REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
06-07-2015	Final Report	1-Apr-2014 - 31-Mar-2015

4. TITLE AND SUBTITLE
Final Report: LA-ICP-MS: Impact on Broad Based Understanding of Military Environment to Solider Protection leading to Materials Innovation and Translation

5a. CONTRACT NUMBER
W911NF-14-1-0143

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
206022

6. AUTHORS
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

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Greensboro, NC 27411 -0001

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
64729-MS-REP.4

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
The instrumentation grant is to establish a laser ablation (LA) Inductively Coupled Plasma Mass Spectrometry (ICP-MS), which can trace metallic elements in various military applications. This capability is critical for alloy innovation and characterization that supports soldiers' protection and further significantly impacts the education and training in Science, Technology, Engineering and Mathematics (STEM) disciplines across departmental boundaries in engineering (biomedical, mechanical and other engineering disciplines), life sciences (biology, animal science) and education (human development and services)

15. SUBJECT TERMS
laser ablation, Inductively Coupled Mass Spectrometry,

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Yeoheung Yun
UU	UU	UU	UU		19b. TELEPHONE NUMBER 336-285-3226

Report Title

Final Report: LA-ICP-MS: Impact on Broad Based Understanding of Military Environment to Solider Protection leading to Materials Innovation and Translation

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The instrumentation grant is to establish a laser ablation (LA) Inductively Coupled Plasma Mass Spectrometry (ICP-MS), which can trace metallic elements in various military applications. This capability is critical for alloy innovation and characterization that supports soldiers' protection and further significantly impacts the education and training in Science, Technology, Engineering and Mathematics (STEM) disciplines across departmental boundaries in engineering (biomedical, mechanical and other engineering disciplines), life sciences (biology, animal science) and education (human development and services).

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper
07/06/2015	3 Youngmi Koo, Vesselin N. Shanov, Sergey Yarmolenko, Mark Schulz, Jagannathan Sankar, Yeoheung Yun. Inverse-Ordered Fabrication of Free-Standing CNT Sheets for Supercapacitor, Langmuir, (07 2015): 0. doi: 10.1021/acs.langmuir.5b00891
TOTAL:	**1**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper
TOTAL:	

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. Yeoheung Yun, Yougseok Jang, Juan Wang, Zhongyun Dong, Vesselin Shanov, Jagannathan Sankar, Youngmi Koo, Leon White, Boyce Collins, "Biodegradable Magnesium Implant: In vivo and In vitro Convergence", Proceedings of the ASME 2014 International Mechanical Engineering Congress & Exposition, IMECE2014-39262, November 14-20, 2014, Montreal, Canada.
2. Yeoheung Yun, ASTM conference, invited talk, Canada 2014

Number of Presentations: 2.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

2014: The first global standardization committee AC 87 (out of American Society for Testing Materials - ASTM, International Standardization Organization - ISO and Deutsches Institut für Normung - DIN; the German Institute for Standardization)

Graduate Students

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

The instrumentation grant is to establish a laser ablation (LA) Inductively Coupled Plasma Mass Spectrometry (ICP-MS), which can trace metallic elements in various military applications. This capability is critical for alloy innovation and characterization that supports soldiers' protection and further significantly impacts the education and training in Science, Technology, Engineering and Mathematics (STEM) disciplines across departmental boundaries in engineering (biomedical, mechanical and other engineering disciplines), life sciences (biology, animal science) and education (human development and services).

Technology Transfer

Award Information

Award Number	64729-RT-REP
Title of Research	LA-ICP-MS: Impact on Broad Based Understanding of Military Environment to Solider Protection leading to Materials Innovation and Translation
Principal Investigator	Yeoheung Yun
Organization	North Carolina A&T State University

Technical Section

The instrumentation grant is to establish a laser ablation (LA) Inductively Coupled Plasma Mass Spectrometry (ICP-MS), which can trace metallic elements in various military applications. This capability is critical for alloy innovation and characterization that supports soldiers' protection and further significantly impacts the education and training in Science, Technology, Engineering and Mathematics (STEM) disciplines across departmental boundaries in engineering (biomedical, mechanical and other engineering disciplines), life sciences (biology, animal science) and education (human development and services).

Technical Report

Instrument Introduction: Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a type of mass spectrometry which can detect metallic elements and some non-metals in concentrations as low as one part in 10^{12} (one part per trillion), the best resolution among analytical tools. Compared with other techniques such as atomic absorption techniques, ICP-MS provides greater speed, precision, and sensitivity for tracing metals, which allows scientific and technical advances in many military applications. However, an ICP-MS by itself can only probe samples that are inherently liquid samples or solutions containing dissolved solids. The inability to analyze solid samples can be overcome by coupling ICP-MS with Laser Ablation (LA) as a means of sample introduction. LA ICP-MS can directly analyze solid samples of bulk military materials. We are proposing to establish a state-of-the-art LA-ICP-MS infrastructure that consists of an Agilent 8800 ICP-MS (Triple Quadrupole ICP-QQQ, Agilent Technologies (Figure. 1)) and an Analyte G2 laser system (excimer Laser Ablation, Photon-Machines Inc. (Figure 2)).

ICP-MS: Agilent Model 8800 is truly ground-breaking - the world's first Triple Quadrupole ICP-MS (ICP-QQQ). It allows ***the best accuracy, performance, stability, flexibility, reliability, and consistency*.** In general, the detection capability of ICP-MS is often limited in real applications by two major factors: contamination and spectral interference. Most interference problems were resolved using Collision/Reaction Cell technology. However, some interference still remains, such as metal oxide ion interference. This next-generation Agilent Model 8800 dramatically reduces interference by adapting two quadrupoles, one before and one after the Collision/Reaction Cell. These two quadrupoles select ions to enter the cell, providing consistent reaction conditions, thereby solving the problem of current cell technologies. This allows analysts to more effectively use reaction mode for a larger number of elements/applications. This technology allows removing

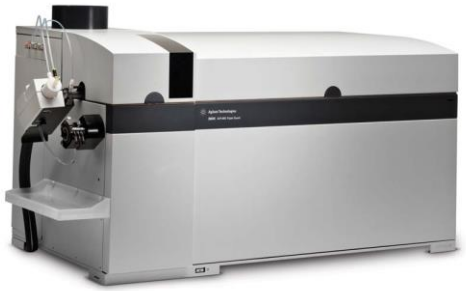

Figure 1. World-first and only Triple Quadrupole ICP-MS (Agilent 8800 ICP-MS).

interference that can't be resolved by any of the other ICP-MS systems in the market. Thus, the 8800 ICP-QQQ has higher sensitivity and lower backgrounds, providing improved performance compared to existing single quadrupole ICP-MS instruments. The accompanying Mass Hunter software provides capabilities from automated startup checks following plasma ignition, through batch and queue method setup and sequencing, to integrated data processing and final report generation. This instrument can seamlessly link with HPLC, GC, CE, and capillary-LC for LC-ICP-MS (strong flexibility and extendibility). In particular, the benefit is the absolute most sensitive detection limits in ICP-MS, which is the key for laser ablation ICP-MS. Incorporation with Laser Ablation (LA) allows analyzing solid sample introduction of any complex sample matrices in military sets.

Laser Ablation: Analyte G2 (Laser Ablation, Photon-Machines Inc.) is a new generation of cutting edge laser ablation products for spatially-resolved analysis of solid samples in ICP-MS. This instrument provides a very sensitive, precise, and accurate tool for analysis of solid samples. Specifically, it uses an excimer laser to selectively remove (ablate) and subsequently analyze discrete areas of a sample at < 1 μm resolution. This is ideal for the trace element analysis of specific areas of a sample and/or for depth profiling through layers within a sample. ***Analyte G2 incorporates an ultra-short sub-4 ns pulse excimer laser from ATL-Lasertechnik with pre-ionization*** and includes a number of innovations including: 1) proprietary beam shaping and homogenization technology enables the Analyte G2 to ablate clean, flat, craters of repeatable shape and size on a wide variety of opaque and transparent materials from powders to quartz to carbonate, 2) the 4 ns pulse length and 193 nm wavelength technology leads to exceptional coupling efficiency resulting in sub-micron particles that ionize readily with less fractionation, 3) high speed X,Y, Z stager with long working distance (100 x 100 mm travel) that accepts large format and specialized sample chamber, 3) high capacity sample cells (up to 150 mm x 150 mm) with ultrafast washout, 4) 30 spot selection technologies ranging from < 3 μm to 250 μm, which makes the most versatile instrument of its kind with unique capabilities, ideal for both micro-feature and bulk analysis, 5) visualization systems including two high definition CCD cameras, video microscope, and laser beam delivery optics, deliver co-linear viewing and lasing perpendicular to the sample (there is no off-axis component that distorts the image or requires correction), 6) fire-on-the-fly motion-controlled lasing, 7) auto evacuation of sample cells for rapid ICP-MS stabilization, 8) a cryostage stager for direct tissue work (spatial resolution < 1um, best resolution in this field). Thus, the reliability and affordability of the Analyte G2 in combination with its deep UV 193 nm wavelength, ultra-short pulse length, flat beam profile, and surplus energy make it the best choice to pair with the Agilent 8800 ICP-QQQ to maximize system performance. This combination of LA and ICP-MS is a unique analytical/bioanalytical tool that can handle even the most difficult samples and applications. ***Thus LA ICP-MS is of high value for the understanding of the influence of military environment to solider protection and the development of materials innovation and translation.***

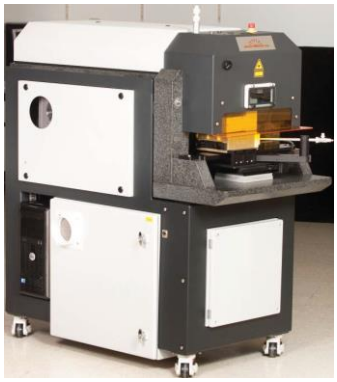

Figure 2. Ultra short pulse excimer LA system from Photon-Machine Inc.

Instruments Acquisition (Laser Ablation and ICP-MS):
Upon receiving the award, our team started the process of instrumentation acquisition under University guidance with its purchasing department. Our purchasing organization routinely pushes back on all large sole source procurements and requires extensive justification. We also have the added hurdle that all procurements over $100K must go to the State Purchasing Office for approval. Our Division of Research and Economic Development has been assisting to speed up the approval process. Eventually the Agilent 8800 ICP-MS system (ICP-MS) was received and is on site as is the Laser Ablation (LA) Unit CETAC/Teledyne Analyte G2 which arrived February 5, 2015 after a lengthy purchasing process.

Space Allocation and Renovation:

The proper space decision has primarily has been hampered by the need to have effluent from the instrument piped away safely from the instrument. The initial lab space planned in the Fort Interdisciplinary Research Center (IRC) at NC A&T State University (NC A&T) to host the equipment became unavailable when it was decided that an old piece of equipment scheduled for surplus was in fact going to be upgraded and incorporated for a new project. An initial study conducted by NC A&T physical plant and an outside engineering firm for a second lab option required the renovation of an existing biological lab, but these expenditures were estimated upwards of $50-75K. The Division of Research and Economic Development assisted this search by offering a laboratory basement lab (#007) in the Fort-IRC building. Though more affordable than the second choice, this space was non-optimal due to the need to plumb the effluent about 60 feet to another lab's chemical hood ductwork and the need to control temperature variation within the room. In mid-June of this year it was decided that the best plan of action was to move infrastructure from a lab that has a chemical fume hood and long central work table and distribute some of those equipment into the basement lab mentioned above while others would be consolidated into existing bioengineering labs. This plan is expected to work because the proximity of the chemical hood to the equipment and the opportunity to make the bioengineering lab workflow streamlined. The process of altering lab space is typically estimated to be 3 to 6 months once the engineering firm designs the project, but we are hopeful that we can bring that number in as the HVAC changes are perceived to be minimal. Steps have been taken to coordinate with the Physical Plant at NC A&T and an outside engineering firm to undertake this project.

We believe this equipment will have an enormously positive impact on the research activities on this campus and the surrounding communities. The LA-ICP-MS system awarded is a very unique instrument that will bring value and collaboration with companies and other universities. It is our desire to demonstrate this progress through publications, research awards, and so on. Dr .Y. Yun has recently submitted a NSF-PREM proposal ($3,000 K) and NIH SC3 grant ($450 K) that will utilize the LA-ICP-MS system.

Future plan:

The LA ICP-MS impacts on various levels of DoD research which will eventually seed scientific and far reaching technological discoveries that enhance DoD-related research capabilities. The research focus initially planned target developing advanced functional materials, biosensors, novel filters, toxicity study, biomechanics, imaging and medical science in military applications. This will be achieved through the well-planned, dynamic team-based and cutting-edge research and education activities by creating thrust areas: (1) Alloys, (2) Analytical Chemistry, (3) Regenerative Medicine, (4) Toxicity, (5) Imaging and (6) Education.

Operation, maintenance, technical support and long-term sustainability: A senior technical personnel, along with support staff, will be responsible for equipment operation and maintenance and training of the students. Faculty members will be involved in the research, research training, translational activities, education and outreach. These critical positions are provided to effectively use the characterization facility and as well to carry out the technical activities related to DoD research. He/she will be in charge of the safety and recordkeeping. Training and operation manuals will be developed and readily provided by the technical team. The instrument will have a one year full warranty, following the University and Center's maintenance protocols. Regarding long-term sustainability, this instrument system will be integrated with existing center resources (see facilities and instruments page), with the ability to keep the system updated and get proper service as necessary. In the meantime, the team will get more involved in various projects related with DoD research and education.

Equipment accessibility, usage and fees: We will develop a web-based reservation system so that users can schedule time on the integrated research instrument from anywhere on or off NCAT's campus. This web-based system will support the multi-institutional and interdepartmental nature of the usage. It is planned that the proposed research instrument will be a part of NCAT's shared facilities, and will be

readily accessible to trained users. Estimated average usage time within the first year after the installation is 6-10 hours per day. We do not initially plan to charge fees for the use because it will be used heavily for ongoing activities. In the future, outside users will be charged on an hourly basis in accordance with university's guidelines on the operation of shared facilities.

Equipment oversight and dissemination of results of the project: A committee comprised of the PI and projects leaders will oversee the integrated research instrument usage and disseminate experimental results as well as activities related to training, operational procedures, new courses, publications, presentations, conferences, and seminars. At the end of the project term, a final project report will be prepared and submitted to DoD.