A. COVER PAGE

Project Title: A Direct-Reading Inhalable Particle Sizer with Elemental Composition Analyzer	
Grant Number: 5R21OH011287-02	**Project/Grant Period:** 09/01/2018 - 08/31/2020
Reporting Period: 09/01/2019 - 08/31/2020	**Requested Budget Period:** 09/01/2019 - 08/31/2020
Report Term Frequency: Annual	**Date Submitted:** 12/17/2021
Program Director/Principal Investigator Information: AZER YALIN , PHD **Phone Number:** 9702325545 **Email:** azer.yalin@colostate.edu	**Recipient Organization:** COLORADO STATE UNIVERSITY COLORADO STATE UNIVERSITY-FORT COLLINS 2002 Campus Delivery - Sponsored Programs FORT COLLINS, CO 805232002 **DUNS:** 785979618 **EIN:** 1846000545A1 **RECIPIENT ID:**
Change of Contact PD/PI: No	
Administrative Official: LINDA LOING 2002 Campus Delivery Fort Collins, CO 80523 **Phone number:** 970-491-6586 **Email:** linda.loing@colostate.edu	**Signing Official:** LINDA LOING 2002 Campus Delivery Fort Collins, CO 80523 **Phone number:** 970-491-6586 **Email:** linda.loing@colostate.edu
Human Subjects: NA	**Vertebrate Animals:** NA
hESC: No	**Inventions/Patents:** No

B. ACCOMPLISHMENTS

B.1 WHAT ARE THE MAJOR GOALS OF THE PROJECT?

Exposure to inhalable aerosols contributes significantly to the burden of occupational morbidity and mortality. While respirable, and to a lesser extent, thoracic aerosols have received attention from instrument developers in recent years, no direct-reading instruments currently exist to determine the size and chemistry of large, inhalable particles (i.e., those greater than 20 μm). Current methods for inhalable aerosols call for the collection of filter-based methods lack temporal and spatial information and provide no information on the size distribution or chemical composition of the aerosols.
Despite the recognition that size and composition are important in determining and preventing health effects, few instruments exist capable of characterizing both, particularly in real time. We have previously developed a virtual, portable inhalable particle separator capable of characterizing the size distribution of particles in the range of ~10-100 μm. The R21 research proposed here will expand the capabilities of the DRIPS instrument to characterize the size-dependent chemical composition of inhalable aerosol particles in situ and in real time. Thus, our research objective is to develop a portable, direct-reading instrument that can characterize both the size and chemical composition of inhalable aerosol hazards (~10-100 μm diameter particles) in the workplace. To achieve this goal, we propose two aims:

Aim 1: Develop and integrate a laser-induced breakdown spectrometer and trigger system into an existing particle sizer system (DRIPS). This aim will evaluate design tradeoffs associated with incorporating a laser-induced breakdown spectroscopy (LIBS) system into the DRIPS device for elemental chemical analysis (ECA). A novel test-bed, based on an electrodynamic balance to provide controlled conditions, will be used to record LIBS emission spectra to examine effects of laser parameters (pulse energy, focusing parameters), particle size and composition, particle location relative to the plasma, and partial particle vaporization. A trigger system to fire the LIBS laser beam to achieve high particle sampling rate and minimize matrix effects will be developed. Calibration curves relating the LIBS signal to analyte mass will be developed. A field testable prototype real-time DRIPS/ECA system will then be constructed based on the findings from these experiments.

Aim 2: Conduct laboratory and field studies to evaluate performance of the combined particle sizer and elemental chemical analysis system (DRIPS/ECA). Laboratory testing will be conducted in a calm air chamber to evaluate LIBS detection efficiency, i.e. fraction of particles admitted through the tube that are also detected by LIBS. The calibration curves will be challenged using metal alloys and mixtures to identify and assess matrix effects, including for beryllium owing to its high importance in occupational settings. The instrument will also be tested in a machine shop to characterize DRIPS/ECA performance in a real-world environment.

B.1.a Have the major goals changed since the initial competing award or previous report?

No

B.2 WHAT WAS ACCOMPLISHED UNDER THESE GOALS?

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B.3 COMPETITIVE REVISIONS/ADMINISTRATIVE SUPPLEMENTS

For this reporting period, is there one or more Revision/Supplement associated with this award for which reporting is required?

No

B.4 WHAT OPPORTUNITIES FOR TRAINING AND PROFESSIONAL DEVELOPMENT HAS THE PROJECT PROVIDED?

NOTHING TO REPORT

B.5 HOW HAVE THE RESULTS BEEN DISSEMINATED TO COMMUNITIES OF INTEREST? NOTHING TO REPORT
B.6 WHAT DO YOU PLAN TO DO DURING THE NEXT REPORTING PERIOD TO ACCOMPLISH THE GOALS? Not Applicable

Direct-Reading Inhalable Particle Sizer with Elemental Composition Analyzer

The present 2-page summary report provides research highlights addressing the following two aims:

Aim 1: Develop and integrate a laser-induced breakdown spectrometer and trigger system into an existing particle sizer system (DRIPS).

Aim 2: Conduct laboratory and field studies to evaluate performance of the combined particle sizer and elemental chemical analysis system (DRIPS/ECA).

Highlight activities are summarized as follows:

Design and Hardware Configuration for Particle Sizing and LIBS Detection.

The setup for the combined sizing and Laser Induced Breakdown Spectroscopy (LIBS) setup is shown in Figure 1. The setup uses a Q-switched Nd:YAG laser (Quantel, Q-smart 100) with a nominal pulse width of 7 ns as a LIBS source. The instrument also employs a pair of laser sheets (from continuous-wave sources) that transect the falling particles above the LIBS beam. These two sheets, in combination, are used to size and count the falling particles, as well as to set the timing (triggering) for the LIBS micro-plasma formation. We have also developed a custom setup, on discrete bursts of compressed air through an aerosol dispersion nozzle, to reliably disperse particles in the size range of interest (20-100 μm). The test particles are allowed sufficient vertical distance to reach their terminal settling velocity in relatively calm air before entering the device inlet. We have used multiple proximately located filters and optical microscopy to confirm reasonable uniformity in the particle generation and dispersion with the setup.

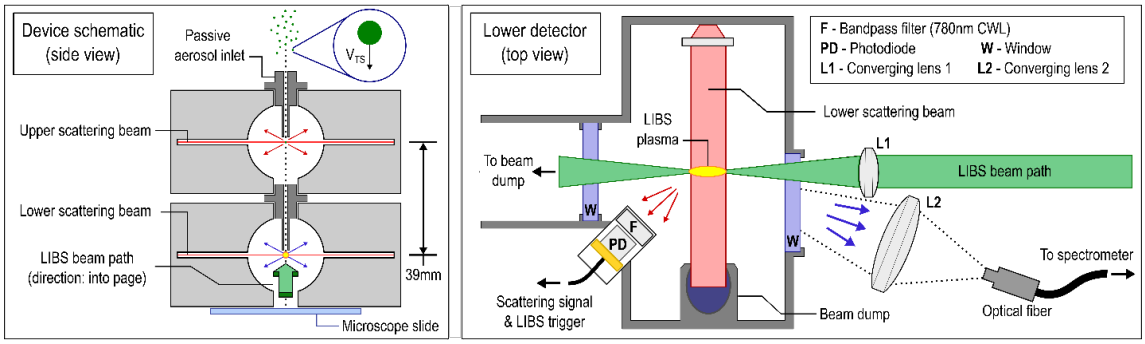

Fig. 1: Setup for combined sizing and Laser Induced Breakdown Spectroscopy (LIBS) for elemental analysis.

Summary of Test Results on Counting and Sizing

We have conducted a series of tests to develop the methods for particle sizing, counting, and triggering. An important advance (not anticipated in the proposal) was to adopt commercial particle counting and sizing hardware as a means to accelerate this development. Specifically, we have developed an informal partnership with the company Particles Plus (PP), who has provided us several particle sensors (their model 9301-OEM). The sizing and counting sensor is based on Mie scattering methods. A diode laser (wavelength of 785 nm and power up to ~50 mW) is formed by a lens-pair into a sheet of laser light (thickness of ~50 μm and width of ~3 mm). Particle counting (in our size range) is straightforward with this approach when particle count numbers are low enough that we do not have issues with coincidence error and our signals (given the large particles) are well above the noise floor. Airborne particles greater than ~20 μm in diameter that enter the inlet of the prototype sampler are detected and counted using light scattering signals produced as the particles transit the pair of low power continuous laser beams. The aerodynamic diameter of the particle is found by the time-of-flight between the two scattering beams which have a fixed vertical separation of 39 mm. By measuring the time elapsed between the peaks of successive light scattering signals, the terminal settling velocity—and, thus, the aerodynamic diameter—of each particle can be directly calculated. To verify the aerodynamic diameter measurements device by time-of-flight, a glass microscope slide was placed directly beneath the outlet of the sampler to collect

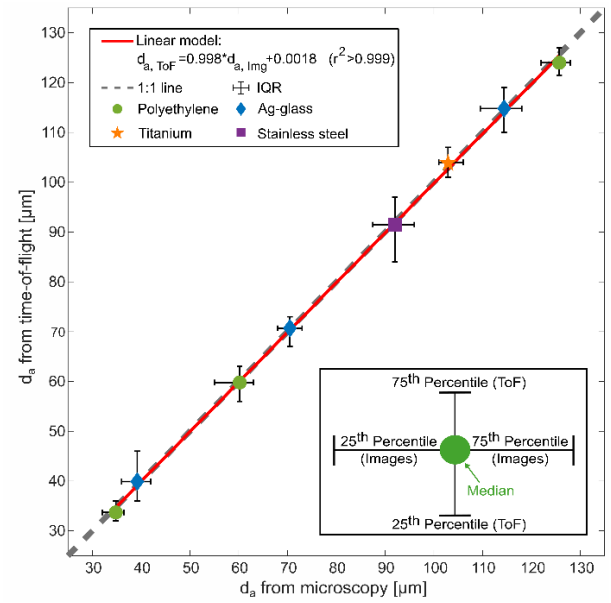

Fig. 2: Time-of-flight aerodynamic diameter sizing results verified with optical microscopy.

the particles detected in each experiment. Figure 2 shows relationship between the median aerodynamic diameters measured by time-of-flight and optical microscopy was linear and strongly correlated (r^2 > 0.999). The mean absolute difference between the median aerodynamic diameters measured by each method over all eight test aerosol types was 0.9 µm with a mean difference in interquartile range of 1.9 µm.

Summary of Test Results on Species Identification by LIBS

In addition to the second signal for the time-of-flight calculation, the scattering signal generated when a particle enters the lower laser beam is used to provide a trigger which activates the LIBS system and initiates a micro-plasma spark coincident with the position of the particle. The same trigger pulse starts the 0.5 ms spectrometer integration period which collects the light emitted from the plasma. The plasma emission spectrum recorded by the spectrometer during each laser plasma is examined to detect peaks at specific wavelengths that would indicate the presence of an element of interest within the analyte. Every element in the analyte volume within the plasma will contribute to the emission spectrum. Thus, spectral features from the room air constituents (N, O, etc.) are present in every experimental LIBS signal. The LIBS spectra analysis process eliminates as much of the contribution of the air as possible, leaving only the peaks that result from ablation of a solid particle. After suppression of the air plasma features, the wavelengths of the remaining peaks are used to determine the elemental composition of the ablated aerosol mass. If no strong peaks are present in the signal following air plasma correction, this indicates the LIBS plasma "missed" the falling particle or the ablated mass was below the limit of detection of the current system. A MATLAB script was developed and tested to automate this spectrum post-processing and material classification procedure. The LIBS system was tested in the laboratory with the silver-coated glass and polyethylene microspheres used in the particle sizing tests as well as polydisperse copper (<75 µm) and titanium (<45 µm) powders. The automated peak detection algorithm was used to classify a set of experimental spectra containing signals from these 4 test aerosols in addition to air-only signals. When compared against manual classification of the same test spectra, the peak detection algorithm was able to correctly distinguish the test aerosol materials from each other and the air signals with an overall accuracy of 91%.

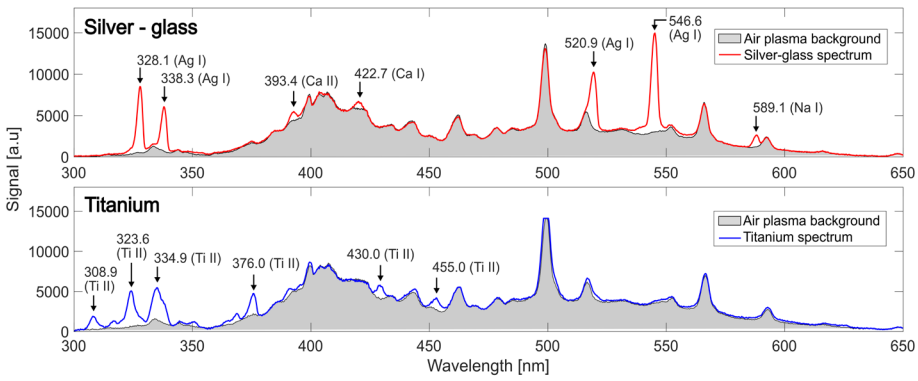

Fig. 3: Experimental LIBS spectra with analyte emission lines identified.

C. PRODUCTS

C.1 PUBLICATIONS

Are there publications or manuscripts accepted for publication in a journal or other publication (e.g., book, one-time publication, monograph) during the reporting period resulting directly from this award?

Yes

Publications Reported for this Reporting Period

Public Access Compliance	Citation
N/A: Not NIH Funded	Sipich J, L"Orange C, Anderson K, Limbach C, Volckens J, Yalin A. A direct-reading particle sizer with elemental composition analysis for large inhalable particles. Aerosol Science and Technology. Forthcoming.

C.2 WEBSITE(S) OR OTHER INTERNET SITE(S)

NOTHING TO REPORT

C.3 TECHNOLOGIES OR TECHNIQUES

NOTHING TO REPORT

C.4 INVENTIONS, PATENT APPLICATIONS, AND/OR LICENSES

Have inventions, patent applications and/or licenses resulted from the award during the reporting period? No

If yes, has this information been previously provided to the PHS or to the official responsible for patent matters at the grantee organization?

C.5 OTHER PRODUCTS AND RESOURCE SHARING

NOTHING TO REPORT

D. PARTICIPANTS

D.1 WHAT INDIVIDUALS HAVE WORKED ON THE PROJECT?

Commons ID	S/K	Name	Degree(s)	Role	Cal	Aca	Sum	Foreign Org	Country	SS
PIYALIN	Y	Yalin, Azer	PHD	PD/PI	0.0	0.0	1.0			NA
JVOLCKENS	Y	Volckens, John	BS,MS,PHD	PD/PI	0.0	0.0	0.5			NA
CHRISTIAN.L	N	L'Orange, Christian	PHD	Postdoctoral Scholar, Fellow, or Other Postdoctoral Position	0.0	0.0	0.5			NA
J_SIPICH	N	Sipich, James		Graduate Student (research assistant)	6.0	0.0	0.0			NA

Glossary of acronyms:
S/K - Senior/Key
DOB - Date of Birth
Cal - Person Months (Calendar)
Aca - Person Months (Academic)
Sum - Person Months (Summer)
Foreign Org - Foreign Organization Affiliation
SS - Supplement Support
RE - Reentry Supplement
DI - Diversity Supplement
OT - Other
NA - Not Applicable

D.2 PERSONNEL UPDATES

D.2.a Level of Effort

Not Applicable

D.2.b New Senior/Key Personnel

Not Applicable

D.2.c Changes in Other Support

Not Applicable

D.2.d New Other Significant Contributors

Not Applicable

D.2.e Multi-PI (MPI) Leadership Plan

Not Applicable

E. IMPACT

E.1 WHAT IS THE IMPACT ON THE DEVELOPMENT OF HUMAN RESOURCES? Not Applicable
E.2 WHAT IS THE IMPACT ON PHYSICAL, INSTITUTIONAL, OR INFORMATION RESOURCES THAT FORM INFRASTRUCTURE? NOTHING TO REPORT
E.3 WHAT IS THE IMPACT ON TECHNOLOGY TRANSFER? Not Applicable
E.4 WHAT DOLLAR AMOUNT OF THE AWARD'S BUDGET IS BEING SPENT IN FOREIGN COUNTRY(IES)? NOTHING TO REPORT

G. SPECIAL REPORTING REQUIREMENTS SPECIAL REPORTING REQUIREMENTS

G.1 SPECIAL NOTICE OF AWARD TERMS AND FUNDING OPPORTUNITIES ANNOUNCEMENT REPORTING REQUIREMENTS

NOTHING TO REPORT

G.2 RESPONSIBLE CONDUCT OF RESEARCH

Not Applicable

G.3 MENTOR'S REPORT OR SPONSOR COMMENTS

Not Applicable

G.4 HUMAN SUBJECTS

G.4.a Does the project involve human subjects?

Not Applicable

G.4.b Inclusion Enrollment Data

NOTHING TO REPORT

G.4.c ClinicalTrials.gov

Does this project include one or more applicable clinical trials that must be registered in ClinicalTrials.gov under FDAAA?

G.5 HUMAN SUBJECTS EDUCATION REQUIREMENT

NOT APPLICABLE

G.6 HUMAN EMBRYONIC STEM CELLS (HESCS)

Does this project involve human embryonic stem cells (only hESC lines listed as approved in the NIH Registry may be used in NIH funded research)?

No

G.7 VERTEBRATE ANIMALS

Not Applicable

G.8 PROJECT/PERFORMANCE SITES

Not Applicable

G.9 FOREIGN COMPONENT
No foreign component
G.10 ESTIMATED UNOBLIGATED BALANCE
Not Applicable
G.11 PROGRAM INCOME
Not Applicable
G.12 F&A COSTS
Not Applicable

I. OUTCOMES

I.1 What were the outcomes of the award?

Exposure to inhalable aerosols contributes significantly to the burden of occupational morbidity and mortality. While respirable, and to a lesser extent, thoracic aerosols have received attention from instrument developers in recent years, no direct-reading instruments currently exist to determine the size and chemistry of large, inhalable particles, i.e., those greater than 20 μm. Current methods for inhalable aerosols call for the collection of filter-based samples over an 8-hr work shift, after which the sample is shipped to a lab for gravimetric and/or chemical post facto analysis. These filter-based methods lack temporal and spatial information and provide no information on the size distribution or chemical composition of the aerosols. Knowledge of particle size and chemistry are critical to the evaluation, recognition, and control of aerosol hazards, as these properties are key drivers of adverse health outcomes. While particles smaller than 20 μm penetrate into (and tend to deposit in) the lower respiratory system, particles larger than 20 μm target the throat and head airways. Thus, large inhalable aerosols are suspected of driving health effects like sinusitis, rhinitis, nasal cancers, and gastrointestinal disorders (due to particles eventually swallowed). Particle chemistry also drives health risks: A 30 μm particle made from beryllium likely has a different risk profile than one made from copper or elemental carbon. Despite the recognition that size and composition are important in determining and preventing health effects, few instruments exist capable of characterizing both, particularly in real time. We have previously developed a virtual, portable inhalable particle separator (termed DRIPS) capable of characterizing the size distribution of particles in the range of ~10-100 μm.

Research under the present grant has advanced the underlying methods needed to expand the capabilities of the DRIPS instrument to characterize the size-dependent chemical composition of inhalable aerosol particles in situ and in real time. We have developed and characterized an optical counting method, based on Mie scattering, to detect and count particles in the aforementioned 10-100 μm size range. The method uses a pair of laser beams to determine particle (aerodynamic) diameter based on time-of-flight of measurements of falling particles. We have also developed and integrated a laser induced breakdown spectroscopy (LIBS) diagnostic capability to the earlier DRIPS instrument. With appropriate triggering, the LIBS diagnostic uses a pulsed laser beam to form microplasmas by illuminating the falling particles, the spectra of which allow composition measurements of constituent atoms within the particles based on known emission wavelengths. We have developed and optimized methods to determine composition of particles with low rates of false-positives and demonstrated the methods for four particle compositions. Overall, our research has made significant progress towards the development of a portable, direct-reading instrument that can characterize both the size and chemical composition of inhalable aerosol hazards (~10-100 μm diameter particles) in the workplace.