Contract No:

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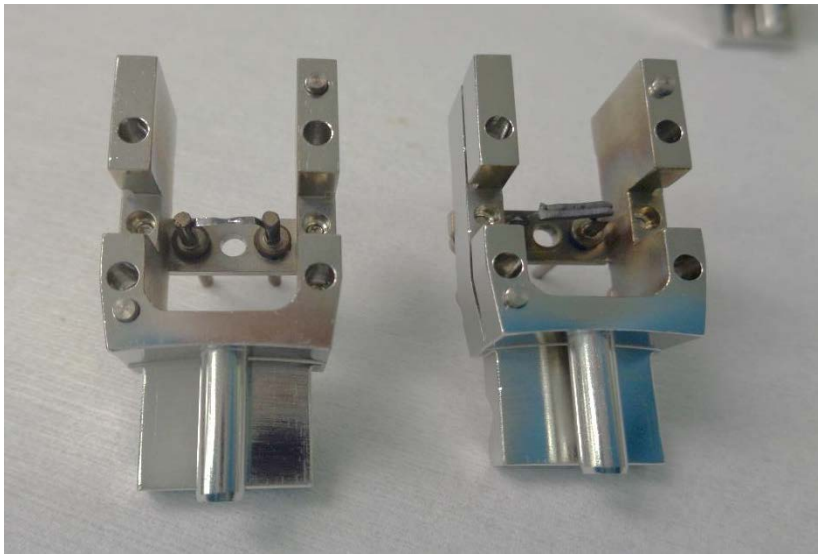
Disclaimer:

Reduced Graphene Oxide as Filament Material for Thermal Ionization Mass Spectrometry with a Focus on Pu and U Analysis

Isotopic information can be informative as to the intended use and/or production history of special nuclear material. For uranium and plutonium samples, thermal ionization mass spectrometry is the benchmark technique for determining isotope ratio data. Sample utilization in thermal ionization is, however, quite low with ionization efficiencies typically between 0.1% and 0.5% - i.e. only 0.1% to 0.5% of the sample consumed actually contributes to the detected signal. Filaments made from reduced graphene oxide have the potential to greatly improve ionization efficiencies and would lead to enhanced analytical capabilities in the fields of nuclear forensics, nuclear safeguards, and environmental monitoring. In the first year of this LDRD project reduced graphene oxide filaments were constructed using 3-D printing techniques. These filaments have been successfully mated to commercial filament posts. Pu ion production was observed from filaments spiked with a small amount (10 pg) of the Pu 128 certified reference materials.



Traditional rhenium filament (left) and reduced graphene oxide filament (right).

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature	**Date**

Title

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The use of graphene oxide materials for thermal ionization mass spectrometry analysis of plutonium and uranium has been investigated. Filament made from graphene oxide slurries have been 3-D printed. A method for attaching these filaments to commercial thermal ionization post assemblies has been devised. Resistive heating of the graphene based filaments under high vacuum showed stable operation in excess of 4 hours. Plutonium ion production has been observed in an initial set of filaments spiked with the Pu 128 Certified Reference Material.

FY2017 Objectives

- Identify background uranium levels in commercially sourced graphene oxide material
- Determine impact of graphene oxide material on thermal ionization efficiency in a typical Re filament TIMS analysis
- 3-D print small form factor graphene oxide filaments
- Mate printed filaments to commercial TIMS filament assemble
- Determine durability of graphene based filaments in a TIMS source chamber when heated to greater than 1000 k

Introduction

Thermal Ionization Mass Spectrometry (TIMS) in an analytical technique that sees widespread use in the fields of nuclear safeguards,[1,2] nuclear forensics,[3,4] and environmental monitoring[5,6] for the measurement and characterization of actinide species. TIMS is currently considered the benchmark technique for determining uranium and plutonium isotopic information.[2] Sample utilization in TIMS is, however, typically quite low due to poor ionization efficiencies – normally in the range of 0.1% - 0.5% for Pu and U. Research has been done to try and increase ionization efficiencies with much of the work focused on geometry modifications of the typical rhenium filament material.[7-9] Because of thermodynamic limits related to work function of the analyte and the ionizing filament entirely new materials (i.e. not Re or W) are needed in order to greatly improve ionization efficiency.

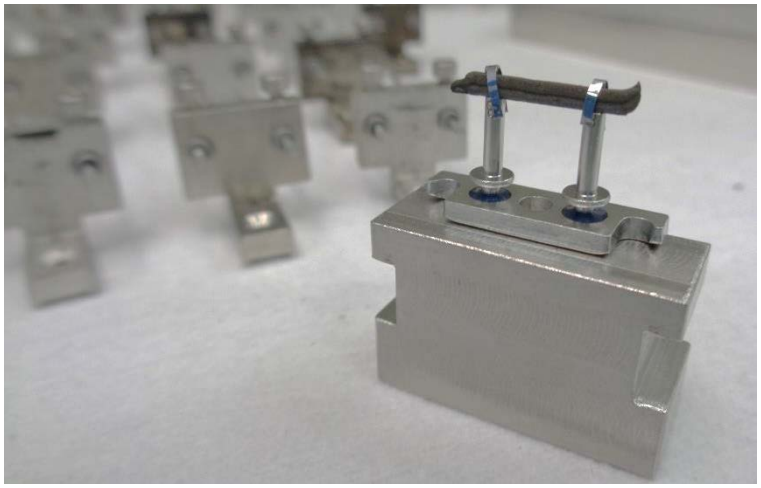

Figure 1. 3-D printed RGO filament mounted on a commercial TIMS post assemble.

Developing new materials to be used as TIMS filaments is, however, non-trivial. In a typical Pu or U analysis the evaporation filament can reach temperatures in excess of 1500 K; therefore, high

temperature stable materials are a must.. Recent work has shown that graphene-based materials can be 3-D printed into small form factors that can be resistively heated to more than 2000 K.[10] This suggests a graphene based TIMS filament is possible and could represent an entirely new substrate material for TIMS analyses. Moreover, because the work function of graphene is tunable[11,12] the thermodynamic constraints that lead to poor ionization efficiency in Re and W based filaments could be overcome. Orders of magnitude increases in ionization efficiency could be realized. Such improvements would directly translated into reduced sample size requirements and/or enhanced analytical capabilities which would support the nonproliferation, safeguards, and forensics communities.

The first year of this LDRD project was focused on baseline project viability studies, developing the technical knowhow to reproducibly manufacture graphene based filaments, testing different methods to mate 3-D printed filaments to commercial TIMS filament assemblies, and initial durability studies of heated filaments under high vacuum conditions. In terms of project viability, we found incorporation of graphene materials into a typical rhenium filament yields ionization efficiencies on par with that of bead loaded samples. We also found reduced graphene oxide slurries can be 3-D printed into small form factor filament shapes that can be mated with commercial TIMS filament posts. Finally, preliminary data has been collected that demonstrates pure graphene filaments can be heated in the source chamber of a commercial TIMS instrument to temperatures in excess of 1500 K with high temperature operation in excess of 4 hours.

Approach

A two pronged research approach was taken in order to quickly establish project viability while also laying the ground work for slower maturing R&D goals. In regard to the former, an initial study of standard Re filaments coated with graphene oxide (GO) was undertaken to screen for potentially negative effects of GO on Pu or U ionization. Results from Pu samples directly loaded onto these hybrid filaments showed reasonably good ionization efficiencies, on par with the standard method of using bead loaded samples, and suggested filaments constructed entirely from GO or other graphene type materials would be compatible with typical TIMS analytical workflows.

Figure 2. Hybrid Re-RGO filaments on GSR stubs being prepped for micro-Raman and SEM characterization.

With positive results from the viability study, efforts were shifted to developing the technical expertise required to reproducibly generate small form factor filaments for TIMS analysis. Multiple synthetic parameters (e.g., ink viscosity, printing speeds, drying times, pre-annealing temperature rates, etc.) were systematically varied to determine optimal filament robustness and durability. R&D associated with attachment of the 3-D printed graphene filaments to commercial TIMS filament assemblies was also conducted.

Results/Discussion

A commercial source of GO/water slurries was identified and initial samples were procured and analyzed. Semi-quantitative ICP-MS found trace amounts of Mn, suggesting Hummers[13] or a modified Hummers[14] method was used for GO production, as well as Na, Mg, and potentially Au. The level of uranium in the RGO slurry was found to be at the level of the blank (Figure 3), which is indicative of sub-1 ppm uranium content in the neat GO paste. This is below that of the zone refined rhenium (10 ppm) typically used in TIMS analysis. Accordingly, for ultra-trace U measurements graphene based filament materials could be superior to the more traditional Re filaments.

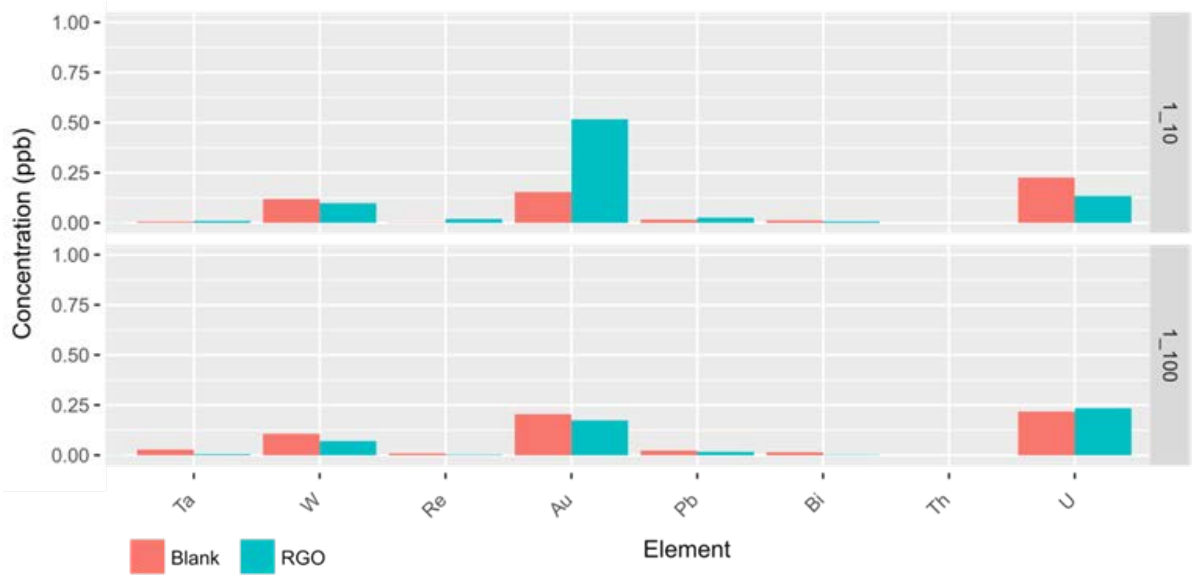

Figure 3. Select element semi-quant ICP-MS results for a 1:10 and 1:100 dilution of a 7.6 mg/mL RGO in 2% nitric acid solution.

Hybrid RGO-Re filaments were characterized at the beginning of the project to assess the influence of graphene type materials on Pu ionization. In this work GO paste was applied to traditional Re filament ribbons (see Figure 2). It was found that upon heating the GO layer on top of the filament would often times delaminate exposing the Re surface. Micro-Raman characterization of the hybrid filaments after heating showed increased sp2 carbon character, which was expected[10], and is indicative of RGO formation. Small islands of sp2-like carbon were observed on areas of the Re filament where the GO/RGO film had exfoliated. The hybrid filaments were also used for Pu sample analysis. 10 pg of CRM Pu 128 was directly loaded on a small number of filaments which were then run using a typical Pu method. Ionization efficiencies for this set was approximately 0.1%, which is within the range observed for bead loaded samples. Accordingly, GO and RGO type materials seem to be compatible with TIMS analysis methodologies.

Printing of the small form factor GO filaments using commercially sourced 3-D instrumentation was found to be relatively straight forward. Difficulty was encountered trying to maintain the 3-D printed shape during the pre-annealing step. This step is required to ensure the filaments are sufficiently conductive for Joule heating in a commercial TIMS source chamber. A precise drying and thermal annealing protocol was determined that allows for filament pre-annealing with minimal loss of 3-D shape and structure. A number of different connection schemes were tested to physical and electrically attach the graphene filament to the commercial filament assembly. Three of the more successful

connection motifs are shown in Figure 4. Carbon tape, copper tape, metallic paint, and Re ribbons were all tested as attachment strip materials. Re ribbons were found to be best.

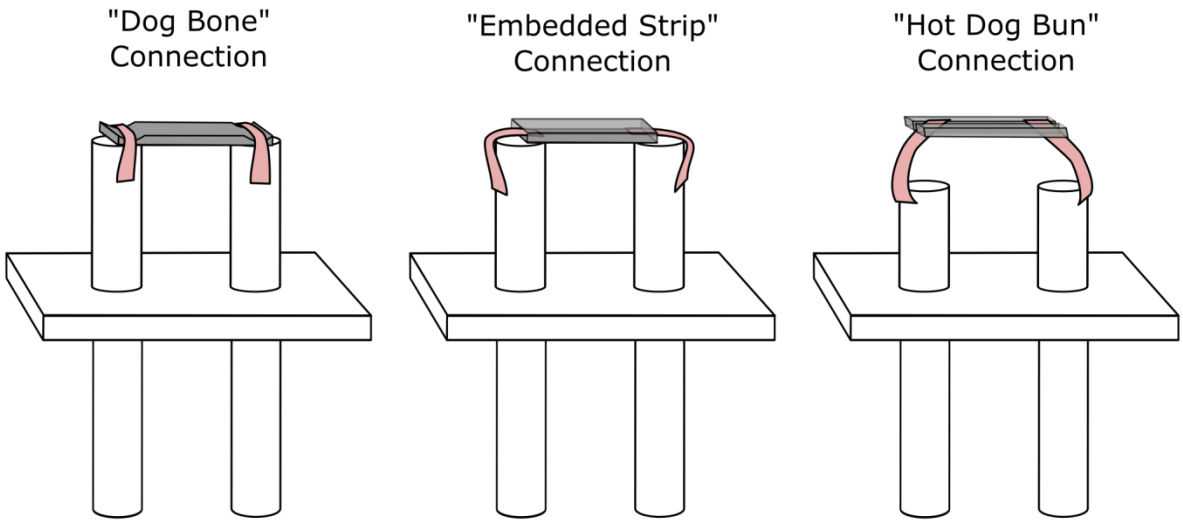

Figure 4. Three of the different connection types investigated for attaching the graphene filament to a commercial TIMS filament assembly. The pink strips are Re ribbons.

The "Embedded Strip" and "Hot Dog Bun" connection types were found to have the best electrical connectivity. An initial set of the "Hot Dog Bun" style filaments was been loaded into a commercial TIMS instrument (Isotopx) and characterization is currently underway. Initial results are promising with neat RGO filament operating at greater than 1500 K for more than 4 hours. Pu ion production has also been observed from a filament spiked with 10 pg of CRM Pu 128.

FY2017 Accomplishments

- Uranium content of commercial RGO found to be sub 1 ppm making it suitable substrate for ultra-trace uranium analysis.
- Ionization efficiency of hybrid Re-RGO filaments measured at approximately 0.1%
- Three different filament attachment schemes manufactured and characterized
- Graphene based filament operated in a commercial TIMS source for more than 4 hours at temperatures in excess of 1500 K
- Pu ion production observed from a 3-D printed RGO filament

Future Directions

- Iterate graphene-post attachment scheme to maximize robustness
- Injection molded filaments vs. 3-D printed
- Measure ionization efficiency of graphene based filaments for pg Pu loads
- Measure ionization efficiency of graphene based filaments for pg U loads
- Print and characterize new filament geometries (i.e. cavities)
- Develop doped/functionalized graphene materials to increase work function

FY 2017 Publications/Presentations

None

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Acronyms

CRM – Certified Reference Material
GO – Graphene Oxide
ICP-MS – Inductively Coupled Plasma Mass Spectrometry
R&D – Research and Development
RGO – Reduced Graphene Oxide

TIMS – Thermal Ionization Mass Spectrometry

Intellectual Property

Invention Disclosure - SRS-16-019 – "*Graphene Based Filaments for Thermal Ionization"*

Patent application - 15/435,976 - *"Graphene/Graphite-Based Filament for Thermal Ionization*"

Total Number of Post-Doctoral Researchers

1