REPORT DOCUMENTATION PAGE	Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
06-01-2019	Final Report	4-Mar-2013 - 28-Feb-2015

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Final Report: Plasmonic Nanosensors for Chemical Warfare Agents	
	5b. GRANT NUMBER W911NF-13-C-0051
	5c. PROGRAM ELEMENT NUMBER 665502
6. AUTHORS	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES	8. PERFORMING ORGANIZATION REPORT NUMBER
MKS Technology PO Box 74 Centennial, WY 82055 -0074	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)	10. SPONSOR/MONITOR'S ACRONYM(S) ARO
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	11. SPONSOR/MONITOR'S REPORT NUMBER(S) 62358-CH-SB2.1

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for public release; distribution is 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

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Keith Carron
UU	UU	UU	UU		19b. TELEPHONE NUMBER 307-460-2089

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

RPPR Final Report
as of 24-Apr-2019

Agency Code:

Proposal Number: 62358CHSB2 **Agreement Number: W911NF-13-C-0051**

INVESTIGATOR(S):

Name: Keith Carron
Email: kcarron@wysri.com
Phone Number: 30746020890303
Principal: Y

Organization: **MKS Technology**
Address: PO Box 74, Centennial, WY 820550074
Country: USA

DUNS Number: 830205980 EIN: 264611015
Report Date: 31-Mar-2015 Date Received: 06-Jan-2019
Final Report for Period Beginning 04-Mar-2013 and Ending 28-Feb-2015
Title: Plasmonic Nanosensors for Chemical Warfare Agents
Begin Performance Period: 04-Mar-2013 **End Performance Period:** 28-Feb-2015
Report Term: 0-Other
Submitted By: Keith Carron Email: kcarron@wysri.com
Phone: (307) 460-20890303
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1 **STEM Participants:** 0

Major Goals: MKS Technology
1. Design and evaluate a removable cartridge for our porous me mbranes (months 1-3)
2. Develop an air sampling system to pull ambient air through the porous SERS membranes (months 3-6)
3. Develop firmware algorithms for library matching routines. (months 1-18)
• Routines will account for variation between SERS substrates and will accept multiple coatings for enhanced agent adsorption.
4. Evaluate the reader and SERS membranes with VX and Lewisite at ECBC (months 12-24)
5. Design and evaluate a MIL-STD 810G system that is compliant to: (months 6-12)
• drop
• splash
• ambient temperature
• decontamination
6. Coordinate with DOD specialist and design the reader for field connectivity (months 6-12)

iFyber
1. iFyber will synthesize, test and compare a series of alpha-effect sensors for trace nerve agent detection (months 1-9)
• Minimalistic sensor (simple alpha-effect nucleophile)
• Rapidly rearranging sensor for enhanced detection time
• Rapidly rearranging SERRS sensor for enhanced detection time and sensitivity
2. iFyber will prepare, evaluate, and compare the performance of SERS-active porous substrates from various base materials including nylon (original design), cellulose, glass, and ceramic. (months 1-9)
• Evaluate coating homogeneity
• Test sensitivity to laser degradation
• Test SERS performance with known compounds
• Identify and optimize best performing SERS membranes
3. iFyber will perform pilot scale production of optimized SERS-active substrates (months 12-24)
• Building from the foundational lab scale production exper iments planned for the Phase 1 Option (? 1 meters), substrates will be produced in ? 10 meter batches to validate large scale SERS-active surface production.
• Establish performance and reproducibility metrics of scaled up SERS-active membrane product.

Northwestern University
1. Conduct studies to maximize the enhancement factor with iFyber SERS (months 1-12)
• Compare solution LSPR spectra to spectra obtained by the integrating sphere technique to determine plasmon of nanoparticles adsorbed to the iFyber

• Perform wavelength scanned measurements and correlate to LSPR data to determine optimal parameters for SERS sensing
2. Evaluate and validate the effectiveness of various surface chemistries (created by iFyber and NU) for optimal design of iFyber SERS sensing of trace nerve agent simulants (months 12-24)
• Determine DLt of nerve agent simulants
• Test specificity of SERS sensor for different nerve agent simulants
• Evaluate the use of SAMs for detection of nerve agent simulants (as an alternative scheme to iFyber's work)
• Compare different detection platform schemes using a multiplex, multi-molecule SERS screening technique
• Evaluate the use of the air sampling system (provided by MKS) with iFyber SERS to significantly improve the Dlt of several nerve agent simulants.

Accomplishments: See attached .pdf.

Training Opportunities: Dmitry Kurouski, Nicolas Large, Naihao Chiang, Nathan Greeneltch , Tamar Seideman,

The above are students at Northwestern University that were trained during this project.

Results Dissemination: Unraveling near-field and far-field relationships for 3D SERS substrates – a combined experimental and theoretical analysis.

Dmitry Kurouski, Nicolas Large, Naihao Chiang, Nathan Greeneltch, Keith T. Carron, Tamar Seideman, George C. Schatz and Richard P. Van Duyne

Analyst, 2016,141, 1779-1788

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Keith Carron
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Co PD/PI
Participant: Richard Palmer Van Duyne
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: Y
Other Collaborators:

Participant Type: Co PD/PI
Participant: Aaron Strickland
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:

International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Accomplishments:

MKS Technology

1. Design and evaluate a removable cartridge for our porous membranes (months 1-3)

- **This was accomplished and tested with very low vapor pressure simulants.**
- **A system was provided to ECBC for parallel evaluations**

2. Develop an air sampling system to pull ambient air through the porous SERS membranes (months 3-6)

- **This was accomplished with a small battery powered (1-AA) pump.**
- **We tested two systems, a pull through the membrane and a blow across the membrane.**

3. Develop firmware algorithms for library matching routines. (months 1-18)

- **This was accomplished with a Pierson's correlation.**

Routines will account for variation between SERS substrates and will accept multiple coatings for enhanced agent adsorption.

- **This was accomplished with a mixture matching routine that included the surface coatings in its library.**

4. Evaluate the reader and SERS membranes with VX and Lewisite at ECBC (months 12-24)

- **A system was sent to ECBC.**

5. Design and evaluate a MIL-STD 810G system that is compliant to: (months 6-12)

- **The system was drop tested and certified internally. This eventually led to a commercial product called the CBExM (Military).**

6. Coordinate with DOD specialist and design the reader for field connectivity (months 6-12)

- **Not accomplished. Discussion about connectivity took place, but the DOD did not have a standard format and we could not determine a proper format.**
-

iFyber

1. iFyber will synthesize, test and compare a series of alpha-effect sensors for trace nerve agent detection (months 1-9)

- Minimalistic sensor (simple alpha-effect nucleophile) -- **Accomplished**
- Rapidly rearranging sensor for enhanced detection time -- **Accomplished**
- Rapidly rearranging SERRS sensor for enhanced detection time and sensitivity – **Not Accomplished. A sensors that also provided a resonance Raman signal was not fabricated.**

2. iFyber will prepare, evaluate, and compare the performance of SERS-active porous substrates from various base materials including nylon (original design), cellulose, glass, and ceramic. (months 1-9)

- Evaluate coating homogeneity -- **Accomplished**
- Test sensitivity to laser degradation – **Accomplished (Measurements with and without the MKS ORS (Orbital Raster Scan) were performed)**
- Test SERS performance with known compounds – **Accomplished (Performed largely at the University of Wyoming with the assistance of Dr. Carron)**
- Identify and optimize best performing SERS membranes – **Accomplished with assistance from MKS. Nylon was an optimal material.**

3. iFyber will perform pilot scale production of optimized SERS-active substrates (months 12-24)

- Building from the foundational lab scale production experiments planned for the Phase 1 Option (≤ 1 meters), substrates will be produced in ≥ 10 meter batches to validate large scale SERS-active surface production. – **Partially accomplished, discussion with Eastman Kodak took place and it was determined that a roll-to-roll process would be viable for large scale production.**

Northwestern University

1. Conduct studies to maximize the enhancement factor with iFyber SERS (months 1-12)

- Compare solution LSPR spectra to spectra obtained by the integrating sphere technique to determine plasmon of nanoparticles adsorbed to the iFyber**. Accomplished, and published.**
- Perform wavelength scanned measurements and correlate to LSPR data to determine optimal parameters for SERS sensing. **Accomplished and published.**

2. Evaluate and validate the effectiveness of various surface chemistries (created by iFyber and NU) for optimal design of iFyber SERS sensing of trace nerve agent simulants (months 12-24)

- Determine DLt of nerve agent simulants. **Not accomplished, safety required this work to be performed at ECBC.**
- Test specificity of SERS sensor for different nerve agent simulants. **Not accomplished due to toxicity. This is redundant to ECBC's evaluation with VX.**
- Evaluate the use of SAMs for detection of nerve agent simulants (as an alternative scheme to iFyber's work). **Accomplished. SAMs are inferior to a reactive method developed by i-Fyber.**
- Compare different detection platform schemes using a multiplex, multi-molecule SERS screening technique. **Not accomplished.**
- Evaluate the use of the air sampling system (provided by MKS) with iFyber SERS to significantly improve the Dlt of several nerve agent simulants. **Accomplished by MKS.**