PIGE as a PFAS field-screening test

Dr. Graham Peaslee – University of Notre Dame

December 5, 2019

SERDP • ESTCP SYMPOSIUM
25 YEARS OF ESTCP
2019 | Enhancing DoD's Mission Effectiveness

Outline

- Motivation — Why is a “Total Fluorine” method needed?
- Introduction — What is PIGE?
- Technical Details — Current Method, Sensitivity, Specificity, Speed
- Advantages/Disadvantages of common total fluorine methods
- Project Description — 3 objectives
- Project Update — Progress to date
- Conclusions
- Questions

Why is a "Total Fluorine" method needed?

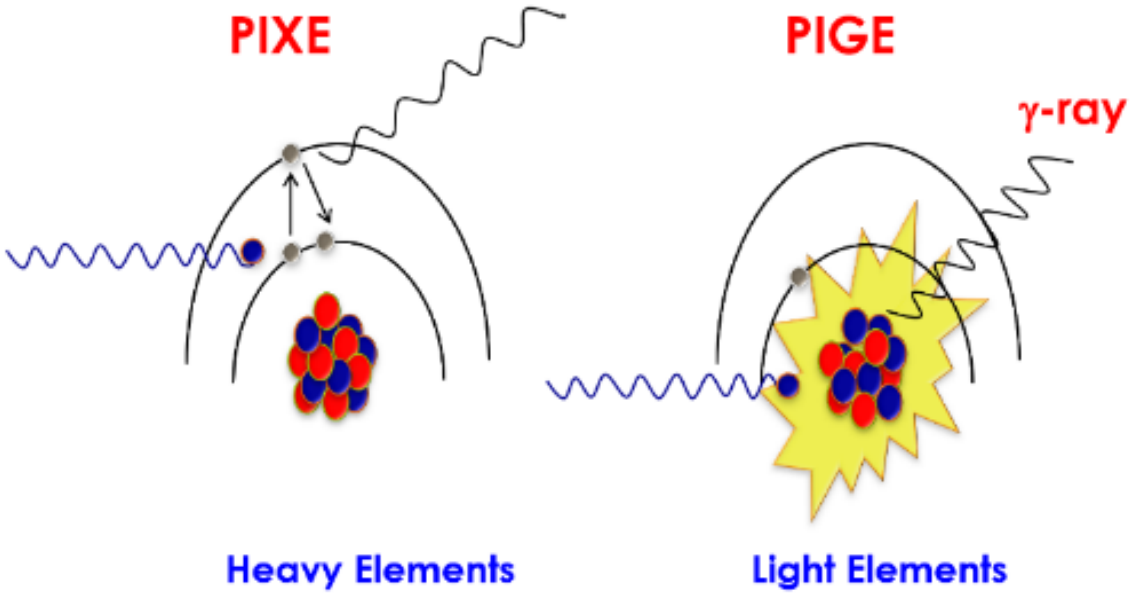
- There are 4700+ known PFAS…less than 1% are currently targeted
- Non-targeted analytes can be precursors to regulated PFAS
  - Example of textile side-chain fluoropolymers

    n-Et-FOSE → n-Et-FOSAA → PFOA

- Potential for **screening**: Site identification and delineation
  - Identifying the reservoir of PFAS
- Potential for **monitoring**: Site remediation and treatment

What is PIGE?

- **Particle Induced Gamma-ray Emission (PIGE) Spectroscopy**
- Light ions as excitation source
- Nuclear de-excitation of ^{19}F
- Identification of characteristic γ-rays



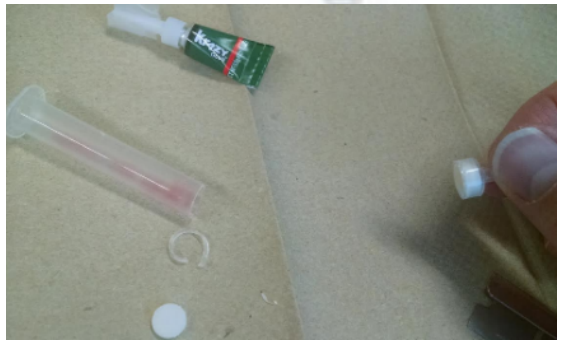
Sensitive, specific, rapid, non-destructive

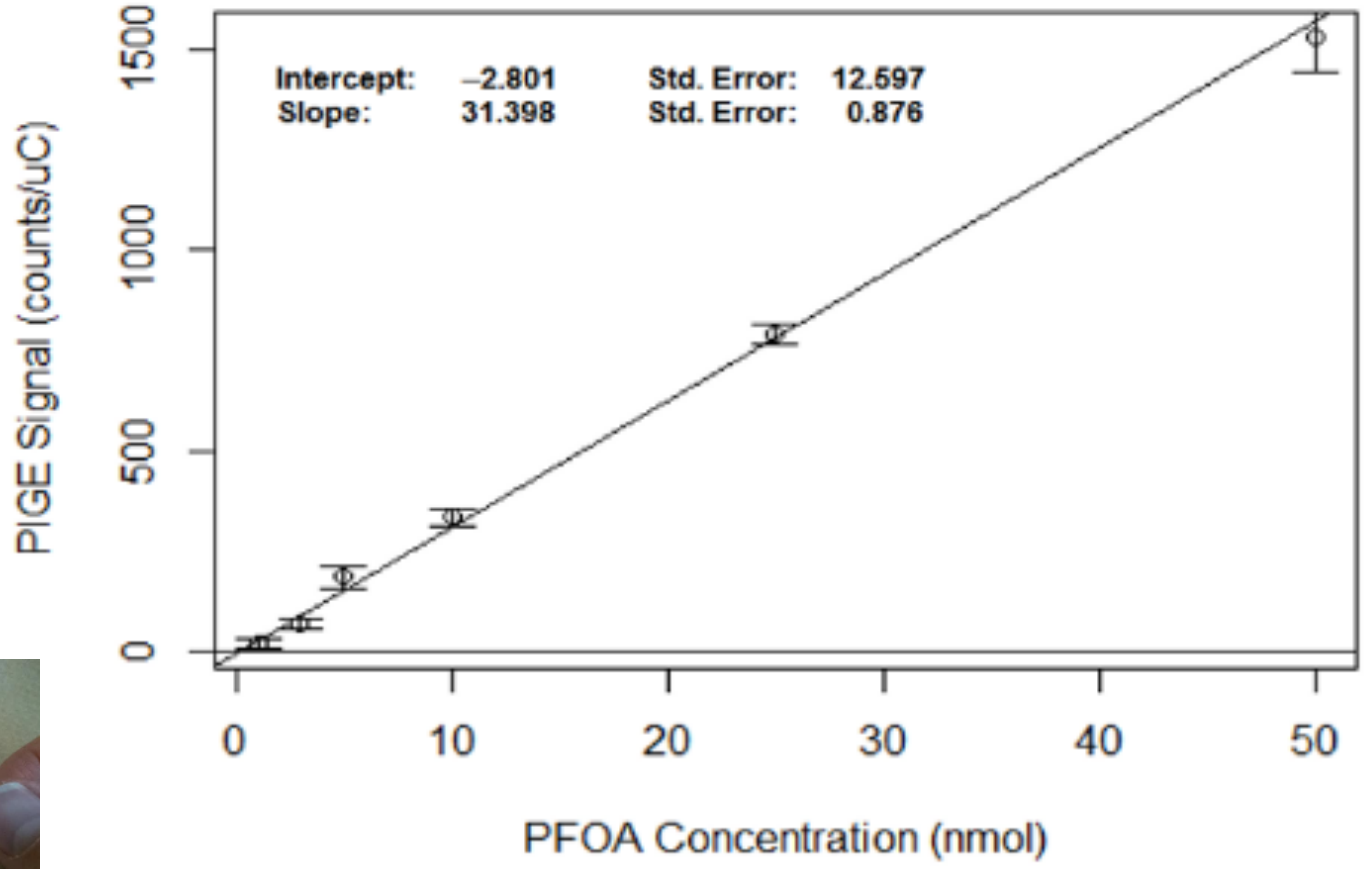
What is PIGE?

- Particle Induced Gamma-ray Emission (PIGE) Spectroscopy

What is PIGE?

- **Sensitivity**
- 50 mL aliquot
- Concentrated by SPE
- Analyzed for 3 min
- MDL = 5 ppb F



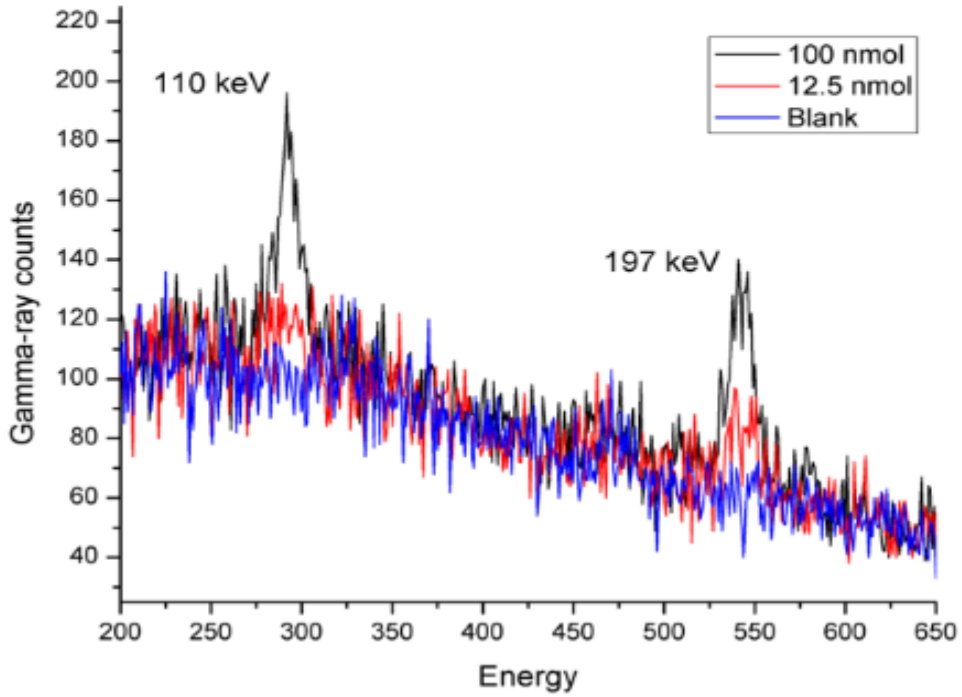


SERDP • ESTCP SYMPOSIUM
#SerdpEstcp2019

What is PIGE?

- **Specificity**
- 50 mL aliquot
- Concentrated by SPE
- Analyzed for 3 min
- No interferents
- No matrix effects
- Identifies all PFAS on SPE
- Inorganic F removed by wash

Figure 3: PIGE spectra of PFOA extracted onto the surface of WAX cartridges. The two gamma rays detected at 110 keV and 197 keV arise from excitations of ^{19}F nuclei.



Advantages/Disadvantages

- Comparison with other techniques published

Environmental Science & Technology Letters

Letter

Cite This: *Environ. Sci. Technol. Lett.* XXXX, XXX, XXX−XXX

pubs.acs.org/journal/estlcu

Total Fluorine Measurements in Food Packaging: How Do Current Methods Perform?

Lara Schultes,[*,†] Graham F. Peaslee,[‡] John D. Brockman,[§] Ashabari Majumdar,[‡] Sean R. McGuinness,[‡] John T. Wilkinson,[‡] Oskar Sandblom,[†] Ruth A. Ngwenyama,[§] and Jonathan P. Benskin[†]

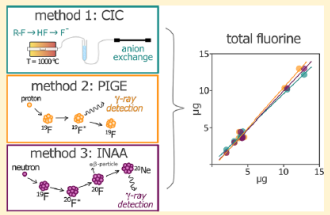
[†]Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Svante Arrhenius väg 8, SE-10691 Stockholm, Sweden

[‡]Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, United States

[§]Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States

Supporting Information

ABSTRACT: Per- and polyfluoroalkyl substances (PFASs) represent a class of more than 4000 compounds. Their large number and structural diversity pose a considerable challenge to analytical chemists. Measurement of total fluorine in environmental samples and consumer products is therefore critical for rapidly screening for PFASs and for assessing the fraction of unexplained fluorine(i.e., fluorine mass balance). Here we compare three emerging analytical techniques for total fluorine determination: combustion ion chromatography (CIC), particle-induced γ-ray emission spectroscopy (PIGE), and instrumental neutron activation analysis (INAA). Application of each method to a certified reference material (CRM), spiked filters, and representative food packaging samples revealed good accuracy and precision. INAA and PIGE had the advantage of being nondestructive, while CIC displayed the lowest detection limits. Inconsistencies between the methods arose due to the high aluminum content in the CRM, which precluded its analysis by INAA, and sample heterogeneity (i.e., coating on the surface of the material), which resulted in higher values from the surface measurement technique PIGE compared to the values from the bulk volume techniques INAA and CIC. Comparing CIC-based extractable organic fluorine to target PFAS measurements of food packaging samples by liquid chromatography−tandem mass spectrometry revealed large amounts of unidentified organic fluorine not captured by compound-specific analysis.



Environmental Science & Technology

Article

pubs.acs.org/est

Closing the Mass Balance on Fluorine on Papers and Textiles

Alix E. Robel,[†] Kristin Marshall,[†] Margaret Dickinson,[‡] David Lunderberg,[‡] Craig Butt,[§] Graham Peaslee,[∥] Heather M. Stapleton,[§] and Jennifer A. Field[*,†]

[†]Department of Environmental and Molecular Toxicology, 2750 Campus Way, Oregon State University, Corvallis, Oregon 97331, United States

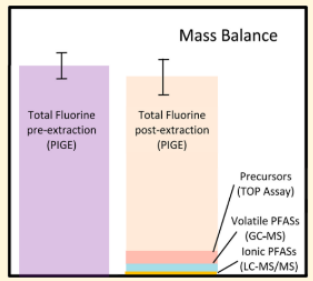
[‡]Science Center Rm 2106A, 35 East 12th Street, Holland, Michigan 49422-9000, United States

[§]Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States

[∥]Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, United States

Supporting Information

ABSTRACT: Papers and textiles that are treated with per- and polyfluoroalkyl substances (PFASs) are sources of human and environmental exposure. Data for individual PFASs, such as perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), are not placed into the context of total fluorine for papers and textiles. Gas chromatography−mass spectrometry (GC−MS) and liquid chromatography−tandem mass spectrometry (LC-MS/MS) were used to quantify volatile and ionic PFASs, respectively, and the total oxidizable precursor (TOP) assay was used to quantify precursors that form perfluoroalkyl carboxylates. Molar sums of PFASs obtained by GC-MS, LC-MS/MS, and precursors were compared to total fluorine (nmol F/cm^2) determined by particle-induced gamma ray emission (PIGE) spectroscopy, measured before and after extraction. Volatile and ionic PFASs and unknown precursors accounted for 0−2.2%, 0−0.41%, and 0.021−14%, respectively, of the total nmol F/cm^2 determined by PIGE. After extraction, papers and textiles retained 64 ± 28% to 110 ± 30% of the original nmol F/cm^2 as determined by PIGE, indicating that the



SERDP • ESTCP SYMPOSIUM
#SerdpEstcp2019

Advantages/Disadvantages

- PIGE is spectroscopic: **Rapid** > 1000 samples per day possible
- PIGE is non-destructive: Same sample can be extracted for LC-MS/MS
- PIGE is inclusive: All PFAS (known and unknown) simultaneously
- PIGE MDL depends on volume sampled…70 ppt any PFAS = 3 L

- PIGE is largely academic tool to date – limited commercialization
- PIGE is laboratory-based to date – large & specialized equipment

Project Objectives

- **PIGE as a PFAS field-screening test**
  - Reduce time/cost for site identification and delineation of impacted groundwater
  - Allow on-site rapid monitoring of remediation and environmental transport

- **Tasks:**
- Determine the Efficiency of PIGE as a Function of Beam Energy
- Determine MDL for PIGE as a Function of Sample Volume
- Design of a Field-Deployable PIGE System

Project Description: Task 1

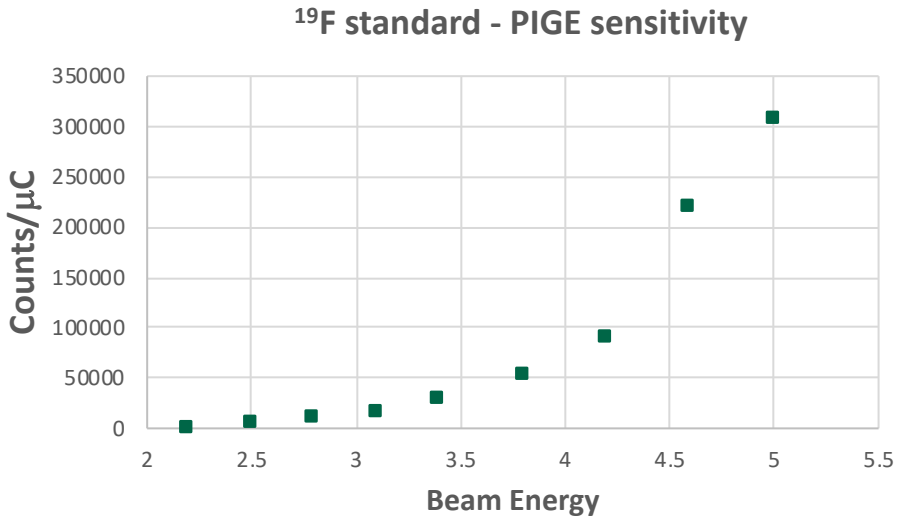
- **Determine the Efficiency of PIGE as a Function of Beam Energy**

  What is the minimum size of particle accelerator needed?

- Preliminary Results:

Sensitivity of PIGE for ^{19}F increases with beam energy markedly

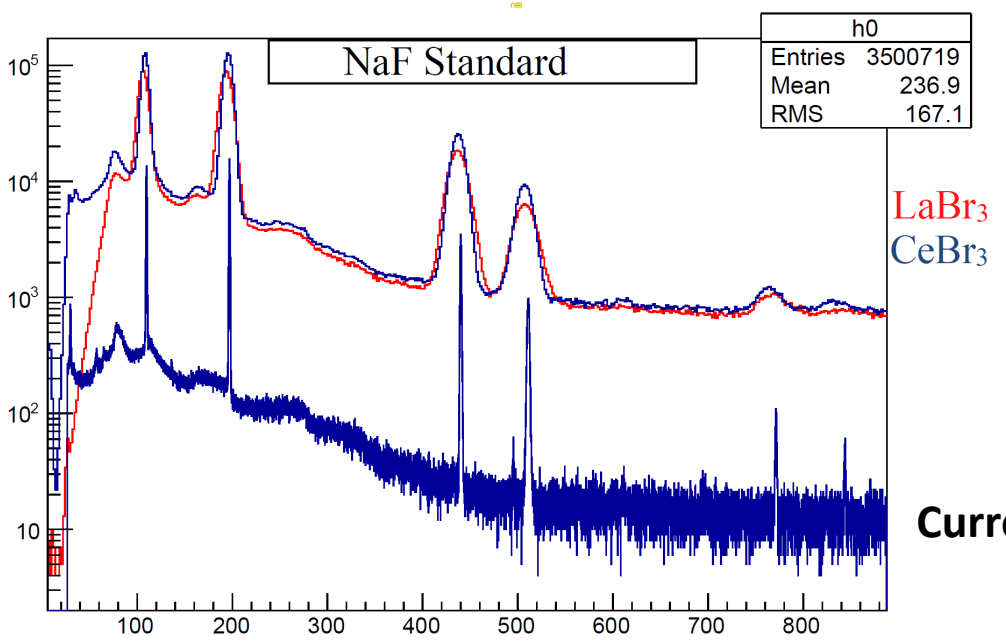
Can't go above 5 MeV without activation though…



Project Description: Task 1

- **Determine the Efficiency of PIGE as a Function of Beam Energy**
- Preliminary Results:

  Detection efficiency can be improved with $CeBr_3$ scintillators



Current: HPGe

SERDP • ESTCP SYMPOSIUM
#SerdpEstcp2019

Project Description: Task 2

- **Determine MDL for PIGE as a Function of Sample Volume**

  What is the minimum sample volume needed?

- Preliminary Results:

MDL does scale linearly with sample volume (for WAX SPE)

5 ppb @ 50 mL

120 ppt @ 2.0 L

5000 ppt x 50 mL = 125 ppt x 2000 mL

Project Description: Task 2

- **Determine MDL for PIGE as a Function of Sample Volume**

  What is the minimum sample volume needed?

- Preliminary Results:

  We have identified faster and more complete preconcentration method:

Commercially available GAC felt

Cost < 10 cents / sample

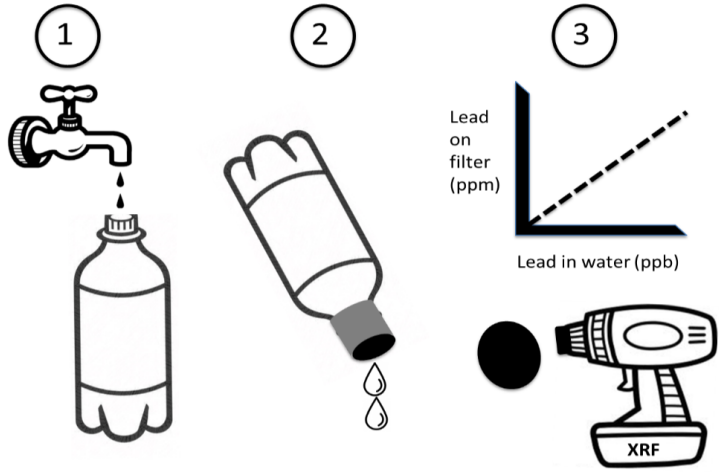
Can gravity filter 5 L in less than 3 min

A Sensitive XRF Screening Method for Lead in Drinking Water

Meghanne Tighe[1], Mark Wilson[1], George Ruscio-Atkinson[1], Graham F. Peaslee[2], Marya Lieberman[1]

1. Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556
2. Department of Physics, University of Notre Dame, Notre Dame, IN 46556

Table of Content Art



SERDP • ESTCP SYMPOSIUM
#SerdpEstcp2019

Project Description: Task 3

- Design of a Field-Deployable PIGE System

  Can a practical field deployable instrument be designed?

DARPA initiative for DHS: starfire industries

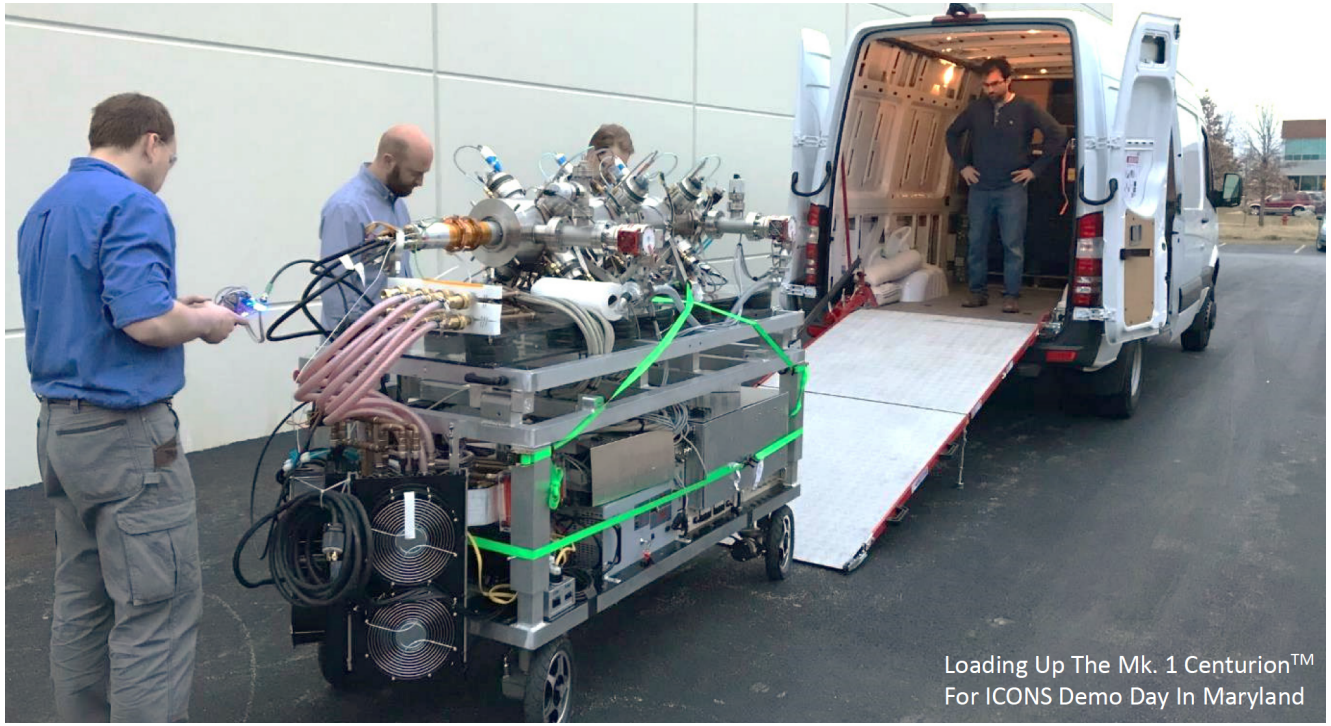
Portable accelerator to screen ports for SNM

Produces 4 MeV deuteron beams…

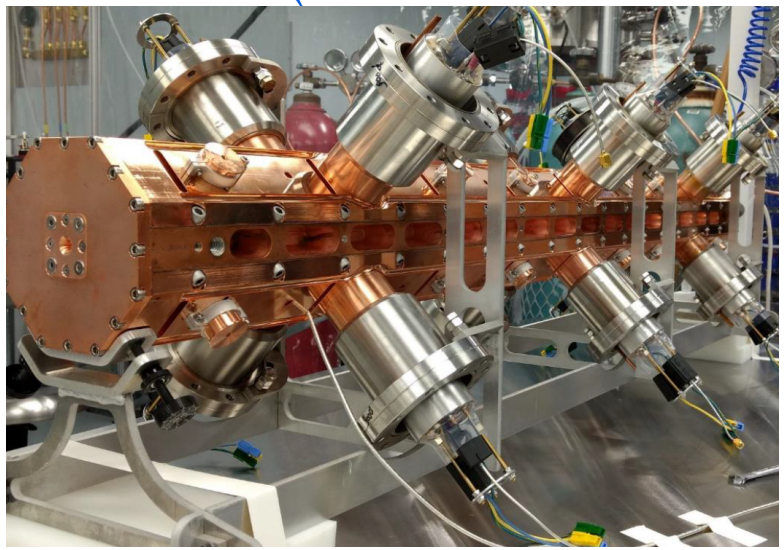
Project Description: Task 3

- Design of a Field-Deployable PIGE System

  Can a practical field deployable instrument be designed?



starfire industries



SERDP • ESTCP SYMPOSIUM
#SerdpEstcp2019

Conclusions

- Significant progress in demonstrating PIGE as a viable total F method
- Envision prototype system on a truck = field-deployable
- Envision commercialization and multiple units (leased/sold)
- SOP:

  Run 2 L of well water through GAC felt filter (minutes in field)

  Dry filters (hours in truck)

  Analyze filters by PIGE in truck (minutes per sample)

  Identify all sum of all PFAS present > 50 ng/L (ppt) on site

  (If targeted analytes needed, can elute PFAS for LC-MS/MS)

Questions?

gpeaslee@nd.edu