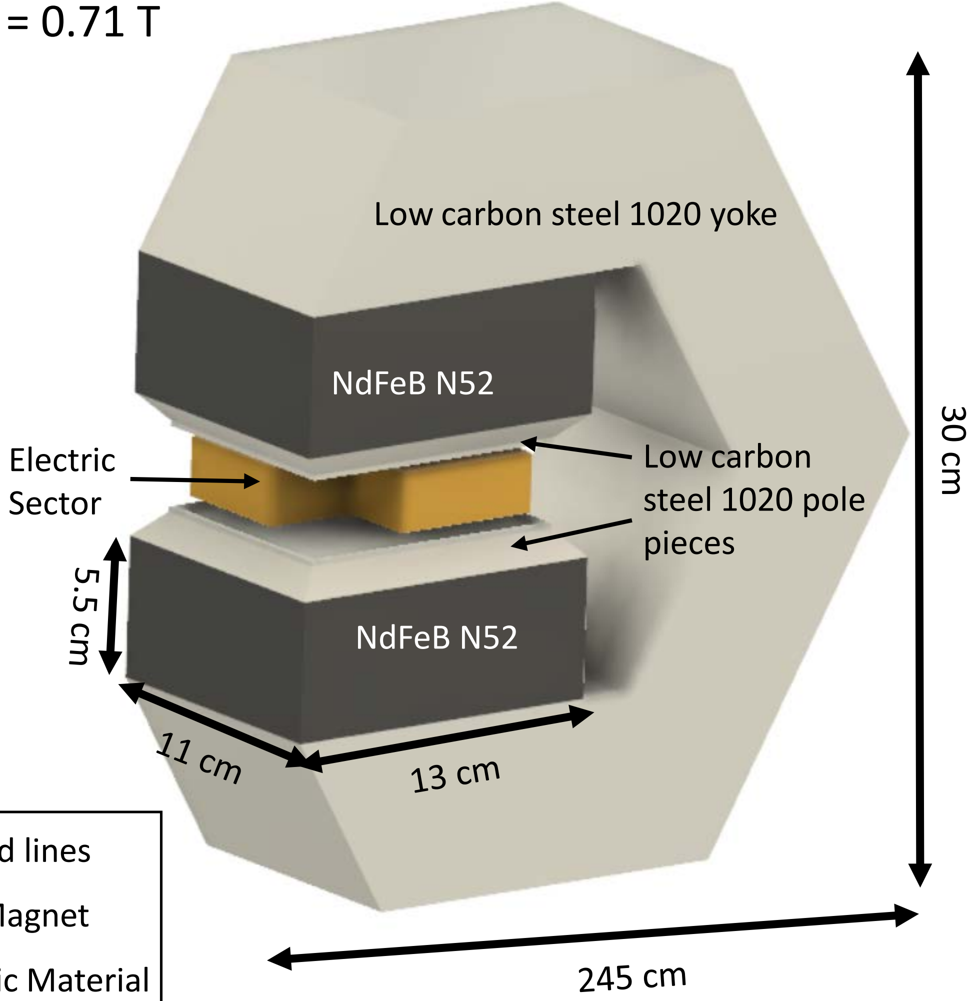
$$a_i = \frac{m_i}{z}\frac{2\pi E}{B^2}$$



Magnetic Sector Design

Magnetic Sector Design
B-field = 0.71 T





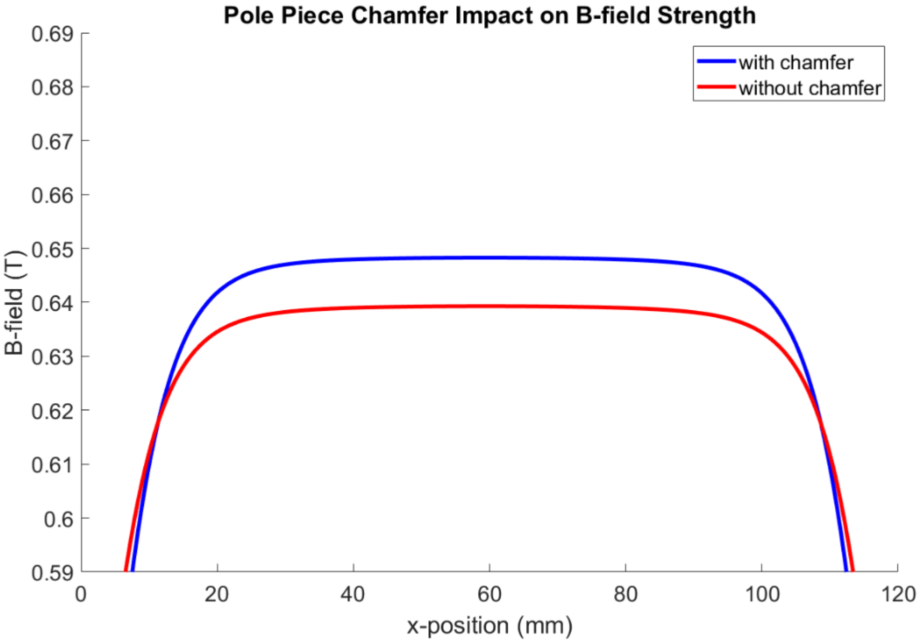
This design increases magnetic field in air gap and reduces leaked B-field

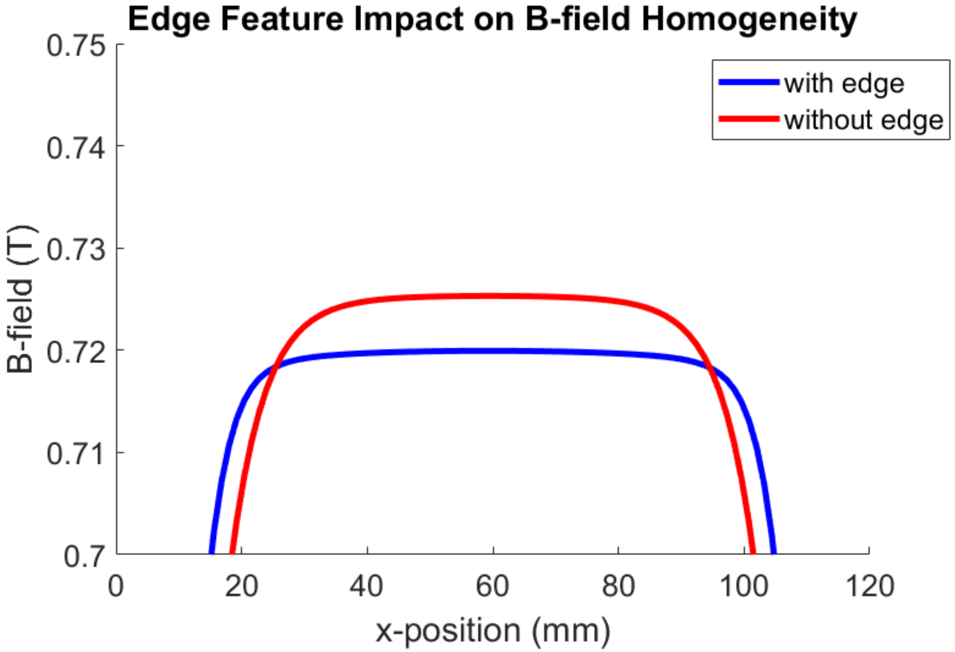
$$\vec{E} = -E\hat{y}$$
$$\vec{B} = -B\hat{z}$$

→	Magnetic field lines
■	Permanent Magnet
□	Yoke Magnetic Material
■	Electric Sector

Magnetic sector weighs ~45 lbs.

Design and B-field Uniformity





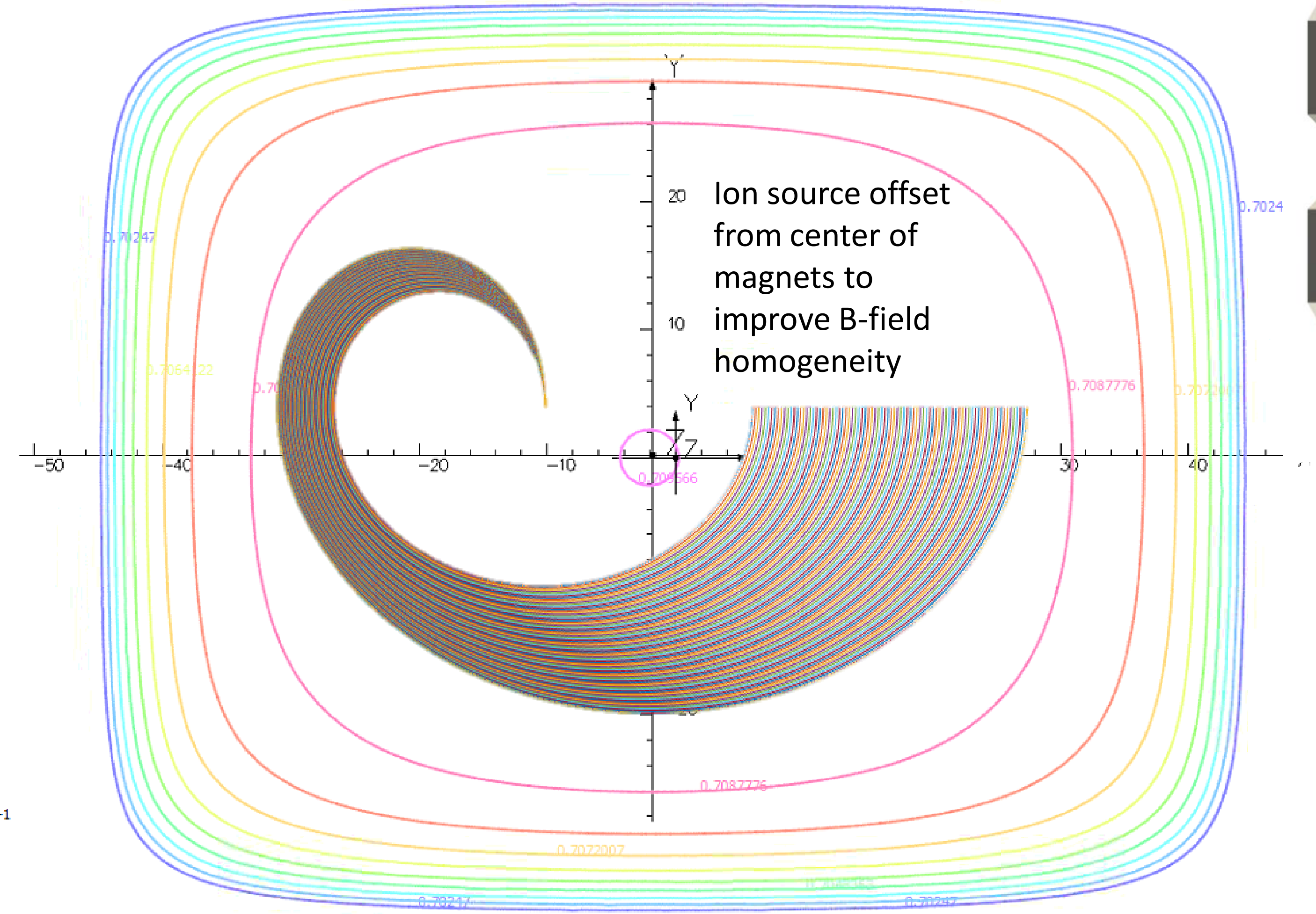
The chamfered pole piece increases the magnetic field strength

The edge pieces (or shimming rods) reduce the magnetic field strength but extend the uniformity of the region

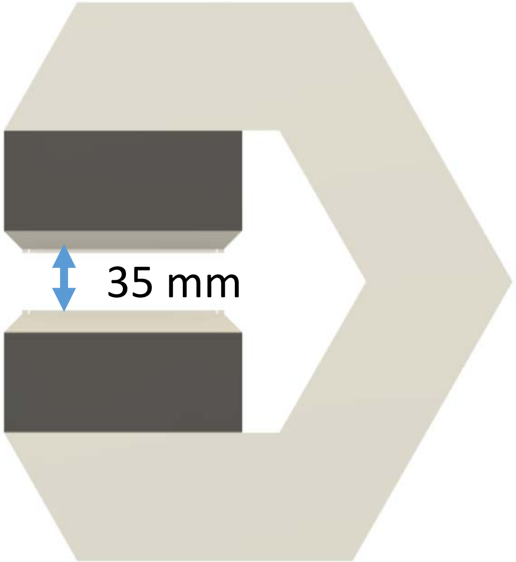
Magnetic Sector Homogeneity

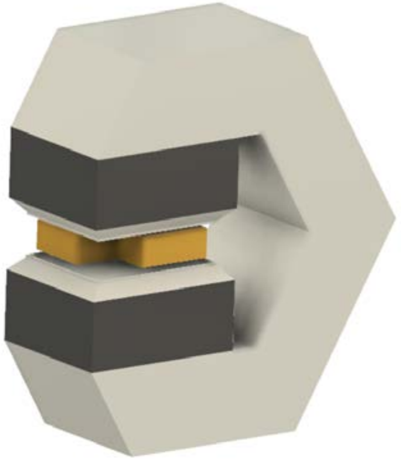
Region of uniformity for area of 80 mm (x-direction) by 60 mm (y-direction)

Max 0.71 T, showing map of region with < 1% B-field change



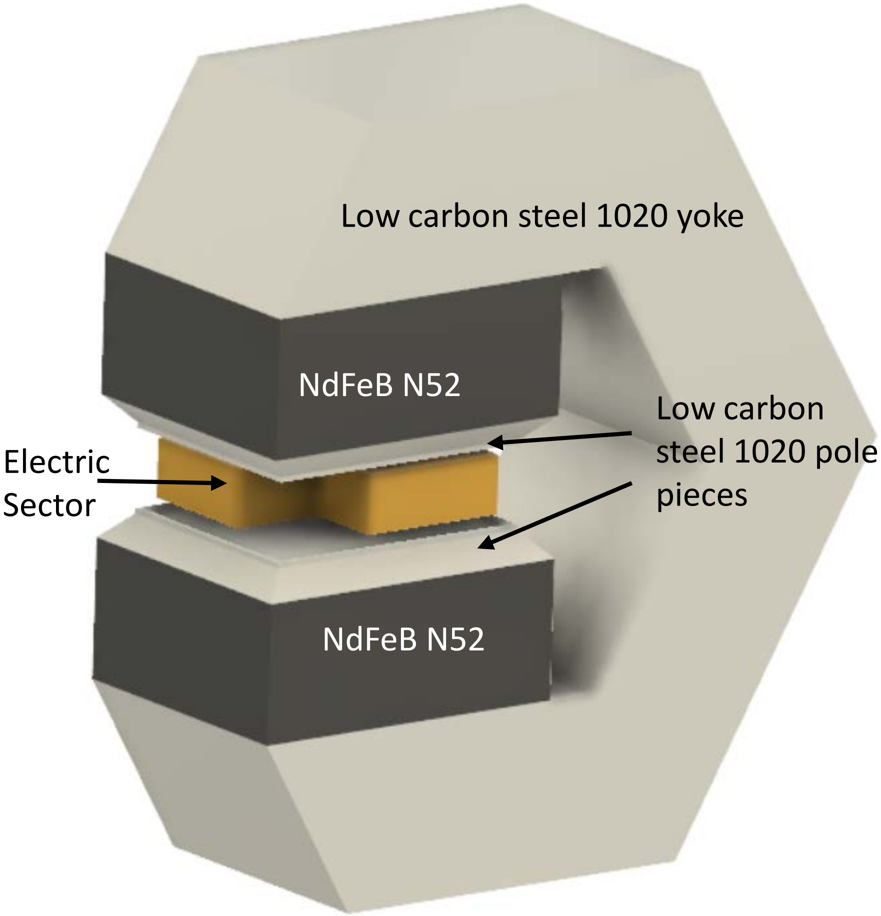
Ion source offset from center of magnets to improve B-field homogeneity

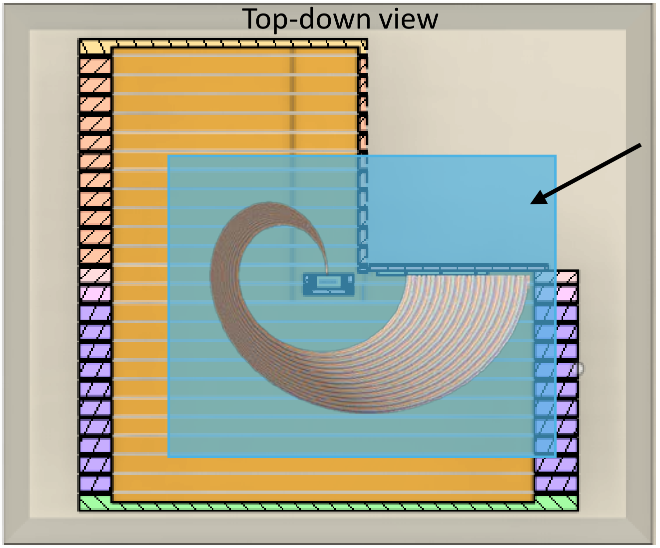




Mass Analyzer Design

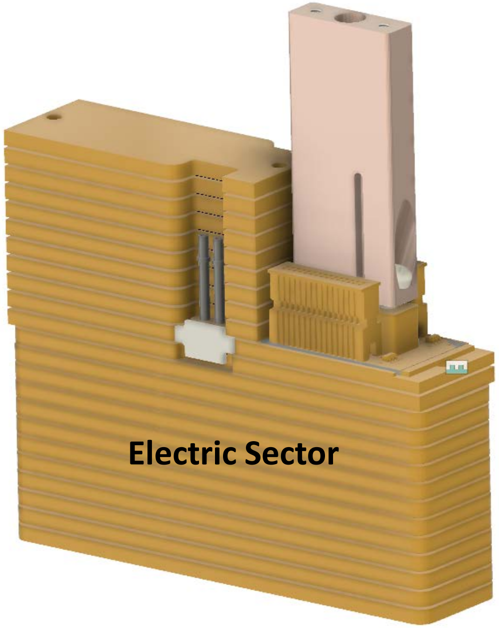
We are manufacturing the magnetic sector





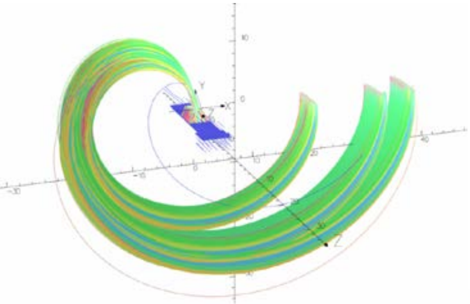
Necessary region of B-field homogeneity <1%

B-field is least uniform near the edges of the blue box

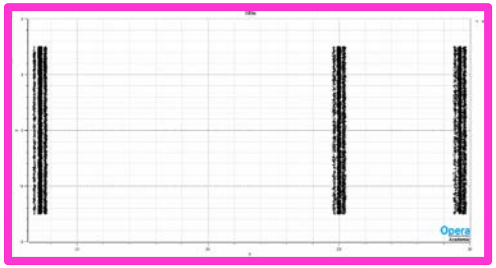


Electric sector is being designed to fit the air gap of the magnetic sector, the size of the ion trajectories, and improvements since the CAMMS design

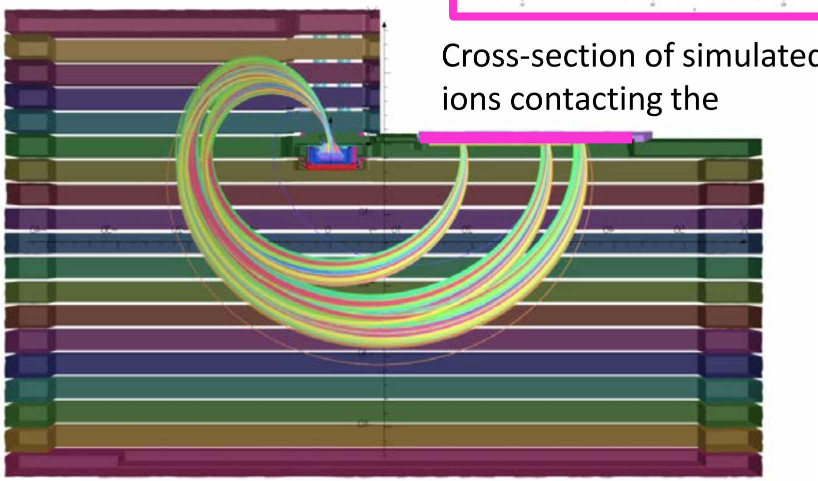
Mass Analyzer Design

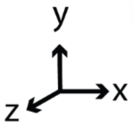


PFC 69, PFC 119, PFC 131amu



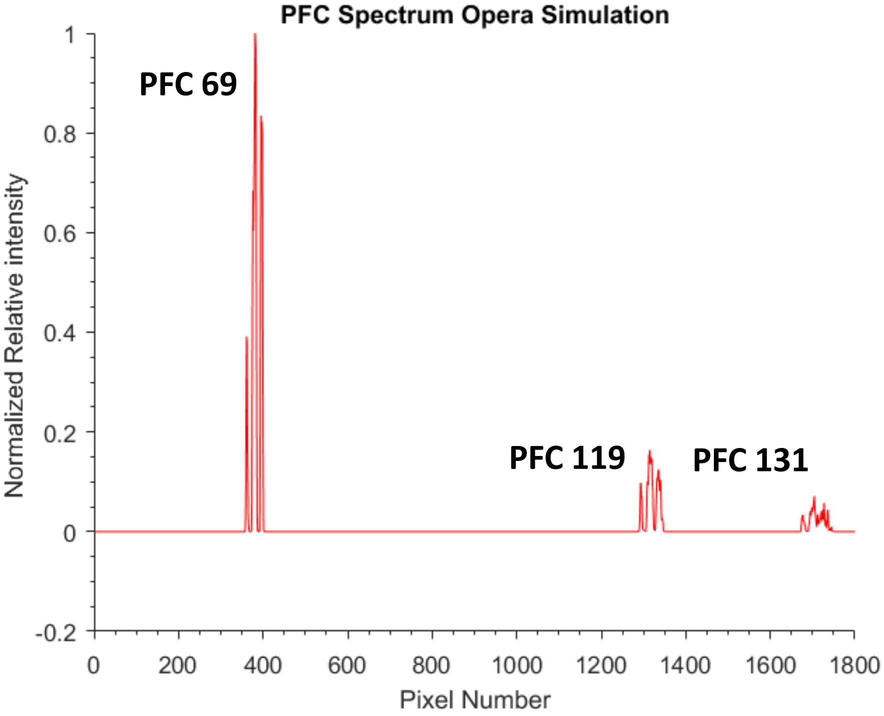
Cross-section of simulated PFC ions contacting the





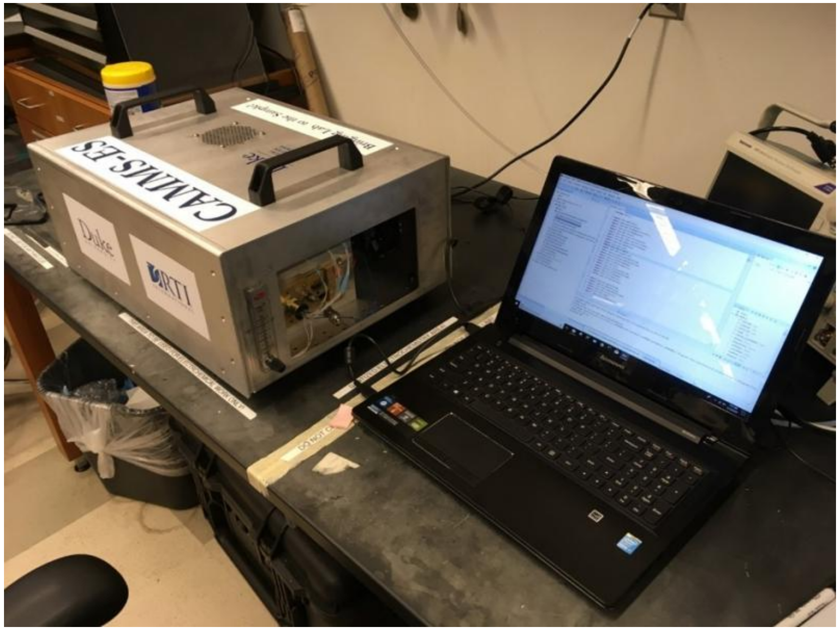
$$\vec{E} = -E\hat{y} = 1881.1\,V/m$$
$$\vec{B} = -B\hat{z} = 0.7T$$

Simulated PFC Mass Spectrum shows coded aperture image with 3-slits



Out of the Lab

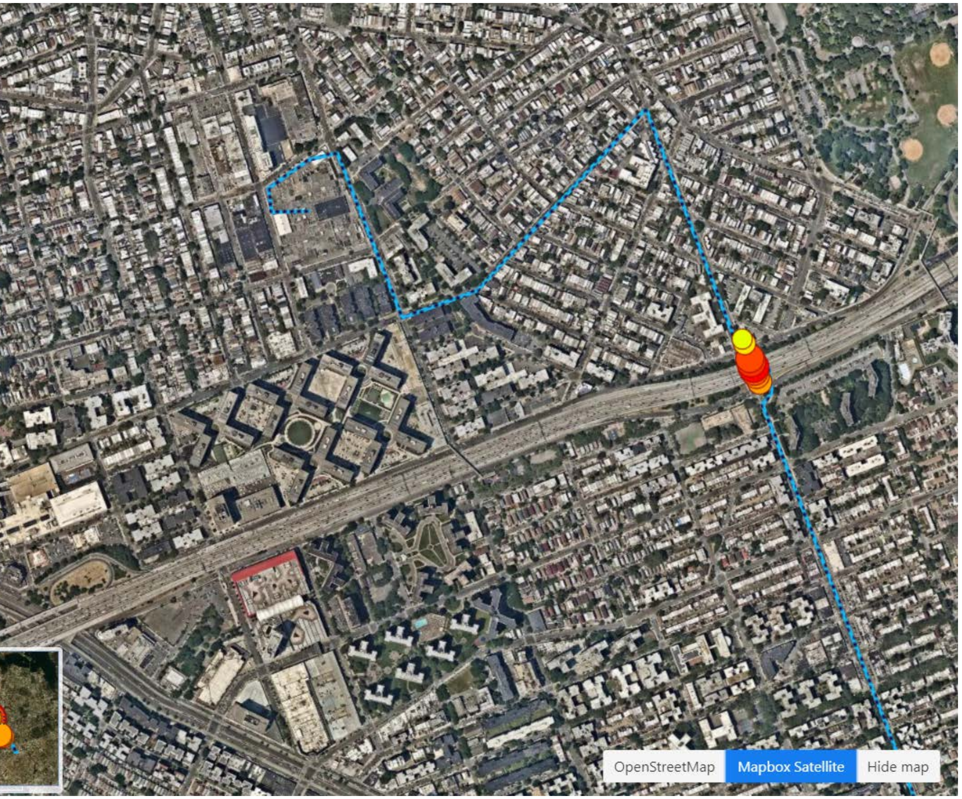
So, how do we take our lab instrument and turn it into a "smart," leak detector?

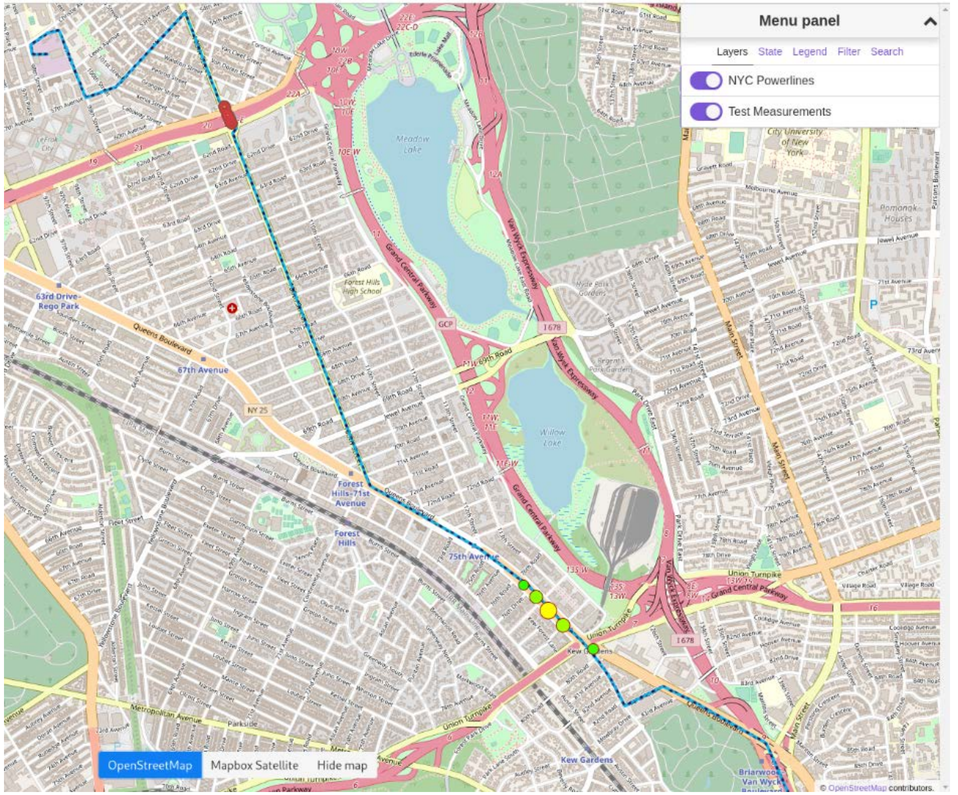


renci

RENCI Data Collection Software – Maps

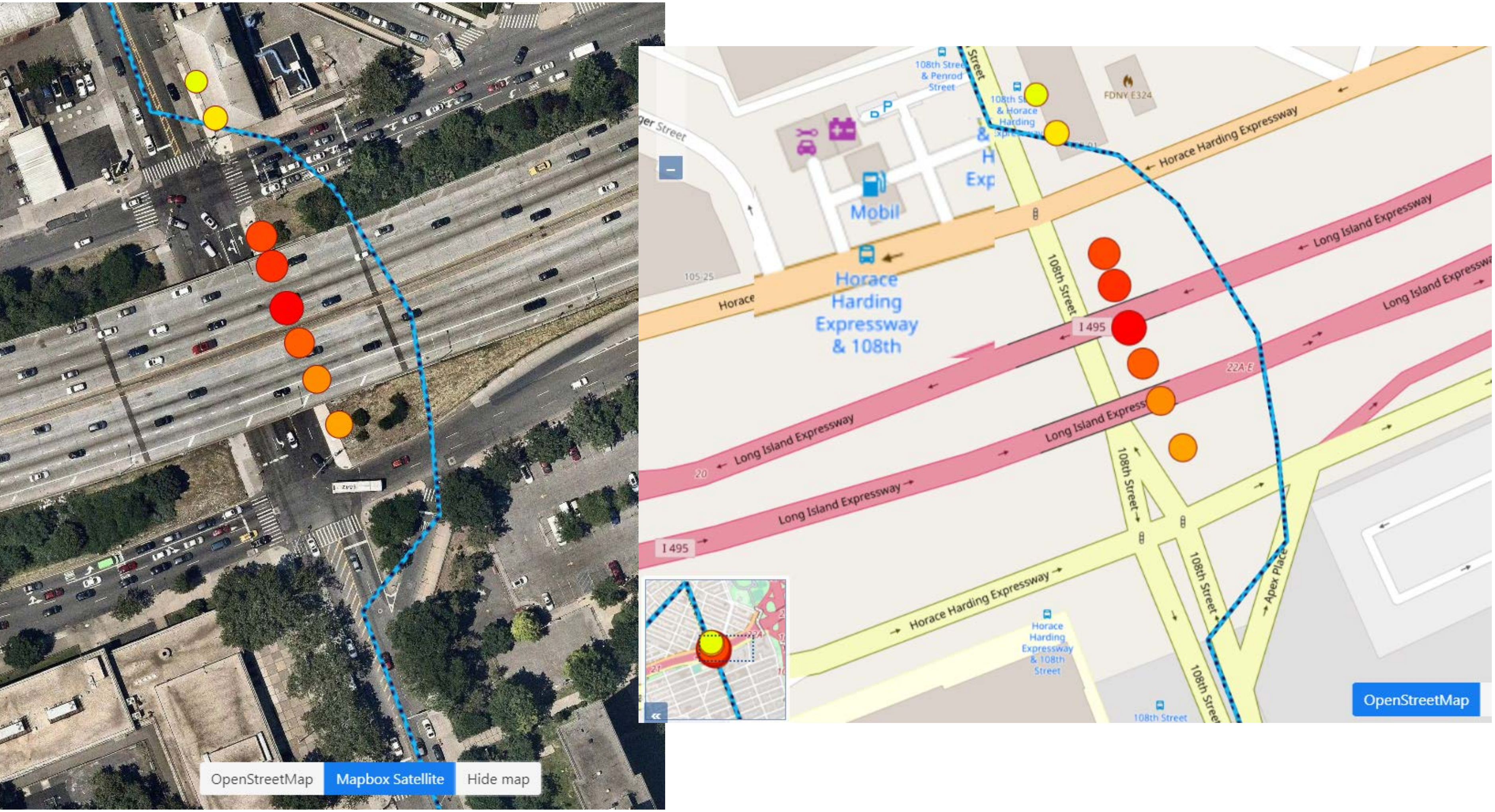
- RENCI combined multiple open-source frameworks and libraries to create a measurement collection software
- Overlay google maps (physical maps) with High Voltage Transmission Cables (HVTC) maps (or of other infrastructure)





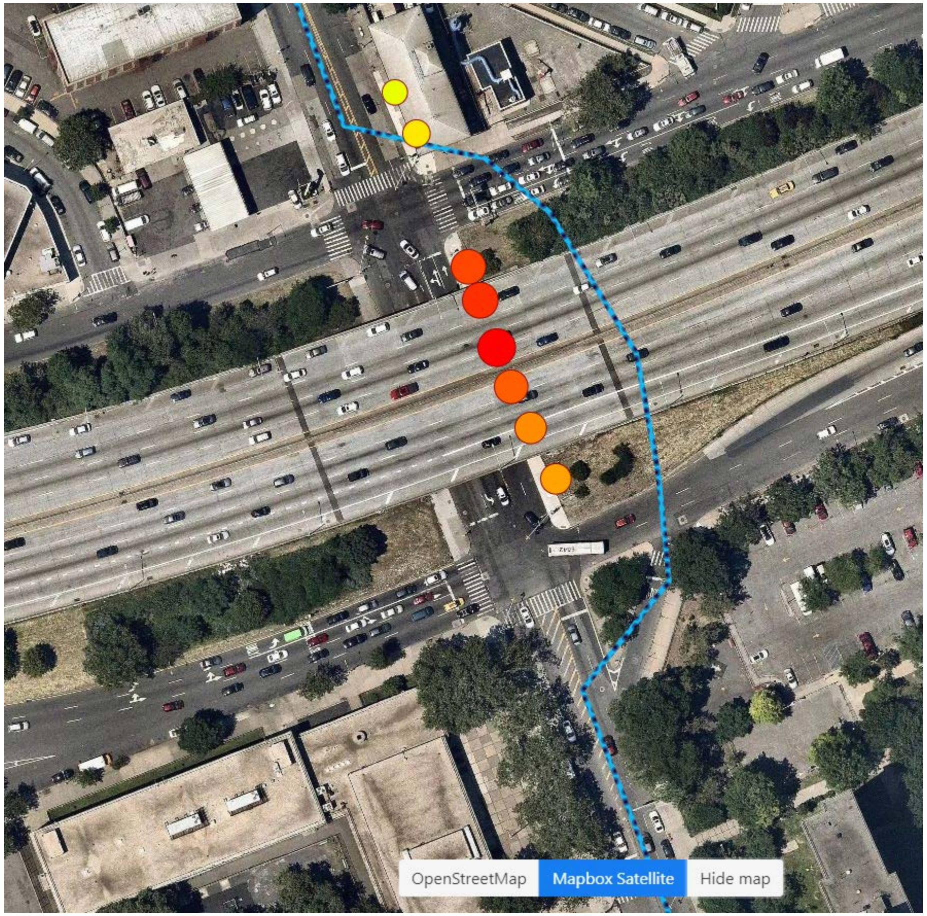
RENCI Data Collection Software – Data Points

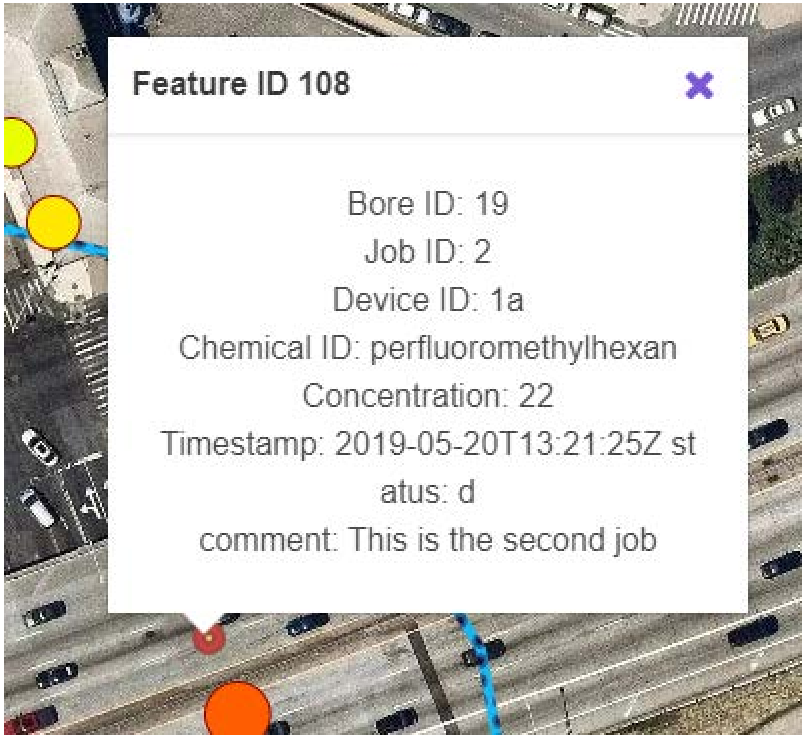
- Collect data points for PFC along HVTC



RENCI Data Collection Software – Data Points

- Data points will collect PFC concentration, GPS coordinates, time stamp, job information, and additional comments
  - Data points can be entered automatically (Connected to the mass spec) or entered manually

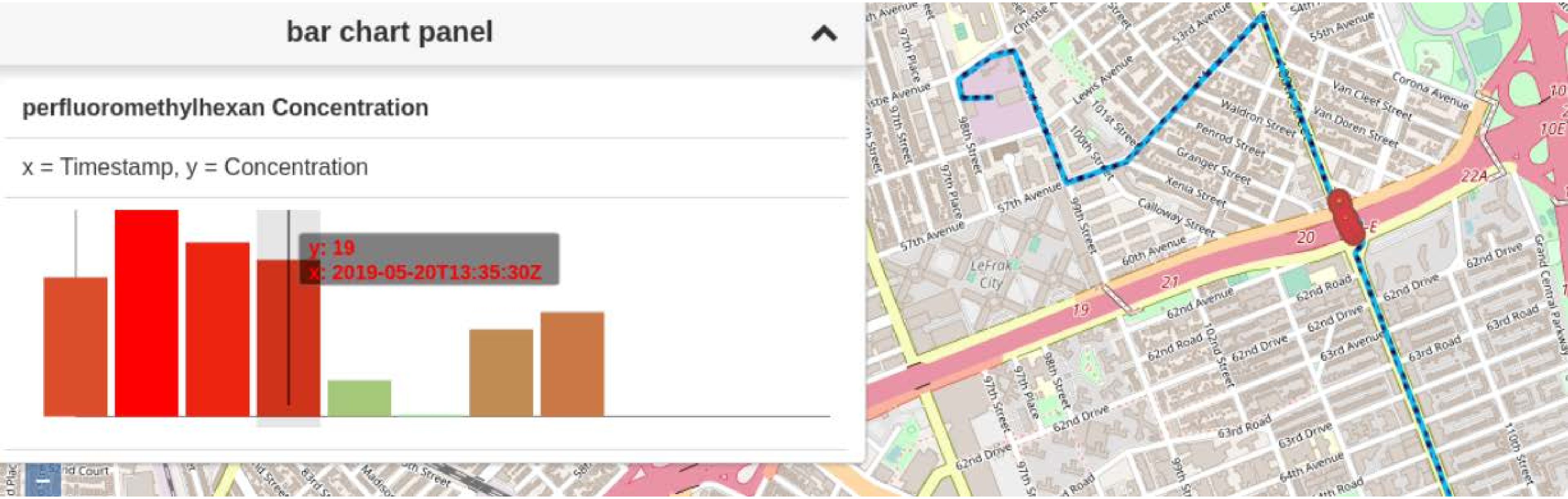




Bore ID: 19
Job ID: 2
Device ID: 1a
Chemical ID: perfluoromethylhexan
Concentration: 22
Timestamp: 2019-05-20T13:21:25Z st
atus: d
comment: This is the second job

RENCI Data Collection Software – Time Range

- Data points can also be used to reflect changes in PFC concentration over time (by filtering the time range for a specific region)



bar chart panel

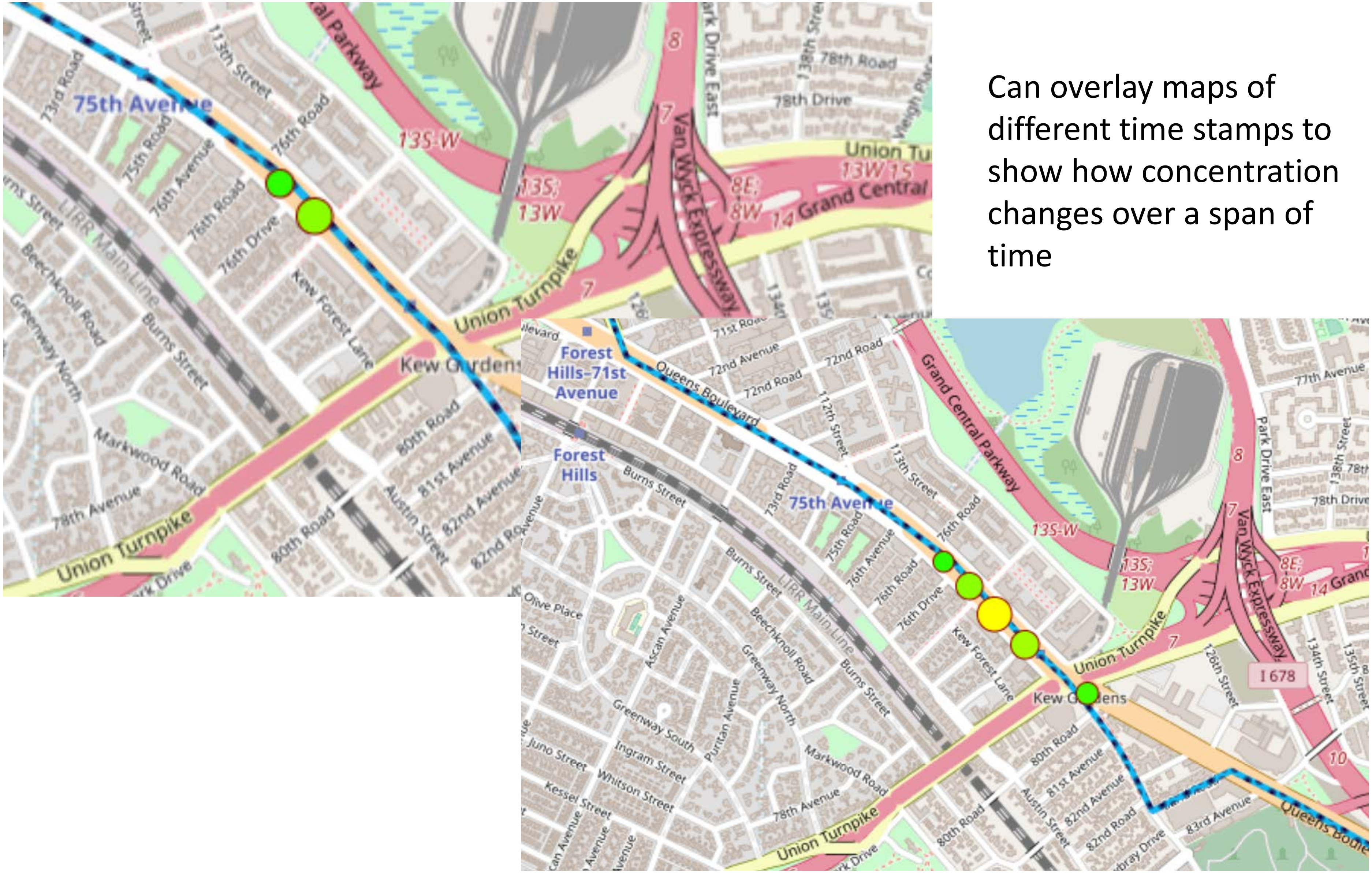
perfluoromethylhexan Concentration

x = Timestamp, y = Concentration

y: 19
x: 2019-05-20T13:35:30Z

Bar chart showing the relative concentrations of the PFC at the various sample collection locations over time

RENCI Data Collection Software – Time Range



Can overlay maps of different time stamps to show how concentration changes over a span of time

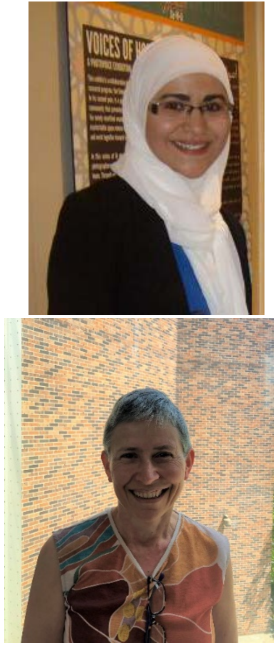
Field Testing Plan

- Fall 2019 – go to NYC and test software alongside PFT Tech and their GC
- Spring 2020 – local hardware field test on Duke's campus
- Summer 2020 – go to NYC and test the new mass spectrometer hardware and software package alongside the PFT Tech's gas chromatograph
- If field testing goes well, we will market the technology to PFT Tech's customers, utility providers who would benefit from our mass spectrometer and improved PFC detection

Conclusions

- Discussed the problem of leaking high voltage transmission cables
    - Estimated $2 billion annual problem worldwide
- Discussed how a portable mass spectrometer could be used to detect perfluorocarbon tracers for this application
- Talked about how I’ve been designing the new mass analyzer
- Detailed our plans to test the mass spectrometer in the **Harsh Environment** of New York City along with it’s software package

Thank you!



Thank you Dr. Jason Amsden and Dr. Jeff Glass for their guidance and support!

Contact me at klh93@duke.edu

Funding Agencies:

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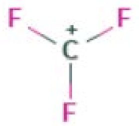
Other Molecules with Peaks Near PFC Fragments

69 amu – CF_3^+



68.99	CH3ClF
68.99	AlNNN
68.99	MeF..Cl anion
68.99	Trifluoromethyl cation
69.00	Trifluoromethyl radical
69.00	CF3 anion
69.00	Beryllium carbonate
69.00	Ammonium hypochlorite
69.00	hydroxylammonium chloride
69.00	FCCCN+
69.00	2-Propynenitrile, 3-fluoro-
69.00	c-LiOONO
69.00	t-LiOONO
69.00	lithium nitrate
69.01	NNBeO2
69.02	tetrazolide anion
69.02	Isoxazole
69.02	Oxazole
69.02	vinyl isocyanate
69.02	Acetyl cyanide
69.02	Propiolamide

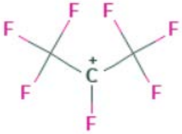
119 amu – $C_2F_5^+$

118.94	Acetonitrile, bromo-
118.98	Chloroacetyl isocyana
118.99	2-Thiazolidinethione
119.00	2-Butynenitrile, 4,4,4-trifluoro-
119.00	Methanesulfonylacetonitrile
119.02	Acetic acid, nitro-, methyl ester
119.04	Benzene, isocyanato-
119.04	Cyanic acid, phenyl ester
119.04	2,1-Benzisoxazole
119.04	1,2-Benzisoxazole
119.04	Benzoxazole
119.04	Benzonitrile, 2-hydroxy-
119.04	Benzonitrile, 4-hydroxy-
119.04	Benzonitrile, 3-hydroxy-
119.04	Benzonitrile, N-oxide
119.04	Acetamide, N-(β-mercaptoethyl)-
119.05	5-Azabenzimidazole
119.05	Benzene, azido-
119.05	1H-Benzotriazole

131 amu – $C_3F_5^+$

130.99	Sodium tetrafluoroberyllate(ii)
130.99	2(3H)-Thiazolethione,3-methyl-
130.99	Allyl, pentafluoro-, radical
131.00	H2O..CF3CO2 anion
131.00	1,1,1-Trifluoro-N-methyl methanesulfenamide
131.00	(H2O)2..MeSO3 anion
131.00	Ethoxycarbonyl isothiocyanate
131.00	Methyl 2-isothiocyanatoacetate
131.01	(FCH2)2CHOH..Cl anion
131.01	Methyl(trifluoromethyl) phosphinic acid amide
131.01	1,2,3-trifluorophenide anion
131.01	1,2,4-trifluorophenide anion
131.01	1,3,5-trifluorophenide anion
131.01	3-Chloro-tetrahydro-furan-2-carbonitrile

169 amu – $C_3F_7^+$

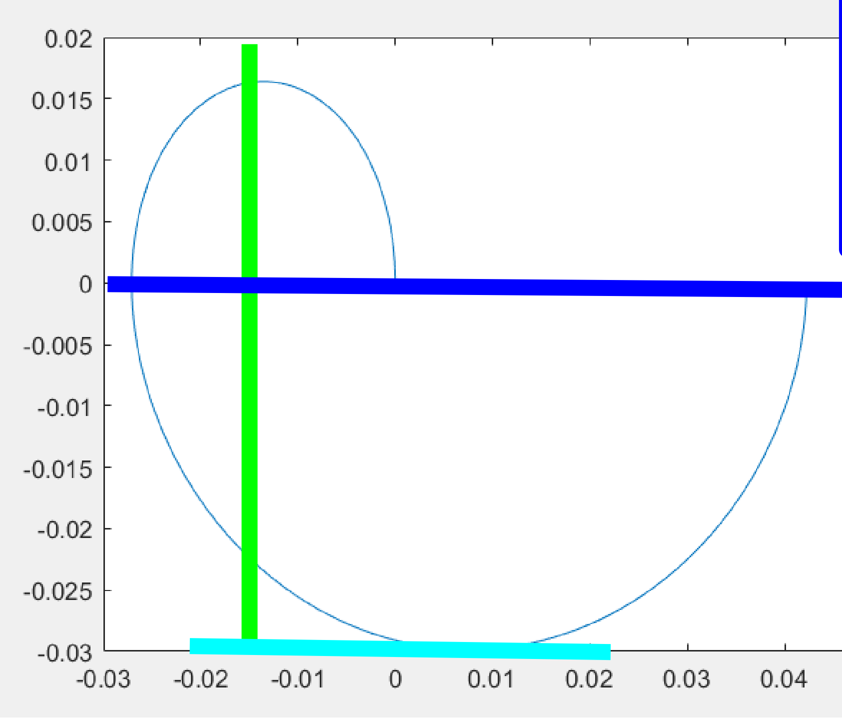


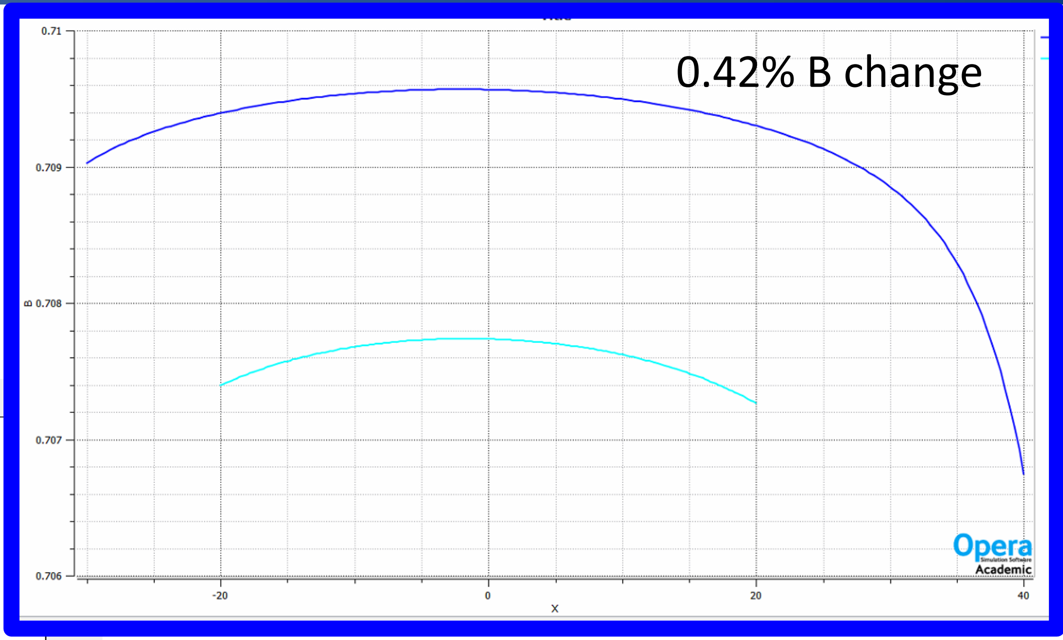
168.98	4-Chlorophenyl isothiocyanate
168.98	3-Chlorophenyl isothiocyanate
168.98	2-Chlorophenyl isothiocyanate
168.98	Benzothiazole, 2-chloro-
168.98	Methane, fluorotrinitro-
168.99	2-Amino-5-trifluoromethyl-1,3,4-thiadiazole
168.99	2(3H)-Benzoxazolone, 6-chloro-
168.99	Chlorzoxazone
169.00	Pyridine, pentafluoro-
169.01	2-Chloro-6-fluorobenzyl cyanide
169.02	Methyl 4-nitrophenyl sulphide
169.03	Carbamic chloride, methylphenyl-
169.03	o-Chloroacetanilide
169.03	Acetamide, N-(4-chlorophenyl)-
169.03	Acetamide, N-(3-chlorophenyl)-
169.03	Phosphoramidothioic acid, O,O-diethyl ester
169.04	Phenol, 4-methoxy-2-nitro-
169.04	4-Nitroguaiacol
169.04	4-Hydroxy-3-nitrobenzyl alcohol
169.04	3,4,5-Trihydroxybenzamide

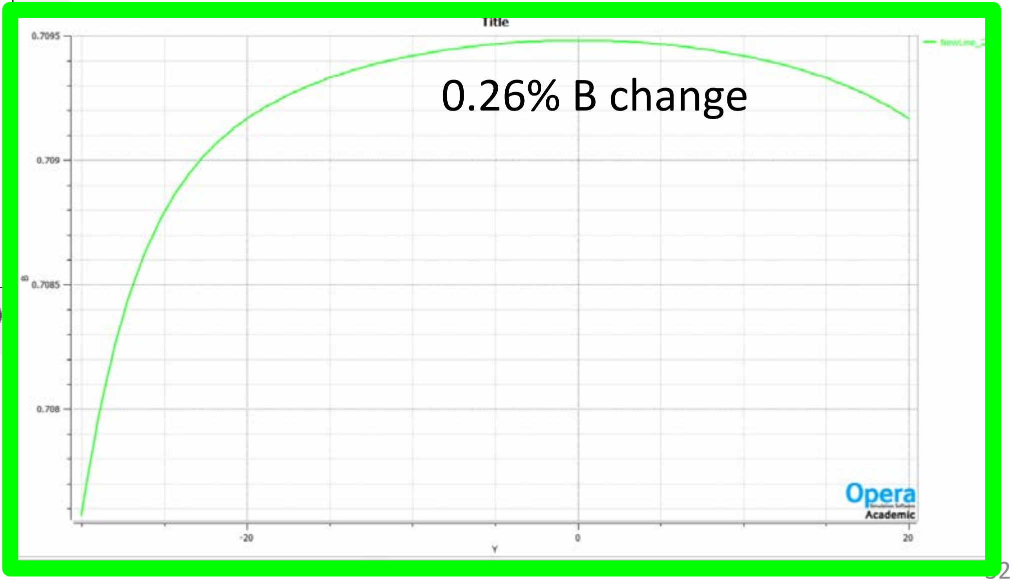
Magnetic Field Uniformity

For mass of 169 (largest peak we are target

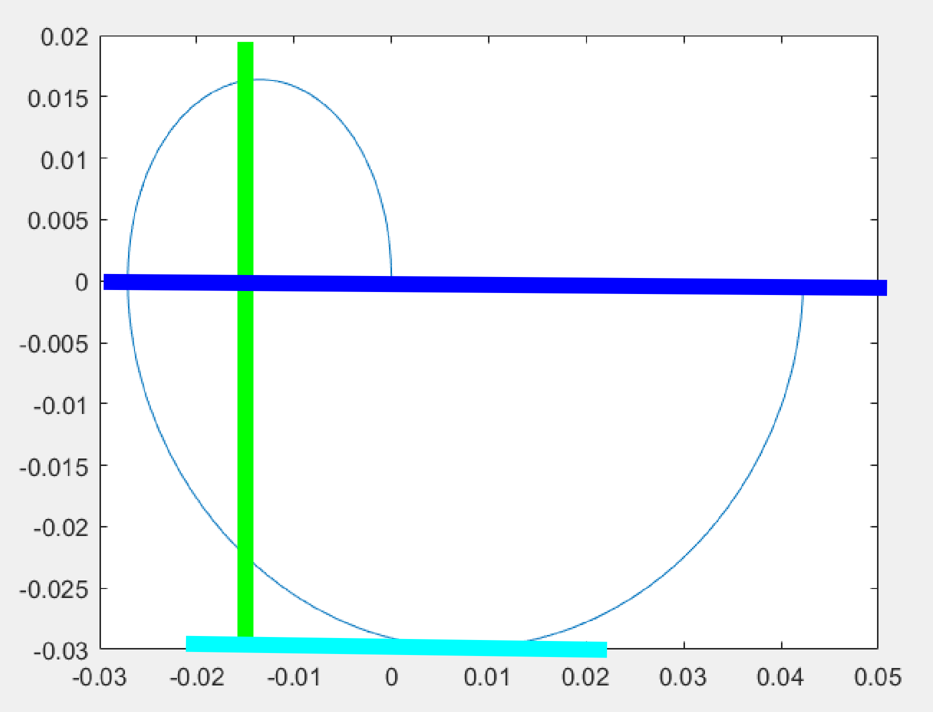
x_distance = 53.45 +20 = 73.45mm
y_distance = 46.235 +20 = 66.23mm

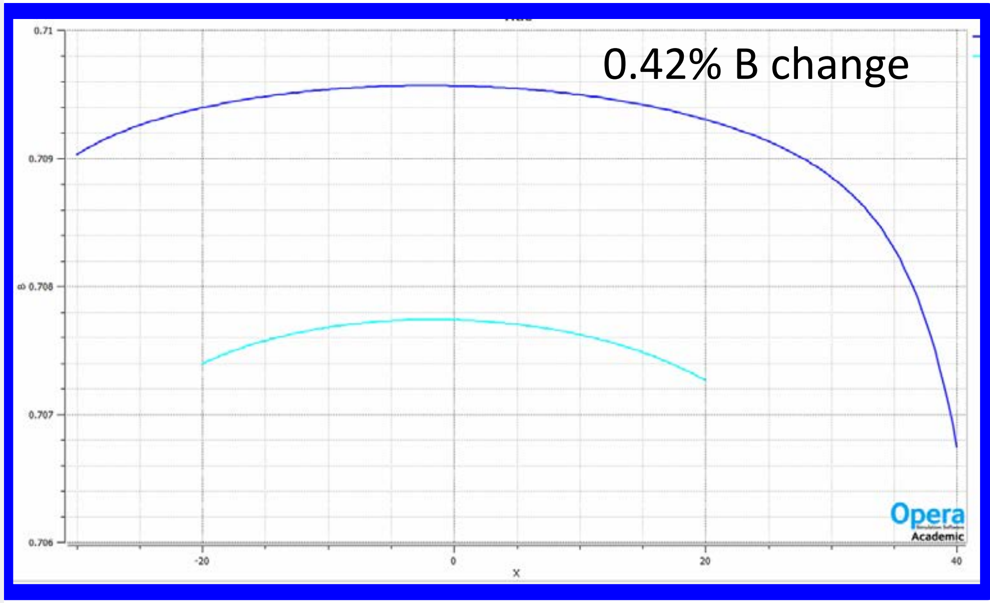



0.42% B change


0.26% B change

Magnetic Sector Homogeneity

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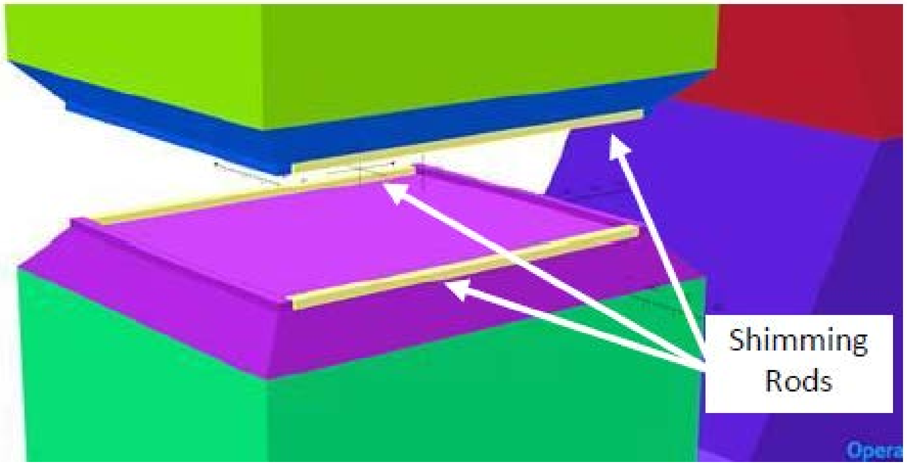

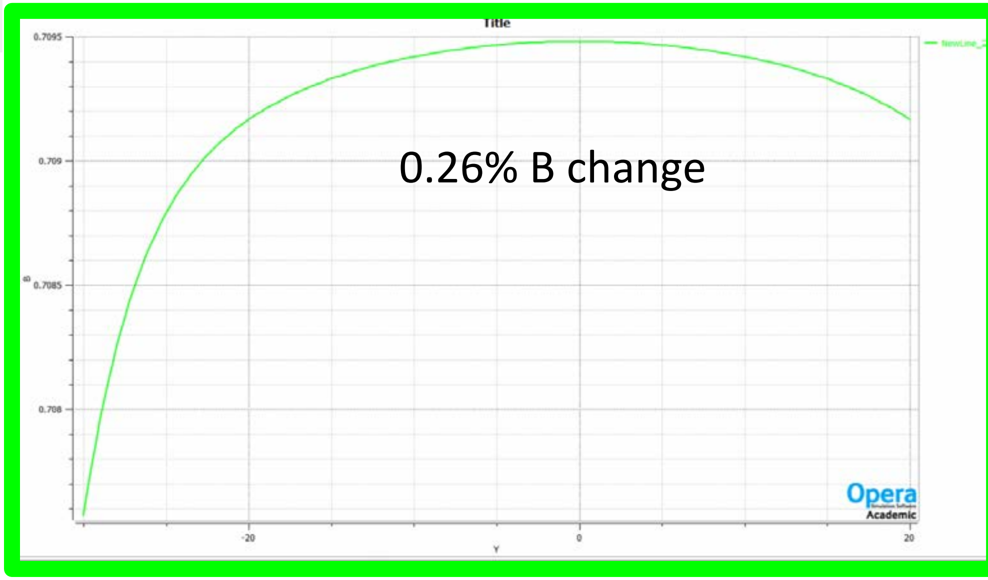
0.26% B change

RENCI Measurement Application Components

- Django, a Python web framework that provides an interface to backend databases
- Django Rest Framework, uses Django to provide a REpresentational State Transfer (REST), Application Programming Interface (API), to data stored in a database
- Vue.js, a JavaScript framework for building interfaces and single page applications
- Quasar a front-end JavaScript framework that works with Vue.js to build user interfaces (UI)
- Openlayers, a JavaScript library for displaying map data in web browsers as slippy maps
- D3.js a JavaScript library for producing dynamic, interactive data visualizations in web browsers

Abstract

High voltage transmission cables (HVTCs) exist buried underground as part of the electrical utility grid. These HVTCs degrade over time and the petroleum-based dielectric fluid can leak into the surrounding environment posing a safety, economic, and environmental concern. Current HVTC leak detection methods involve detecting perfluorocarbon tracer (PFT) molecules injected into the dielectric fluid with a truck mounted custom modified gas chromatograph. The gas chromatograph is extremely sensitive, but suffers from poor dynamic range, high cost, and limited portability. Duke University is collaborating with PFT Technology to develop a cycloidal coded aperture portable mass spectrometer capable of detecting PFT molecules for locating leaks in HVTCs in the field. This work presents a preliminary design and finite element analysis simulations of the proposed cycloidal mass analyzer including a 0.7 T NdFeB magnet, aluminum electric sector, electron ionization source, and focal plane capacitive transimpedance amplifier array detector. The mass analyzer is designed to detect fragments of PFT molecules in the mass range of 59-160 amu with a resolution of 0.5 amu. The anticipated footprint of this mass analyzer is 30 cm x 27 cm x 11 cm and will weigh ~ 40 kg.