FINAL REPORT

Developing PIGE into a Rapid Field-Screening Test for PFAS

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University Of Notre Dame
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This limited scope project was designed to determine the operating parameters needed to take a laboratory technique called PIGE (Particle Induced Gamma-ray Emission Spectroscopy) and turn it into a field-deployable approach to rapidly screen for the presence of PFAS in groundwaters at AFFF-impacted sites. Since these “forever” chemicals are released into the environment from legacy use of AFFF, and several are already known to be toxic, this method for screening for the presence of organic fluorine as a surrogate for PFAS in groundwater could potentially save significant time and money in characterizing their presence, and monitoring their removal or destruction.

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PFAS, PIGE, total fluorine screening, groundwater contamination, field-deployable system

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List of Acronyms

AFB – Air Force Base
AFFF – Aqueous Film-Forming Foams
CIC – Combustion Ion Chromatography
DoD – Department of Defense
EPA – Environmental Protection Agency
GEN-X – Perfluoro-2-propoxypropanoic acid
HAL – Health Advisory Limits
ICP – Inductively Coupled Plasma Spectroscopy
KEV– Kilo-Electron Volts
LC-MS/MS – Liquid Chromatography – tandem mass spectrometry
MDL – Method Detection Limit
MEV– Mega-Electron Volts
NAA – Neutron Activation Analysis
NMR – Nuclear Magnetic Resonance
PFAS – Per- and Polyfluorinated Substances
PFBS – Perfluorobutane Sulfonate
PFDA– Perfluorodecanoic Acid
PFHpA– Perfluoroheptanoic Acid
PFHXA– Perfluorohexanoic Acid
PFHXS– Perfluorohexane Sulfonate
PFNA– Perfluorononoic Acid
PFOA – Perfluorooctanoic Acid
PFOS – Perfluorooctanesulfonic Acid
PFPeA – Perfluoropentanoic Acid
PIGE – Particle Induced Gamma-ray Emission Spectroscopy
PPM – Parts per million (mg/L)
PPB– Parts per billion (µg/L)
PPT – Parts per trillion (ng/L)
RFQ – Radio Frequency Quadrupole
SERDP – Strategic Environmental Research and Development Program
SOP – Standard Operating Procedures
SPE – Solid Phase Extraction
TOP – Total Oxidizable Precursor assay
US – United States
WAX – Weakly Anionic Exchange

Keywords
PFAS, PIGE, total fluorine screening, groundwater contamination, field-deployable system.

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Abstract

Introduction and Objectives:
This limited scope project was designed to determine the operating parameters needed to take a laboratory technique called PIGE (Particle Induced Gamma-ray Emission Spectroscopy) and turn it into a field-deployable approach to rapidly screen for the presence of PFAS in groundwaters at AFFF-impacted sites. Since these “forever” chemicals are released into the environment from legacy use of AFFF, and several are already known to be toxic, this method for screening for the presence of organic fluorine as a surrogate for PFAS in groundwater could potentially save significant time and money in characterizing their presence, and monitoring their removal or destruction.

Technical Approach:
During this project we determined the precise beam energy of protons required to make these measurements, that could be produced by modifying a field-deployable accelerator system previously developed by DARPA. The modifications were made to the design plans of the commercial system, and the method detection limits were estimated based on a series of laboratory measurements on existing and new solid-phase extraction media.

Results:
The preliminary results were very promising, as a 3.5 MeV portable accelerator system, based off the existing model has been designed by Starfire Industries, LLC. We have shown that this modified system would be theoretically capable of making rapid PIGE measurements (minutes per sample) at a field site. The discovery of an inline filter material that would allow PIGE measurement detection limits in the 10-50 ppt range for all anionic PFAS simultaneously, means that this system could be used in a variety of situations to facilitate site characterization, remediation and long-term monitoring.

Benefits:
The results of this project significantly reduce the risk to develop a new technology that could be a “game-changer” in the field. Having the capability to determine total aqueous PFAS concentrations within hours on site, will allow field operations to respond immediately to the data obtained. This could potentially cut down the time on site for characterization and remediation significantly – which results in overall cost savings. Although not quite as simple as a pH meter, its impact on field operations concerned with identifying and remediating PFAS contamination may be just as high. The ability to react immediately to changing conditions, to characterize more fully, or to monitor more regularly for less cost are the biggest benefits of this project.

Graphical abstract:

Conceptual figure of what a portable PIGE unit would look like, based on this work.
Executive Summary

Introduction

Because of the environmental longevity of PFAS, AFFF-impacted DoD installations and petrochemical facilities, as well as industrial fluorochemical manufacturing sites, civilian airports and waste-water treatment facilities leaching PFAS-treated materials all contribute PFAS contamination to ground water and surface water. Because these “forever chemicals” have been associated with a myriad of the human health hazards each of these sources of PFAS contamination will require site characterization at very low concentrations of PFAS (parts per trillion), where the mixture of PFAS present depends upon the original AFFF formulation, the site geochemistry, and the presence of other co-contaminants. After characterization, each site may require site-specific remediation strategies. Finally, each of these contaminated site remediation efforts will require years of subsequent monitoring and re-sampling. The initial site characterization of each AFFF-impacted DoD installation typically costs millions of dollars and can take a year or more to perform. With the potential number of AFFF-impacted sites in the US in the thousands, just the characterization efforts for DoD sites will be very costly and time-consuming.

In addition, proposed remediation strategies at each of these sites are varied and include sequestration technologies as well as both in situ and ex situ methods of destruction. Simultaneously, the number of targeted PFAS analytes that can be measured in commercial laboratories is increasing, and different US states are responding to the drinking water health threat by enacting different regulatory limits in the absence of a national regulatory limit. This leads to the concern that present regulatory interest in two analytes (PFOA and PFOS) that have been used to benchmark most site characterization studies to date, may be expanded to include other PFAS (including PFHxS, PFNA, Gen-X) which may require a re-appraisal of existing sites.

The potential cost of expanding the number of analytes of concern in each of the various treatment strategies when multiplied by the number of PFAS-impacted sites is significant. One of the most expensive pieces of this analysis is just the time involved to obtain site-specific analytical data. For example, the on-site crews required to drill test bores are doing their job based entirely on modeled estimates of ground water flow and known AFFF use locations. When the analytical results indicate additional previously unknown areas of AFFF use, or unexpected ground water behavior, these results arrive weeks after the field crews have moved to another site. The cost to re-allocate these crews back to previous sites is significant. To address this problem, we propose to develop a method of in situ total fluorine screening that will allow AFFF-impacted site characterization to be accurate, rapid and inexpensive. In addition, this methodology is so rapid that additional sampling (both geospatial and temporal) can be performed to give much higher resolution data sets before, during and after remediation efforts have been performed. Similarly, long-term monitoring of site remediation often does not require the complete PFAS identification and quantification for every location and every time point, and having the ability to drive to an existing site and characterize the overall features of the existing well field within a day could save considerable time and expense.

The current state-of-the-art detection method for aqueous solutions of PFAS is the Liquid Chromatography – Tandem Mass Spectrometer (LC-MS/MS). It can achieve part-per-trillion sensitivity and identify which specific PFAS are present. Soils and sediments can be analyzed as well, after an extraction process. However, because of the nature of preparing each sample for multiple PFAS standards, and the chromatographic separation steps required to identify the
individual PFAS, any LC-MS/MS method are inherently slow. In addition, LC-MS/MS techniques require a library of known compounds to which to compare – which means that although it is very sensitive, it is blind to most PFAS precursors that may subsequently degrade into regulated chemicals.

Because of these limitations, we have developed a rapid total fluorine method using Particle-Induced Gamma-ray Emission (PIGE) spectroscopy that is well established with respect to the analysis of total fluorine in solid materials such as papers and textiles. Since 2018, we have developed a PIGE method to rapidly measure fluorine levels in the ppt range in environmental water samples. The technique is rapid (typically requiring only three minutes of analysis per sample or less) and non-destructive. Similar to x-ray analysis, the samples measured are not destroyed nor rendered radioactive.

Since PIGE works with highest sensitivity on solid surfaces, we analyze the PFAS concentration in water samples by using commercially available solid-phase extraction (SPE) technology. For WAX cartridges, for example, approximately 50 mL of sample is passed through the extraction column, and then the surface of the SPE column itself is analyzed by PIGE. This procedure and a representative spectrum are shown in panels of Figure 1 as well.

**Figure 1:** The PIGE method and the instrumentation used at the University of Notre Dame facility.

**Objectives**

The primary objective of this proposal was to take an established total fluorine method and to develop it into a field-screening method for Per- and Polyfluorinated Alkyl Substances (PFAS). Specifically, we proposed to develop the Particle-Induced Gamma-ray Emission (PIGE) spectroscopic method of total fluorine detection to a stage where routine analysis of aqueous samples could be rapidly performed in the field. This required understanding the beam-energy dependence of the spectroscopic signal for fluorine, as well as optimizing the method detection...
limits (MDL) for samples that undergo solid-phase extraction. Finally, knowing the exact operating parameters required for these measurements in a laboratory setting, we proposed to modify the design of an existing field-deployable accelerator that would be capable of rapidly and reliably screening groundwater and surface water samples for the presence of environmentally relevant concentrations of PFAS in the field. If all three of these tasks were successful, then it would be possible to submit a full proposal to build and test a prototype field-deployable system.

Since the spectroscopic measurement of total fluorine has never been used to screen for the presence of PFAS in the field before, there were two “high risk” aspects to this proposal: (i) the miniaturization of an accelerator system that can perform these measurements in the field and (ii) the development of the pre-concentration methods that would achieve sensitivity to PFAS in concentrations down to and below the current Health Advisory Limits (HALs). Thus, we offered to perform this limited scope proposal to identify the minimum beam energy as well as the best solid-phase extraction method detection limits (MDLs) to demonstrate feasibility of this approach with commercially available and existing equipment within one year.

**Technical Approach**

Three tasks were identified to accomplish the goals of this project:

*Task 1 – Determine the Efficiency of PIGE as a Function of Beam Energy*

The goal of this task was to determine the optimum efficiency for detection of fluorine by an accelerated beam of protons as a function of the beam energy. This is a critical design feature of any accelerator, and the energy required for the proton beam will dictate the resultant footprint of the accelerator system. There have been no scientific studies of the sensitivity of PIGE analysis for fluorine in environmental samples as a function of accelerator energy to date, mostly because there has been little interest in measuring fluorine until now. Some early studies suggest the sensitivity goes up with beam energy, but we performed a careful analysis of inorganic fluoride target standards between proton beam energies of 2.1 and 5.0 MeV to determine the sensitivity (and MDL) achievable at each energy.

*Task 2 – Determine MDL for PIGE as a Function of Sample Volume*

The primary goal of this task was to perform a systematic evaluation of the accuracy and precision of the PIGE method on environmental samples likely to be encountered at AFFF-impacted sites. To this end, we verified the linearity of the PIGE response for total fluorine for a selection of anionic PFAS standards as a function of sample volume in two types of solid-phase extraction media.

The first set of MDLs were determined using Waters Weakly Anionic Exchange (WAX) cartridges, which are commercially available and have been shown to be effective for most long-chain anionic PFAS. Initially the MDLs were determined using 50 mL aliquots of seven different aqueous concentrations of PFOA, and then a series of different volumes between 50 mL and 2.0 L of a single concentration of PFOA were measured to demonstrate the linearity of response with increased volume. Similar studies were performed on PFOS and PFHxS.

The second set of MDLs were determined using a novel graphitized activated carbon (GAC) felt, that is commercially available as conductive pads for battery terminals. These felt materials were laser cut to 1”-diameter circles that were approximate 3 mm thick and used as inline filters, through
which 2 L of sample were gravity-filtered. Typical filtration times were on the order of minutes for a 2 L bottle, the filter to air dry for about an hour before sealing into a small pre-labeled resealable plastic bag. This bag was directly taped to a target mount for PIGE analysis. Calibration curves with 6 – 7 different concentrations were obtained with 2.0 L sample volumes for 10 representative PFAS: Gen-X, PFBS, PFPeA, PFHxA, PFHxS, PFHpA, PFOA, PFOS, PFNA, and PFDA. In the case of the GAC felt targets, the PFAS could be washed off with acetone, leaving any inorganic fluoride that adhered to the GAC behind. Thus, both methods had a mechanism for distinguishing total fluorine from inorganic fluoride content in aqueous samples.

Task 3 – Design of a Field-Deployable PIGE System

Once the hypotheses from Task 1 and Task 2 have been confirmed, and optimal accelerating voltages and sample preparation methods determined, the design of a field-deployable PIGE system was addressed. Ideally, such a system would be mobile, and could be deployed to rapidly screen groundwater samples in the field for total organic fluorine. Electrostatic accelerator design is a well-established field, and several US companies manufacture them routinely for medical, industrial or defense purposes. Small accelerators are an engineering challenge that has already been conquered and we partnered with Starfire Industries, LLC in Champaign, IL to take advantage of the DoD investment in their DARPA-funded project to make a portable accelerator for defense purposes. In the final phase of this limited scope proposal, we asked Starfire to modify their existing plans to incorporate what was optimal for a portable PIGE system.

The accelerator design is the key component for the portable PIGE system. The gamma-ray detector systems and appropriate shielding could all be purchased commercially as well for such a system. Similarly, the sample processing hardware which could incorporated into any truck that could drive the PIGE system would be commercially available plumbing and laboratory systems. However, the optimization of the entire system for PIGE analysis of fluorine in both aqueous and solid samples will require the data acquired in Task 1 and 2 in order to prepare a realistic cost estimate to build a turn-key system that could be used in the field. Such turn-key systems could be operated by a trained technical assistant and with no moving parts are quite rugged in the field.

Results and Discussion

The first task was readily accomplished using the Notre Dame Ion Beam Analysis facility. Figure 2 shows the quantity of fluorine gamma rays detected per microcoulomb of beam delivered to target, as a function of proton bombarding energy. Prior to this study, PIGE studies had been routinely conducted at 3.4 MeV of bombarding energy, but the yield was observed to sharply rise with beam energy. Similarly yields drop off significantly below 3 MeV, and this led to our first design consideration that we should use the highest energy possible above 3 MeV. As the bombarding energy at the Notre Dame facility was capable of going all the way to 6 MeV, we began to explore higher energies but beams above 5 MeV in energy were observed to create radioactive products (primarily short-live nitrogen-13 and oxygen-15 isotopes in the atmosphere surrounding the target. While another factor of 10 in PIGE sensitivity appears achievable between 3.5 MeV and 4.5 MeV, anything above 3 MeV would be manageable.
Figure 2: The production of characteristic $^{19}$F gamma rays as a function of proton bombarding energy from a known inorganic standard. The error bars on the individual measurements are encompassed within the symbol for each measurement.

The beam intensity available at the University of Notre Dame for this study was limited to about 50 nA on target, and significantly more beam (a factor of ~100) would be available from the RFQ type of accelerator proposed here, which would more than offset this lack of sensitivity. The most important information from this study is that the beam energy requirement for the portable accelerator system has been defined.

The goal of task 2 was to optimize and determine the MDL for PFAS detection by PIGE. This was done for two types of SPE media: Waters Weakly Anionic eXchange (WAX) cartridges, and a novel Graphitized Activated Carbon (GAC) felt textile used as an in-line filter.

Although WAX cartridges are routinely used for the pre-concentration of anionic PFAS prior to LC-MS/MS analysis, the PIGE analysis of fluorine is done on the top surface of the WAX cartridge before elution is performed, so a new measurement of sensitivity is required for this method as described previously. The initial measurements were all performed with replicate 50 mL samples of diluted aqueous PFOA standards as shown in Figure 3.

Figure 3: A standard calibration curve of PIGE signal recorded in gamma-ray counts per microcoulomb of beam delivered plotted against concentration of 50 mL aqueous samples of PFOA. Three replicate measurements are recorded for six different concentrations of PFOA and a distilled water blank.
The linearity of the response is good and no saturation is observed even with a concentration of almost 20,000 ppt PFOA. The method detection limit can be calculated from this curve based on the standard deviation of response ($S_y$) at levels near the limit of detection, using the formula $\text{MDL} = 3.3 \left( \frac{S_y}{S} \right)$. Using the entire curve, this results in an MDL of 3.3 ppb, but using lowest five points (within a factor of 10 of the MDL) this results in a more accurate MDL of 1.2 ppb PFOA for a 50 mL sample volume. These measurements were repeated for PFOS as well as PFHxS, and resulted in MDLs of approximately 1.1 ppb for PFOS, and 1.4 ppb for PFHxS. This means that with no significant modifications, all anionic PFAS can be measured by this method to a detection limit close to 1000 ppt. For every AFFF-impacted site for which we have measured PFAS (see figures 2 and 3, for example), there have been multiple known PFAS analytes present and between 30% and 90% of the total fluorine signal has come from unknown PFAS analytes or “precursors”. This accounts for the reliability of PIGE already seen from this method using 50 mL sample volumes. There is a lot of organic fluorine available in groundwater at AFFF-impacted sites. However, as PFAS regulatory levels change, they are driven by better detection limits available on LC-MS/MS systems as well as observed health effects seen for PFAS concentrations in the low ppt range in drinking water studies. We have assumed that the MDLs for the PIGE detection method are linearly dependent on sample volume. This means that if we have an established MDL around 1.2 ppb PFOA for a 50 mL sample volume, if we wish to detect a single analyte such as PFOA down to a detection limit of 50 ppt, then we simply need to put a larger volume (= $\frac{1200}{50} \times 50$ mL) of 1.2 L through the WAX cartridge to achieve this limit. However, it was observed that the time and personal attention needed to measure large volumes through a small WAX cartridge, even with commercially available sample extension holders available, was extensive. This would not be a field-friendly method. However, we discovered another SPE method that shows greater promise for practical field measurements.

A similar set of measurements were performed for a novel GAC felt cut to 1-inch diameter circles as used as an inline filter for 2.0 L volumes of water. We used 2.0-L bottles for the laboratory assessment of their performance in collecting PFAS, but of course in the field, in-line filter assemblies could be attached to any bore hole pump and left to run for minutes to hours, and the sampling volume could range between 1 and 100 L readily. In the laboratory, the samples were left to gravity filter through the felt, and 2 L passed through typically within 3 minutes. Unless significant turbidity was encountered, then 10 L of ground water could be passed through this filter in approximately 15 minutes by gravity filtration, or in less time if connected to a bore hole pump.

The results of testing with ten different individual PFAS analytes are shown in Figure 4. The MDLs calculated for these compounds for a 2L volume are: 330 ppt for PFOA, 550 ppt for PFOS, and 200 ppt for PFHxS. While these are better than 50 mL volumes passed through WAX cartridges, the design of in-line filters connected directly to a bore pump allows much greater volumes to be sampled readily. This means if 20 L can be sampled (typically in less than 20 minutes), this method would have the analytical sensitivity for individual analytes of interest in the 20 – 50 ppt range. This method brings the practicality to the field sampling aspect of this project.
Figure 4: The average PIGE signal recovered from 2 L volumes of various PFAS solutions passed through a GAC felt filter by gravity filtration. Only one replicate was measure for this test, but the linearity for all PFAS tested is good, and the slope in each plot represents the relative sensitivity of binding for each PFAS.

The success of these measurements allowed us to commission the re-design of Starfire’s existing Centurion™ accelerator system to produce a proton ($p$) beam suitable for fluorine detection via proton-induced gamma emission (PIGE). Experiments conducted as part of Task 1 have determined that F-detection via PIGE will require a $p$-beam at $\geq 3$ MeV. Modifications to the Centurion’s™ vane tip profile are required to achieve this, as the existing design is capable of outputting deuterons ($d$) at 3.86 MeV and $p$ at 1.93 MeV for use as a neutron generator. While the Centurion™ system is capable of outputting protons at 1.93 MeV, increasing the output energy to at least 3 MeV requires increasing substantially the vane-tip voltages over what is required for the 1.93 MeV case as well as modifying the tip profile to take advantage of the increased electric field.

Since the operating frequency, mid-cell radial aperture, and vane-tip radius of curvature are all unchanged from the existing Centurion™ system, no modifications to the resonator cross section or end regions are required. This simplifies the design process considerably, as changes in vane-tip length will merely require changes to the length of the resonator, without modifying the end-region geometry.

Although a large number of simulations were run, the final result (see Section III) ended up as a balance of 1) the physics relevant to the RFQ accelerator and the PIGE application and 2) practical considerations such as size, weight, and power. Despite the fact the growth of the output energy with respect to the length of the accelerator is sublinear, the physics relevant to fluorine detection via PIGE dictate that additional energy is still indeed favorable throughout the 3—5 MeV range (and beyond). However, building this accelerator into a mobile system does require setting some practical limits on size, weight, and power. As such, a practical limit of 150 cm was placed on the accelerator section, which corresponds to an output energy of approximately 3.5 MeV. Figure 5
shows RFQ length as a function of output energy over a series of simulations where the accelerator section of the RFQ was lengthened to increase the output energy. For this series of simulations, the radial matcher (RM), shaper (SH), and gentle buncher (GB) were all unchanged.

Figure 5: RFQ accelerator length as a function of output energy. For this series of simulations, the radial matcher (RM), shaper (SH), and gentle buncher (GB) were all unchanged. Only the accelerator section was altered.

The parameters of the ultimate result of the iterative design process are shown below, in Table 1. In general, this RFQ operates at 600 MHz, is approximately 147 cm in length, and requires approximately 212 kW of RF cavity-fill power.

Table 2: Operating parameters for the final PIGE RFQ design.

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<tr>
<th>Operating Parameter</th>
<th>Value</th>
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<td>Operating frequency</td>
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<td>Injection energy</td>
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<td>Final beam energy</td>
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<td>Transmission at 10 mA</td>
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<td>Input transverse emittance (normalized)</td>
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<tr>
<td>Output emittance (normalized)</td>
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<tr>
<td>Output beam FWHM energy spread at 10 mA</td>
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<td>Linac operating repetition rate</td>
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<td>Output beam width</td>
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<tr>
<td>Vane length</td>
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<td>Pulsed cavity RF power</td>
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<td>Pulsed beam power (10 mA)</td>
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<td>Pulsed RF input power</td>
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<tr>
<td>Average rf power requirement</td>
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Shown in Figure 6 is the existing, Centurion™ system. The only significant changes that are required to this platform are that 1) the accelerator section will increase in length by approximately 8”, and 2) the RF drive electronics will need to be modified to accommodate four additional RF power injectors. Since the total instantaneous power capability of the existing RF drive chain is beyond what is required here, the only major changes from the existing hardware will be to replace the 12-way splitter in the present system with a 16-way splitter and to add four sets of triode control electronics.

Finally, it is worth noting that the envisioned fluorine-detection system does not have the accelerator implemented as a separately mobile cart, rather as an installation within a larger vehicle containing a small area for the wet chemistry needed to prepare samples for analysis in this machine. To that extent, the wheels and accompanying drive system from the existing cart can be removed. If necessary, the vacuum, cooling, and HV/RF subsystems can also be moved around to better utilize the space allotted for installation within the mobile lab.

Figure 6: The existing Centurion™ system. In this figure, each of the major subsystems has been outlined and labelled. The proposed system will have the RFQ accelerator section lengthened by approximately 8” and will require RF drive electronics for an additional four RF power injectors.

Implications for Future Research and Benefits
In the next proposal for future research, we will take advantage of a previously-funded DARPA project that built a prototype field-deployable accelerator system for Homeland Security purposes. We will propose only minor modifications to that existing system, in order to accomplish the goals of a field prototype that could screen for PFAS in the field. This approach effectively minimizes the risk for the construction of a prototype field system, as we know that the science works at the
appropriate scale from this limited scope study, and the field-deployable system has already been built once, and with the design modifications developed in this study, it is just a question of executing the design for a new prototype system in a full proposal.

This effort addresses a high-priority need identified by the ER19-C2 SON for *In Situ* and *Ex Situ* Remediation of PFAS-Contaminated Groundwater. The development of a field-deployable system that could screen groundwater samples for all PFAS simultaneously within minutes would be a game-changer in both site characterization and site remediation efforts, as well as for routine long-term monitoring of PFAS-impacted sites. This capability would not just significantly reduce costs of off-site analysis by traditional methods, but the rapidity of the results and the inclusivity of all PFAS would save significant time in the characterization of where to remediate, as well as to cut the time needed to assess the effectiveness of the remediation strategies (both *in situ* and *ex situ*) under varying circumstances, and to routinely check the remediation process for long-term changes.

What this means is that further basic research into this method is not needed before proposing to build a prototype portable PIGE system. This is a significant advance of our understanding over even one year ago. The obvious next steps are to propose to build such a system and field-test it at several representative AFFF-impacted sites or active remediation sites. Potential components of this proposal would include a formal partnership between Starfire Industries and the University of Notre Dame and one of the large environmental consulting firms (Jacobs). The goal would be for Starfire Industries to build the modified Centurian system for this project, and to mount it in a commercially available light truck. The University of Notre Dame would adapt commercially available gamma-ray detectors, appropriate shielding and target mechanisms that would fit in the space allowed by the vehicle to provide routine PIGE analysis using the accelerator. The Notre Dame team would also produce a selection of in-line filter devices using the new GAC felt material, that could be independently tested in the laboratory and the field to optimize design and cost. It is likely that the filters will cost only dollars per device, so that a thousand or more could be kept on the portable PIGE system for any site visit. The environmental consultants would provide field personnel and access to known AFFF-impacted groundwater sites and help to design and to perform the field validation study and to help create SOPs for field personnel to use the prototype portable PIGE system.

In summary, completion of a portable PIGE prototype system would allow the following scenarios to unfold as needed:

**Example #1:** For a new site characterization, where well-boring is actively underway, the portable system could be brought to any preferably level location on site. It has self-contained power systems as needed. Pre-labeled inline filters would be distributed to the well heads by field personnel and samples collected with timed “draws” through the filters. This could be 10-20 minutes per well, or if higher sensitivity were desired, they could be left on for an hour, while field personnel continue to add filters to other bores. At the end of deployment of these filters, they would be collected and returned to the PIGE truck, where a single technician could unpack 100 or more filters, dry them for an hour, and then analyze them by PIGE all within the same vehicle within a single 8-hour day. The results could be electronically distributed and analyzed before the next day of boring were to commence. This would allow plume tracing to be done all in a matter of days, instead of repeated visits to the site months apart. The PIGE truck would work
collaboratively with the site characterization team to steer the efforts towards the areas with the highest PFAS impact.

Example #2: For an existing AFFF-impacted site with complete characterization and an active remediation or sequestration effort on-going, the portable PIGE unit could be driven to the site, set up within hours, and used to monitor total fluorine at hundred of locations per day. In this case it would be possible to complete the entire survey periodically (quarterly, monthly) within one or two days, and then drive to another site to repeat the process. The data would confirm the nature of the PFAS contamination at that moment in time, and catch concerning trends early, or reduce the need for complete analytical work-ups of which PFAS are where, if just monitoring of the total F concentration will suffice to say that the plume has not increased. Instead of regular full LC-MS/MS analysis, monthly or quarterly screening could be performed at very low cost and full analysis could be done once a year.

There are undoubtedly many more situations where a portable field measurement of all PFAS (as measured by total anionic organic fluorine) could be practical and cost-saving, but we list just a few of the obvious cases here. Field testing will undoubtedly lead to more situations where a robust and rapid PFAS screening technique could be useful.
Objective

The primary objective of this proposal was to take an established total fluorine method and to develop it into a field-screening method for Per- and Polyfluorinated Alkyl Substances (PFAS). Specifically, we proposed to develop the Particle-Induced Gamma-ray Emission (PIGE) spectroscopic method of total fluorine detection to a stage where routine analysis of aqueous samples could be rapidly performed in the field. This required understanding the beam-energy dependence of the spectroscopic signal for fluorine, as well as optimizing the method detection limits (MDL) for samples that undergo solid-phase extraction. Finally, knowing the exact operating parameters required for these measurements in a laboratory setting, we proposed to modify the design of an existing field-deployable accelerator that would be capable of rapidly and reliably screening groundwater and surface water samples for the presence of environmentally relevant concentrations of PFAS in the field. If all three of these tasks were successful, then it would be possible to submit a full proposal to build and test a prototype field-deployable system.

Since the spectroscopic measurement of total fluorine has never been used to screen for the presence of PFAS in the field before, there were two “high risk” aspects to this proposal: (i) the miniaturization of an accelerator system that can perform these measurements in the field and (ii) the development of the pre-concentration methods that would achieve sensitivity to PFAS in concentrations down to and below the current Health Advisory Limits (HALs). Thus, we offered to perform this limited scope proposal to identify the minimum beam energy as well as the best solid-phase extraction method detection limits (MDLs) to demonstrate feasibility of this approach with commercially available and existing equipment within one year. The successful results of this project are described in this final report.

In the next proposal for future research, we will take advantage of a previously-funded DARPA project that built a prototype field-deployable accelerator system for Homeland Security purposes. We will propose only minor modifications to that existing system, in order to accomplish the goals of a field prototype that could screen for PFAS in the field. This approach effectively minimizes the risk for the construction of a prototype field system, as we know that the science works at the appropriate scale from this limited scope study, and the field-deployable system has already been built once, and with the design modifications developed in this study, it is just a question of executing the design for a new prototype system in a full proposal.

This effort addresses a high-priority need identified by the ER19-C2 SON for In Situ and Ex Situ Remediation of PFAS-Contaminated Groundwater. The development of a field-deployable system that could screen groundwater samples for all PFAS simultaneously within minutes would be a game-changer in both site characterization and site remediation efforts, as well as for routine long-term monitoring of PFAS-impacted sites. This capability would not just significantly reduce costs of off-site analysis by traditional methods, but the rapidity of the results and the inclusivity of all PFAS would save significant time in the characterization of where to remediate, as well as to cut the time needed to assess the effectiveness of the remediation strategies (both in situ and ex situ) under varying circumstances, and to routinely check the remediation process for long-term changes.
Background

Because of the environmental longevity of PFAS, AFFF-impacted DoD installations and petrochemical facilities, as well as industrial fluorochemical manufacturing sites, civilian airports and waste-water treatment facilities leaching PFAS-treated materials all contribute PFAS contamination to ground water and surface water (Domingo2019, Sunderland2019, Hu 2016, Sun2016). Because these “forever chemicals” have been associated with a myriad of human health hazards (Sunderland2019, Liu2018, Grandjean2015, Lau2007), each of these sources of PFAS contamination will require site characterization at very low concentrations of PFAS (parts per trillion), where the mixture of PFAS present depends upon the original AFFF formulation, the site geochemistry, and the presence of other co-contaminants. After characterization, each site may require site-specific remediation strategies. Finally, each of these contaminated site remediation efforts will require years of subsequent monitoring and re-sampling. The initial site characterization of each AFFF-impacted DoD installation typically costs millions of dollars and can take a year or more to perform. With the potential number of AFFF-impacted sites in the US in the thousands, just the characterization efforts for DoD sites will be very costly and time-consuming.

In addition, proposed remediation strategies at each of these sites are varied and include sequestration technologies as well as both in situ and ex situ methods of destruction. Many of these methods are still under development using this SON and other similar SERDP and ESTCP SONs and still need large-scale field validation studies. Simultaneously, the number of targeted PFAS analytes that can be measured in commercial laboratories is increasing, and different US states are responding to the drinking water health threat by enacting different regulatory limits in the absence of a national regulatory limit(Post2020). This leads to the concern that present regulatory interest in two analytes (PFOA and PFOS) that have been used to benchmark most site characterization studies to date, may be expanded to include other PFAS (including PFHxS, PFNA, Gen-X) which may require a re-appraisal of existing sites. The potential cost of expanding the number of analytes of concern in each of the various treatment strategies when multiplied by the number of PFAS-impacted sites is significant. One of the most expensive pieces of this analysis is just the time involved to obtain site-specific analytical data. For example, the on-site crews required to drill test bores are doing their job based entirely on modeled estimates of ground water flow and known AFFF use locations. When the analytical results indicate additional previously unknown areas of AFFF use, or unexpected ground water behavior, these results arrive weeks after the field crews have moved to another site. The cost to re-allocate these crews back to previous sites is significant. To address this problem, we propose to develop a method of in situ total fluorine screening that will allow AFFF-impacted site characterization to be accurate, rapid and inexpensive. In addition, this methodology is so rapid that additional sampling (both geospatial and temporal) can be performed to give much higher resolution data sets before, during and after remediation efforts have been performed. Similarly, long-term monitoring of site remediation often does not require the complete PFAS identification and quantification for every location and every time point, and having the ability to drive to an existing site and characterize the overall features of the existing well field within a day could save considerable time and expense.

The current state-of-the-art detection method for aqueous solutions of PFAS is the Liquid Chromatography – Tandem Mass Spectrometer (LC-MS/MS). It can achieve part-per-trillion sensitivity and identify which specific PFAS are present. Soils and sediments can be analyzed as
well, after an extraction process. However, because of the nature of preparing each sample for multiple PFAS standards, and the chromatographic separation steps required to identify the individual PFAS, any LC-MS/MS method are inherently slow. In addition, LC-MS/MS techniques require a library of known compounds to which to compare – which means that although it is very sensitive, it is blind to most PFAS precursors that may subsequently degrade into regulated chemicals.

Because of these limitations, we have developed a rapid total fluorine method using Particle-Induced Gamma-ray Emission (PIGE) spectroscopy that is well established with respect to the analysis of total fluorine in solid materials such as papers and textiles (Schultes2019, Ritter2017, Schaider2017, Robel2017, Lang2016). In 2018, the University of Notre Dame brought online a new $2M accelerator laboratory to extend these PIGE measurements to other matrices such as soils, sediments and aqueous samples that were well matched to this SON. Notably, we have developed a PIGE method to rapidly measure fluorine levels in the ppt range in environmental water samples (Tighe2020). Technically, PIGE uses accelerated particles to excite the $^{19}F$ nucleus, which then emits characteristic gamma-rays that are measured to give quantitative and unambiguous identification of all fluorine atoms present in the sample. The technique is rapid (typically requiring only three minutes of analysis per sample or less) and non-destructive. Similar to x-ray analysis, the samples measured are not destroyed nor rendered radioactive. At the time when this proposal was submitted, we demonstrated that the method could be calibrated with external aqueous standards to measure fluorine down to a Method Detection Limit (MDL) of ~10 ppb total fluorine for a 50 mL sample. This was achieved using commercially available solid-phase extraction media (Waters WAX cartridges) that are widely used for PFAS pre-concentration in LC-MS/MS analysis. Because most ground and surface waters in the US are low in natural fluoride ion concentrations, total fluorine measured on the WAX cartridge can be used directly as a surrogate measurement of the PFAS contamination present in most cases. In cases where fluoride contamination is a concern, since inorganic fluoride only weakly adheres to WAX media, it can be selectively removed with a dilute ammonium hydroxide wash(Miyake2007). Finally, each AFFF-contamination site we have investigated so far has so many different PFAS, as well as many different precursor materials present, that total fluorine is often above the 100 ppb range at most sites(Barzen-Hanson2017). However, finding solid-phase extraction methods to increase the sensitivity of the PIGE measurements (lowering the MDLs) became one of the objectives of this proposal. Also, at this time, PIGE is confined to nuclear physics laboratories where the instrumentation and expertise exists to make these measurements, but commercially available instrumentation exists that would allow this method to be miniaturized and put on a mobile platform – suitable for in situ fluorine screening measurements executed by field personnel at AFFF-impacted sites.

Other total fluorine measurements exist, including Total Oxidizable Precursor (TOP) analysis with LC-MS/MS, Combustion Ion Chromatography (CIC), and Neutron Activation Analysis (NAA). Even Nuclear Magnetic Resonance (NMR) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) can measure total fluorine in water samples, however these last two methods do not have sufficient sensitivity to be useful for environmental samples. The TOP assay does reproduce PIGE measurements well on most samples, but can miss some PFAS that volatilize(Robel2016) or do not oxidize to laboratory knowns for the LC/MS-MS, or some precursors are not oxidized because of other contaminants in the matrix that use up the oxidizing agent. In addition, the TOP assay includes a wet chemistry step with the slow LC-MS/MS analysis that is typically run twice
(before and after oxidation), so it is even slower and more expensive than LC-MS/MS characterization alone. The CIC method seems to work well in a variety of matrices, but because it is a chromatographic separation after a high-temperature combustion process, it too is also 50-100 times slower per sample than PIGE. While NAA is as fast as PIGE, it requires a nuclear reactor and renders the samples radioactive afterwards which is impractical for use in the field. Thus, PIGE emerges as the only technique that is spectroscopic (fast) that could be applied to hundreds of samples per day per instrument if the technique could be brought to the field. It can be a “game-changer” in the way PFAS contamination of groundwater and surface water is assessed.

Currently PIGE is performed in the Peaslee lab at the University of Notre Dame, as well as in a dozen other labs around the world. The instrumentation (shown in Figure 1) is standard for ion beam analysis laboratories, but not portable, nor trivial to operate. However, for the purposes of this limited scope proposal, it was available to be used without cost to develop the method that could be used more widely. Since it works with highest sensitivity on solid surfaces, we analyze the PFAS concentration in water samples by using commercially available solid-phase extraction (SPE) technology. For WAX cartridges, for example, approximately 50 mL of sample is passed through the extraction column, and then the surface of the SPE column itself is analyzed by PIGE. This procedure and a representative spectrum are shown in panels of Figure 1 as well.

**Figure 1:** The PIGE method and the instrumentation used at the University of Notre Dame facility.
We have established a baseline sensitivity to total fluorine of ~10 ppb and a linear response to calibration standards is shown as a panel in Figure 1. As a demonstration for another ESTCP-funded project, we have received 100+ groundwater samples shipped overnight from AFFF-impacted DoD sites, and we have prepared the samples by SPE, analyzed the samples for total F with PIGE, and returned the quantitative results in ~24 hours after receipt of the samples. Representative preliminary results are shown in Figure 2 to demonstrate the utility of the method – although not field-portable at this point.

![Image](image.png)

**Figure 2:** Preliminary data from “Characterization of the Nature and Extent of Per- and Polyfluoroalkyl Substances (PFASs) in Environmental Media at DoD Sites for Informed Decision-Making” by John J. Kornuc, ER-201633. PIGE demonstrated as a good screening method for groundwater concentrations of PFAS at one AFFF-impacted site compared with traditional LC-MS/MS methods from two laboratories.

Traditional LC-MS/MS measurements are be more sensitive (with lower MDLs) than this preliminary study, but most commercial labs cannot return results in less than a month routinely. For this particular AFFF-impacted site in Florida, similar results are shown from the rapid PIGE screen and the LC-MS/MS data obtained two months later. A second example is shown in Figure 3, where 96 different groundwater samples from an AFFF-impacted AFB in Michigan were compared with full LC-MS/MS analysis in an academic lab. Our previously developed method with WAX cartridges appears to work well to screen for PFAS at actual AFFF-impacted sites at this bombarding energy (3.4 MeV protons) and with this sample size (50 mL).
The total anionic organic fluorine measured by SPE and PIGE analysis for 96 different groundwater samples from an AFFF-impacted AFB are compared to the total PFAS fluorine content measured by LC-MS/MS. The sampling volume was 40 mL for these PIGE measurements, and as a result about half are below MDL for PIGE. The relationship is quite linear, but PIGE measures about 40% more total fluorine compared to LC-MS/MS without a total oxidizable precursor assay.

Because of these encouraging preliminary results, we proposed that the technology exists to perform PIGE on a smaller platform, and combined with a higher-efficiency SPE process, it would be possible to take this type of equipment in a truck to site locations and perform these rapid screening measurements in the field. To achieve lower MDLs, it was proposed that we could use existing SPE technology (WAX cartridges) with larger sample volumes of water. Since significantly higher volume sampling is possible in situ, since the samples do not have to be shipped off-site for analysis, by simply increasing the sampling volume ten-fold or a hundred-fold, it would also be possible to attain significantly lower limits of detection – even below the current EPA drinking water health advisory limits (HALs) of 70 ppt for any one PFAS analyte.

There were two technical challenges to overcome in order to demonstrate the feasibility of this approach. The sensitivity of the PIGE method to fluorine detection depends on the bombarding energy of the proton beam. While we have demonstrated that this method works well with 3.4 MeV protons, we do not know how much sensitivity is lost as beam energy is decreased. Only two previous studies have measured bombarding-energy dependence of PIGE spectroscopy (Kiss1984, Räisänen1982), although neither measured fluorine. However, from these studies we hypothesize that there will be a decrease in sensitivity as the beam energy decreases. In order to optimize the equipment needed to add make this technique mobile, the first challenge is to find the lower limit of fluorine sensitivity required for in situ measurements. The size of the accelerator needed is a critical design parameter required to design the mobile platform. The second challenge is that while the current sensitivity of PIGE seems to work well in typical AFFF-impacted sites, in order to be useful in characterizing groundwater concentrations of PFAS near
the EPA drinking water HALs, larger sample volumes need to be run through the solid-phase extraction media. We hypothesized that the limits of detection should decrease proportionally to the increase in sample volume, but this needed to be verified. If both of these objectives were achieved in this one-year limited scope proposal, enough information would be available to then design a prototype mobile PIGE system that could be built based on modifications to the existing Centurion™ accelerator system built by Starfire Industries LLC. This DARPA-funded project resulted in a successful prototype being constructed and tested, shown in Figure 4.

[Image: Starfire Industries, LLC design (left) and actualization (right) of a portable RFQ accelerator system designed to be field-deployable. A system like this could be readily modified to produce the type of beam required for PIGE analysis of water samples at AFFF-impacted sites.]

While this project was underway, our research team also discovered a commercially-available textile (a graphitized activated carbon felt material) that worked exceptionally well as a filter for divalent metals(Tighe2020a). During and after the COVID-19 shutdown, we have adapted this novel filter material for use with in-line filters for solid-phase extraction of PFAS. It works well as a target for PIGE by simply drying the material filter of water, and we have also had the chance to characterize this method in addition to the proposed WAX method. Although this was not in the original scope of this proposal, we completed the other tasks so rapidly that it was possible to include this approach with the original budget and timeline. We report the results from this additional novel material as well, as it will likely be useful in many applications.

Since this is a completely novel approach to speed PFAS analysis in the field by screening for total fluorine spectroscopically, we have proposed and executed three main tasks to reduce the risks in building and testing a prototype field-deployable system. These tasks were specifically to (1) identify the beam-energy dependence of the PIGE signal for F, (2) optimize and identify the likely field-deployable MDL for total F, and (3) make necessarily modifications to the Starfire Industries design of their portable accelerator system to be able to make these measurements routinely. All three tasks were accomplished and are reported here.
Materials and Methods

Task 1 – Determine the Efficiency of PIGE as a Function of Beam Energy

The goal of this task was to determine the optimum efficiency for detection of fluorine by an accelerated beam of protons as a function of the beam energy. This is a critical design feature of any accelerator, and the energy required for the proton beam will dictate the resultant footprint of the accelerator system. The PIGE method for environmental fluorine measurements was developed on a single commercially-available accelerator system that operates at 1.7 MV of terminal voltage. This new ion beam analysis facility at the University of Notre Dame can accelerate protons between ~1 and 6.0 MeV of energy. There have been no scientific studies of the sensitivity of PIGE analysis for fluorine in environmental samples as a function of accelerator energy to date, mostly because there has been little interest in measuring fluorine until now. Some early studies (Räisänen1983, Kiss1985) suggest the sensitivity goes up with beam energy, but we performed a careful analysis of inorganic fluoride target standards between proton beam energies of 2.1 and 5.0 MeV to determine the sensitivity (and MDL) achievable at each energy. The PIGE system has been described fully in McGuinness2019. A set of six homogenized bags of cellulose nitrate powder were mixed with aliquots of sodium fluoride to make homogenous mixtures of fluoride standards between 0 and 1000 ppm F. These inorganic standards were measure by PIGE using approximately 50 nA of protons at each of nine independent beam energies between 2.1 and 5.0 MeV. Replicate 3-minute acquisitions were performed and the spectra analyzed by integrating the background-subtracted 110 keV and 190 keV $^{19}$F gamma rays. The complete accelerator standard operating procedures have been included in the SEMS reporting for this project.

Task 2 – Determine MDL for PIGE as a Function of Sample Volume

The primary goal of this task was to perform a systematic evaluation of the accuracy and precision of the PIGE method on environmental samples likely to be encountered at AFFF-impacted sites. To this end, we verified the linearity of the PIGE response for total fluorine for a selection of anionic PFAS standards as a function of sample volume in two types of solid-phase extraction media.

The first set of MDLs were determined using Waters Weakly Anionic Exchange (WAX) cartridges, which are commercially available and have been shown to be effective for most long-chain anionic PFAS. Initially the MDLs were determined using 50 mL aliquots of seven different aqueous concentrations of PFOA, and then a series of different volumes between 50 mL and 2.0 L of a single concentration of PFOA were measured to demonstrate the linearity of response with increased volume. Similar studies were performed on PFOS and PFHxS. The procedure to load the WAX cartridges with sample involved the typical conditioning of each cartridge with 3 mL of 0.1% ammonium hydroxide in methanol suggested by the manufacturer. Follow by a rinse with 3 mL methanol and 3 mL of distilled water. Vacuum was applied until each solution was fully passed through the cartridge. Then 50 mL of sample was passed through the conditioned WAX cartridge and the sample reservoir rinsed with ~3 mL of distilled water. Vacuum was applied for at least 30 seconds after last rinse to dry the cartridge. The hypothesis is that the PIGE signal will scale with sample volume was verified by altering the amount of sample volume passed through each cartridge, between 50 mL and 2.00 L.

After the sample was dried, approximately 1-2 mL (about half the WAX cartridge) of Shellac was pipetting directly into the WAX cartridge with a disposable pipette and subsequently vacuumed to
and pull the bioadhesive through the cartridge. After the WAX cartridges were dried, the plastic tube of the WAX Cartridge was remove using the pipe cutter and the uppermost white frit was carefully removed. The solidified SPE media underneath the frit was then mounted as a target for measurement by PIGE.

The second set of MDLs were determined using a novel graphitized activated carbon (GAC) felt, that is commercially available as conductive pads for battery terminals. These felt materials were laser cut to 1”-diameter circles that were approximate 3 mm thick and used as inline filters, through which 2 L of sample were gravity-filtered. Typical filtration times were on the order of minutes for a 2 L bottle, the filter to air dry for about an hour before sealing into a small pre-labeled resealable plastic bag. This bag was directly taped to a target mount for PIGE analysis. Calibration curves with 6 – 7 different concentrations were obtained with 2.0 L sample volumes for 10 representative PFAS: Gen-X, PFBS, PFPeA, PFHxS, PFHpA, PFOA, PFOS, PFNA, and PFDA. In the case of the GAC felt targets, the PFAS could be washed off with acetone, leaving any inorganic fluoride that adhered to the GAC behind. Thus, both methods had a mechanism for distinguishing total fluorine from inorganic fluoride content in aqueous samples.

**Task 3 – Design of a Field-Deployable PIGE System**

Once the hypotheses from Task 1 and Task 2 have been confirmed, and optimal accelerating voltages and sample preparation methods determined, the design a field-deployable PIGE system was addressed. Ideally, such a system would be mobile, and could be deployed to rapidly screen groundwater samples in the field for total organic fluorine. Electrostatic accelerator design is a well-established field, and several US companies manufacture them routinely for medical, industrial or defense purposes. Small accelerators are an engineering challenge that has already been conquered and we partnered with Starfire Industries, LLC in Champaign, IL to take advantage of the DoD investment in their DARPA-funded project to make a portable accelerator for defense purposes. In the final phase of this limited scope proposal, we asked Starfire to modify their existing plans to incorporate what was optimal for a portable PIGE system.

The accelerator design is the key component for the portable PIGE system. The gamma-ray detector systems and appropriate shielding could all be purchased commercially as well for such a system. Similarly, the sample processing hardware which could incorporated into any truck that could drive the PIGE system would be commercially available plumbing and laboratory systems. However, the optimization of the entire system for PIGE analysis of fluorine in both aqueous and solid samples will require the data acquired in Task 1 and 2 in order to prepare a realistic cost estimate to build a turn-key system that could be used in the field. Such turn-key systems could be operated by a trained technical assistant and with no moving parts are quite rugged in the field.
Results and Discussion

Task 1 – Determine the Efficiency of PIGE as a Function of Beam Energy

This task was readily accomplished using the Notre Dame Ion Beam Analysis facility in the Nuclear Science Laboratory. Figure 5 shows the quantity of fluorine gamma rays detected per microcoulomb of beam delivered to target, as a function of proton bombarding energy.

![Figure 5: The production of characteristic $^{19}$F gamma rays as a function of proton bombarding energy from a known inorganic standard. The error bars on the individual measurements are encompassed within the symbol for each measurement.](attachment:image.png)

Prior to this study, PIGE studies had been routinely conducted at 3.4 MeV of bombarding energy, but the yield was observed to sharply rise with beam energy. Similarly yields drop off significantly below 3 MeV, and this led to our first design consideration that we should use the highest energy possible above 3 MeV. As the bombarding energy at the Notre Dame facility was capable of going all the way to 6 MeV, we began to explore higher energies but beams above 5 MeV in energy were observed to create radioactive products (primarily short-live nitrogen-13 and oxygen-15 isotopes in the atmosphere surrounding the target. While another factor of 10 in PIGE sensitivity appears achievable between 3.5 MeV and 4.5 MeV, anything above 3 MeV would be manageable.

The beam intensity available at the University of Notre Dame for this study was limited to about 50 nA on target, and significantly more beam (a factor of ~100) would be available from the RFQ type of accelerator proposed here, which would more than offset this lack of sensitivity. The most important information from this study is that the beam energy requirement for the portable accelerator system has been defined.
Task 2 – Determine MDL for PIGE as a Function of Sample Volume

The goal of task 2 was to optimize and determine the MDL for PFAS detection by PIGE. This was done for two types of SPE media: Waters Weakly Anionic eXchange (WAX) cartridges, and a novel Graphitized Activated Carbon (GAC) felt textile used as an in-line filter.

Although WAX cartridges are routinely used for the pre-concentration of anionic PFAS prior to LC-MS/MS analysis, the PIGE analysis of fluorine is done on the top surface of the WAX cartridge before elution is performed, so a new measurement of sensitivity is required for this method as described previously. The initial measurements were all performed with replicate 50 mL samples of diluted aqueous PFOA standards as shown in Figure 6.

![Figure 6: A standard calibration curve of PIGE signal recorded in gamma-ray counts per microcoulomb of beam delivered plotted against concentration of 50 mL aqueous samples of PFOA. Three replicate measurements are recorded for six different concentrations of PFOA and a distilled water blank.]

The linearity of the response is good and no saturation is observed even with a concentration of almost 20,000 ppt PFOA. The method detection limit can be calculated from this curve based on the standard deviation of response ($S_y$) at levels near the limit of detection, using the formula $MDL = 3.3 \left( \frac{S_y}{S} \right)$. Using the entire curve, this results in an MDL of 3.3 ppb, but using lowest five points (within a factor of 10 of the MDL) this results in a more accurate MDL of 1.2 ppb PFOA for a 50 mL sample volume. These measurements were repeated for PFOS as well as PFHxS, and resulted in MDLs of approximately 1.1 ppb for PFOS, and 1.4 ppb for PFHxS. This means that with no significant modifications, all anionic PFAS can be measured by this method to a detection limit close to 1000 ppt. For every AFFF-impacted site for which we have measured PFAS (see figures 2 and 3, for example), there have been multiple known PFAS analytes present and between 30% and 90% of the total fluorine signal has come from unknown PFAS analytes or “precursors”. This accounts for the reliability of PIGE already seen from this method using 50 mL sample volumes. There is a lot of organic fluorine available in groundwater at AFFF-impacted sites.

However, as PFAS regulatory levels change, they are driven by better detection limits available on LC-MS/MS systems as well as observed health effects seen for PFAS concentrations in the low ppt range in drinking water studies. We have assumed that the MDLs for the PIGE detection
method are linearly dependent on sample volume. This means that if we have an established MDL around 1.2 ppb PFOA for a 50 mL sample volume, if we wish to detect a single analyte such as PFOA down to a detection limit of 50 ppt, then we simply need to put a larger volume (= 1200/50 x 50 mL) of 1.2 L through the WAX cartridge to achieve this limit.

Numerous replicate studies of this with WAX cartridges with sample volumes ranging between 50 mL and 2.0 L of a known PFOA standard (1 ppb) were performed. The results of these tests are shown in Figure 7.

![Figure 7: The average PIGE signal recovered from different sample volumes of a 1 ppb PFOA solution. Between 2 and 5 replicate measurements were made for each volume.](image)

The linearity of signal response is clearly observed for these concentrations of PFOA over a wide range of sample volumes. This implies that simply sampling 1 or 2 L volumes with the WAX cartridge technique would work reduce the MDLs to below 50 ppt. However, it was observed that the time and personal attention needed to measure large volumes through a small WAX cartridge, even with commercially available sample extension holders available, was extensive. This would not be a field-friendly method. However, we discovered another SPE method that shows greater promise for practical field measurements.

A similar set of measurements were performed for a novel GAC felt cut to 1-inch diameter circles as used as an inline filter for 2.0 L volumes of water. We used 2.0-L bottles for the laboratory assessment of their performance in collecting PFAS, but of course in the field, in-line filter assemblies could be attached to any bore hole pump and left to run for minutes to hours, and the sampling volume could range between 1 and 100 L readily. In the laboratory, the samples were left to gravity filter through the felt, and 2 L passed through typically within 3 minutes. Unless significant turbidity was encountered, then 10 L of ground water could be passed through this filter in approximately 15 minutes by gravity filtration, or in less time if connected to a bore hole pump.

The results of testing with ten different individual PFAS analytes are shown in Figure 8. Because this material had not been used with PFAS before, it was necessary to ascertain that it behaved...
similarly to bulk GAC systems to capture most PFAS, but with lower efficiency on the short-chain PFAS.

Figure 8: The average PIGE signal recovered from 2 L volumes of various PFAS solutions passed through a GAC felt filter by gravity filtration. Only one replicate was measure for this test, but the linearity for all PFAS tested is good, and the slope in each plot represents the relative sensitivity of binding for each PFAS.

The MDLs calculated for these compounds for a 2L volume are: 330 ppt for PFOA, 550 ppt for PFOS, and 200 ppt for PFHxS. While these are better than 50 mL volumes passed through WAX cartridges, the design of in-line filters connected directly to a bore pump allows much greater volumes to be sampled readily. This means if 20 L can be sampled (typically in less than 20 minutes), this method would have the analytical sensitivity for individual analytes of interest in the 20 – 50 ppt range. This method brings the practicality to the field sampling aspect of this project.

Task 3 – Design of a Field-Deployable PIGE System

The overall goal of this work is to revise the vane-tip profile of Starfire’s existing Centurion™ accelerator system to produce a proton (p) beam suitable for fluorine detection via proton-induced gamma emission (PIGE). Experiments conducted as part of Task 1 have determined that F-detection via PIGE will require a p-beam at ≳ 3 MeV. Modifications to the Centurion’s™ vane tip profile are required to achieve this, as the existing design is capable of outputting deuterons (d) at 3.86 MeV and p at 1.93 MeV for use as a neutron generator. While the Centurion™ system is capable of outputting protons at 1.93 MeV, increasing the output energy to at least 3 MeV requires increasing substantially the vane-tip voltages over what is required for the 1.93 MeV case as well as modifying the tip profile to take advantage of the increased electric field.
Since the operating frequency, mid-cell radial aperture, and vane-tip radius of curvature are all unchanged from the existing Centurion™ system, no modifications to the resonator cross section or end regions are required. This simplifies the design process considerably, as changes in vane-tip length will merely require changes to the length of the resonator, without modifying the end-region geometry.

Although a large number of simulations were run, the final result (see Section III) ended up as a balance of 1) the physics relevant to the RFQ accelerator and the PIGE application and 2) practical considerations such as size, weight, and power. Despite the fact the growth of the output energy with respect to the length of the accelerator is sublinear, the physics relevant to fluorine detection via PIGE dictate that additional energy is still indeed favorable throughout the 3—5 MeV range (and beyond). However, building this accelerator into a mobile system does require setting some practical limits on size, weight, and power. As such, a practical limit of 150 cm was placed on the accelerator section, which corresponds to an output energy of approximately 3.5 MeV. Figure 9 shows RFQ length as a function of output energy over a series of simulations where the accelerator section of the RFQ was lengthened to increase the output energy. For this series of simulations, the radial matcher (RM), shaper (SH), and gentle buncher (GB) were all unchanged.

The parameters of the ultimate result of the iterative design process are shown below, in Table 1. In general, this RFQ operates at 600 MHz, is approximately 147 cm in length, and requires approximately 212 kW of RF cavity-fill power.

![RFQ accelerator length as a function of output energy. For this series of simulations, the radial matcher (RM), shaper (SH), and gentle buncher (GB) were all unchanged. Only the accelerator section was altered.](image_url)

**Table 3:** Operating parameters for the final PIGE RFQ design.

<table>
<thead>
<tr>
<th>Operating Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating frequency</td>
<td>600 MHz</td>
</tr>
<tr>
<td>Injection energy</td>
<td>12.5 keV</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>Final beam energy</td>
<td>3.52 MeV</td>
</tr>
<tr>
<td>Transmission at 10 mA</td>
<td>82.0 %</td>
</tr>
<tr>
<td>Input transverse emittance (normalized)</td>
<td>0.20 $\pi$ mm-mrad</td>
</tr>
<tr>
<td>Output emittance (normalized)</td>
<td>0.14 $\pi$ mm-mrad</td>
</tr>
<tr>
<td>Output beam FWHM energy spread at 10 mA</td>
<td>15 keV</td>
</tr>
<tr>
<td>Linac operating repetition rate</td>
<td>60 Hz</td>
</tr>
<tr>
<td>Output beam width</td>
<td>100 $\mu$s</td>
</tr>
<tr>
<td>Vane length</td>
<td>147 cm</td>
</tr>
<tr>
<td>Pulsed cavity RF power</td>
<td>212 kW</td>
</tr>
<tr>
<td>Pulsed beam power (10 mA)</td>
<td>35 kW</td>
</tr>
<tr>
<td>Pulsed RF input power</td>
<td>247 kW</td>
</tr>
<tr>
<td>Average rf power requirement</td>
<td>1.5 kW</td>
</tr>
</tbody>
</table>

This RFQ takes an input beam of 12.5 keV protons and accelerates them to 3.5 MeV ± 15 keV. The spot size of the beam at the output of the accelerator is approximately 0.5 mm (FWHM). Figure 10 shows both the simulated energy spectrum of the output proton beam (left) and the simulated beam spot at the output of the accelerator (right). Figure 11 shows the transmission of the proposed accelerator simulated over the range of 10 $\mu$A—30 mA. A transmission of > 75% is achieved for an input current $\leq$ 14 mA.

**Figure 10**: A histogram showing the energy distribution of the output proton beam at 10 mA (left) and the beam spot at the output of the accelerator (right).
Figure 11: Transmission as a function of input current. This simulation assumes a normalized input emittance of 0.2 mm-mrad.

As the beam is accelerated, some charge is lost as it falls out of the acceleration envelope. Figure 12 shows a plot of transmission at 5 mA and 10 mA over a range of normalized input emittances. The simulated behavior shows a relatively constant transmission over the approximate range of 0.05—0.35 mm-mrad. A transmission > 75% is maintained for a 10 mA input having a normalized emittance ≤ 0.5 mm-mrad. Figure 13 shows the simulated energy spectrum of lost current within the accelerator. Most of the beam losses during acceleration occur at ~250 keV, and there is a low-intensity but broad loss around 1—2 MeV. This lost charge will be incident on the internal copper walls of the accelerator. Any radiation produced from these lost protons on copper over the range of interest for F-detection via PIGE will be 1) low intensity, 2) diffuse, 3) emitted far away from the sample and detectors, and 4) easily mitigated by shadow-shielding (if necessary).

Figure 12: A plot of transmission at 5 mA and 10 mA for a series of input emittances is shown at left. For each of the inputs, the Courant-Snyder parameters were held constant. The series of ellipses corresponding to the various input particle distributions, spanning 0.05 mm-mrad (blue) to 2 mm-mrad (red), is shown at right.
A perspective view of the proposed RFQ accelerator is shown in Figure 14. Since the length required to achieve 3.5 MeV protons is longer than the present Centurion™ system, the resonator will need to be lengthened. However, as the present design uses the same mid-cell radial aperture, drive frequency, and vane-tip radius of curvature, the resonator cross section and end-regions do not need to be altered from the existing design. Thus, this added length will only require one additional ring of four RF power injectors (also called final power amplifiers, or FPAs), along with additional RF tuning slugs, venting slots, and cavity probe points that accompany each RF power injector. A comparison between the RFQ accelerator section of the existing Centurion™ system and the proposed PIGE RFQ accelerator is shown in Figure 15.

Figure 14: The proposed RFQ, rendered here with the four sets of four RF power injectors attached. Also shown are the cavity tuning slugs (one each to the left and right of every RF power injector), venting slots, and cavity probe points.
Figure 15: A comparison between the proposed RFQ accelerator and the RFQ accelerator section of the existing Centurion™ system (top). A photograph of the accelerator portion of the existing Centurion™ system with the RF power injectors attached during cavity tuning is also shown.

Shown in Figure 16 is the existing, Centurion™ system. The only significant changes that are required to this platform are that 1) the accelerator section will increase in length by approximately 8”, and 2) the RF drive electronics will need to be modified to accommodate four additional RF power injectors. Since the total instantaneous power capability of the existing RF drive chain is beyond what is required here, the only major changes from the existing hardware will be to replace the 12-way splitter in the present system with a 16-way splitter and to add four sets of triode control electronics. A block diagram of the proposed RF drive chain is shown in Figure 17, along with a photograph of one of the existing triode control boards.
Finally, it is worth noting that the envisioned fluorine-detection system does not have the accelerator implemented as a separately mobile cart, rather as an installation within a larger vehicle containing a small area for the wet chemistry needed to prepare samples for analysis in this machine. To that extent, the wheels and accompanying drive system from the existing cart can be removed. If necessary, the vacuum, cooling, and HV/RF subsystems can also be moved around to better utilize the space allotted for installation within the mobile lab.

![Diagram of the existing Centurion™ system with labels for major subsystems. The proposed system will have the RFQ accelerator section lengthened by approximately 8” and will require RF drive electronics for an additional four RF power injectors.]

**Figure 16:** The existing Centurion™ system. In this figure, each of the major subsystems has been outlined and labelled. The proposed system will have the RFQ accelerator section lengthened by approximately 8” and will require RF drive electronics for an additional four RF power injectors.
We have detailed here the results of an iterative design process whereby the design of Starfire’s existing Centurion™ system has been modified to supply 3.5 MeV $p$ for use in a mobile rapid field-screening system for detecting PFAS compounds via PIGE. By maintaining the same mid-cell radial aperture, vane-tip radius of curvature and drive frequency, we are able to keep the existing resonator design and forego the extensive engineering work that would be required had the resonator cross section changed. The final result is an accelerator design that is only 8” longer than the existing Centurion™ system and is able to exceed the requirements for a mobile rapid field-screening PIGE system.
Conclusions and Implications for Future Research

Every aspect of the proof-of-concept study summarized here led to positive conclusions that can be acted upon. A list of conclusions is itemized here.

- The first task determined the minimum proton beam energy required to make the PIGE method work as a screening tool for total fluorine in groundwater samples. Because we had a laboratory system with variable beam energies available, this was a simple experiment to perform, but a critical step in the determination of the accelerator design, and ultimately its size. We have proven that anything above 3 MeV would work for this technique, and that the higher the beam energy the more sensitive the measurement becomes (at least up to 5 MeV). We also have shown that there is no appreciable radiation induced in the target materials at these energies, which means the licensing of these devices will be similar to licensing routine x-ray producing devices such as portable x-ray fluorimeters.

- The second task determined that aqueous sample method developed using standard WAX cartridges and simply solidifying the cartridge with adhesive and placing it in the beam will yield impressive linearity and modest sensitivity for all anionic PFAS – down to about 1 ppb for 50 mL samples. This MDL was proven to be linear with sample volume, so lower environmental limits could be achieved by larger sample volumes if needed. However, this method was found to not scale efficiently with volume, in terms of sample preparation time.

- As an extension to the second task, a novel GAC felt filter method was developed that shows excellent linearity and impressive sensitivity for the 2-liter gravity-filtered laboratory samples. This method, when used as an inline filter will yield individual analyte total fluorine MDLs in the 20-50 ppt range readily. The ease of use and sample preparation for this method reduces analysis time and cost significantly as well. This is a viable method for rapid field sampling of total fluorine when combined with PIGE analysis.

- The third task took the results from the first task and produced a re-design of an existing portable accelerator system, developed with DARPA funding by Starfire Industries, LLC. This redesign demonstrates that only modest modifications are necessary to take the existing accelerator and modify it into a portable PIGE system. This is important because rather than designing a portable system from scratch, we have proven that simply taking a working system and modifying the accelerator tube length by 8-inches and re-designing the internal components appropriately (the vane tips), a prototype device could be constructed rapidly with high-likelihood of success.

What this means is that further basic research into this method is not needed before proposing to build a prototype portable PIGE system. This is a significant advance of our understanding over even one year ago. The obvious next steps are to propose to build such a system and field-test it at several representative AFFF-impacted sites or active remediation sites. Potential components of this proposal would include a formal partnership between Starfire Industries and the University of Notre Dame and one of the large environmental consulting firms (Jacobs). The goal would be for Starfire Industries to build the modified Centurian system for this project, and to mount it in a commercially available light truck. The University of Notre Dame would adapt commercially available gamma-ray detectors, appropriate shielding and target mechanisms that would fit in the space allowed by the vehicle to provide routine PIGE analysis using the accelerator. The Notre Dame team would also produce a selection of in-line filter devices using the new GAC felt material, that could be independently tested in the laboratory and the field to optimize design and
cost. It is likely that the filters will cost only dollars per device, so that a thousand or more could be kept on the portable PIGE system for any site visit. The environmental consultants would provide field personnel and access to known AFFF-impacted groundwater sites and help to design and to perform the field validation study and to help create SOPs for field personnel to use the prototype portable PIGE system.

In summary, completion of a portable PIGE prototype system would allow the following scenarios to unfold as needed:

Example #1: For a new site characterization, where well-boring is actively underway, the portable system could be brought to any preferably level location on site. It has self-contained power systems as needed. Pre-labeled inline filters would be distributed to the well heads by field personnel and samples collected with timed “draws” through the filters. This could be 10-20 minutes per well, or if higher sensitivity were desired, they could be left on for an hour, while field personnel continue to add filters to other bores. At the end of deployment of these filters, they would be collected and returned to the PIGE truck, where a single technician could unpack 100 or more filters, dry them for an hour, and then analyze them by PIGE all within the same vehicle within a single 8-hour day. The results could be electronically distributed and analyzed before the next day of boring were to commence. This would allow plume tracing to be done all in a matter of days, instead of repeated visits to the site months apart. The PIGE truck would work collaboratively with the site characterization team to steer the efforts towards the areas with the highest PFAS impact.

Example #2: For an existing AFFF-impacted site with complete characterization and an active remediation or sequestration effort on-going, the portable PIGE unit could be driven to the site, set up within hours, and used to monitor total fluorine at hundred of locations per day. In this case it would be possible to complete the entire survey periodically (quarterly, monthly) within one or two days, and then drive to another site to repeat the process. The data would confirm the nature of the PFAS contamination at that moment in time, and catch concerning trends early, or reduce the need for complete analytical work-ups of which PFAS are where, if just monitoring of the total F concentration will suffice to say that the plume has not increased. Instead of regular full LC-MS/MS analysis, monthly or quarterly screening could be performed at very low cost and full analysis could be done once a year.

There are undoubtedly many more situations where a portable field measurement of all PFAS (as measured by total anionic organic fluorine) could be practical and cost-saving, but we list just a few of the obvious cases here. Field testing will undoubtedly lead to more situations where a robust and rapid PFAS screening technique could be useful.
Literature Cited


