Development of Methodologies for Evaluating Emissions from Metal-Based Energetic and Pyrotechnic Formulations WP19-F4-1392

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4 December 2019

Goals / SON / Background WP19-F4-1392

Overall Goal: Development of emission factors based on stages of energy release of energetic materials (3 year effort – FY20-22)

SON *Incorporate heterogeneous chemical kinetics into flow dynamics to predict pollutant emissions.*

- **Develop emission characterization methodologies for energetic and pyrotechnic formulations.**
- **Ultimate goal of developing a field ready methodology.**
- **Measure concentrations of airborne metals and chemicals of interest in relevant operating environments, including at the end of gun barrels.**

Background

- **Nominal 1 year effort initiated 2016**
- **Bridging effort 2018**
- **Full proposal (3-year effort) 2019**
- **Experiments conducted at ARL - APG**
- **EPA/UDRI mobile chemical analysis instrumentation and personnel**

Project Team WP19-F4-1392

- **US Army Research Laboratory:** Kevin McNesby*, Eric Johnson, John Schmidt, Mike Nusca, Mike McQuaid, Chiung-Chu Chen

- **US Environmental Protection Agency, Office of Research and Development:** Brian Gullett*, Amara Holder

- **University of Dayton Research Institute:** Johanna Aurell

Experimentation, Pyrotechnics, CFD, Chemical Kinetics, Analytical Chemistry

Previous Work: Key Points - SEED

Gun Firings:

- Average **CO concentrations around 1500 ppm** after firing, suggesting that inhalation studies on firing ranges may be warranted. Levels may exceed air standard.

- Emitted particles had mass median diameters between ≤ **0.389 and 0.575 µm**, a respirable particle size.

- **Cu** was the metal observed in highest concentration for all three round formulations.

- More than 100% of the Pb in the propellant/primer formulations was observed to be emitted for all three round types – possible lead slug contribution.

- Improved estimates of emission factors for chemical species during M4 weapon firing will result from the **combination of accurate flow dynamics, improved IB thermodynamic calculations, and incorporation of a finite rate chemical kinetics** to simulate muzzle flash.

Previous Work: Key Points - SEED

Explosions:

- Emissions from the TNT detonations indicated **combustion efficiencies of about 98%.** Reasonable agreement with simulation.

- Comparison of PM emission factors show that our laboratory results, while consistent with others, are half that of our field values, likely due to detonations in the field entraining sandy soil.

- The addition of Mg/B to the TNT formulations significantly **increased the $PM_{2.5}$ emission** by a factor of 8.

- Performing the **experiments in a blast chamber is misleading** as the transit of the shock wave back and forth within the chamber, following detonation, provides mixing approximating the homogeneous reactor used in the chemical kinetic calculations.

- Incorporation of **finite rate chemical kinetics** for heterogeneous mixtures would improve particle combustion contributions.

Distribution A – Distribution is unlimited

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Technical Objectives for WP19-F4-1392

- **Measure concentration of airborne particles (organics/metals and gases for gun firings (fielded ammo), pyrotechnics (+ alternate formulations), metal-containing explosives.**

- **Use observed/measured stages of energy release during gun firings/explosions/deflagrations to guide mechanism reduction and incorporation of finite rate kinetics.**

- **Compare measurement to simulation results. Modify incorporation of finite rate heterogeneous and homogeneous chemical kinetics into computational flow dynamics to improve Emission Factor estimation.**

Energetic Materials Systems

WP19-F4-1392

- **Gun Firings:** M4 carbine firing M855A1 ammunition (copper-jacketed steel bullet; double base propellant, #41 primer. Army–issue 9 mm handgun / ammunition.

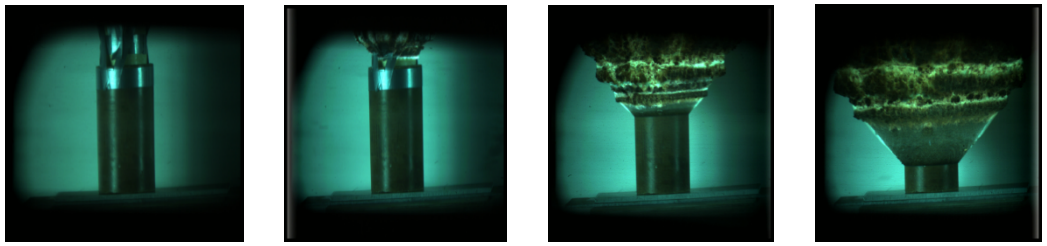
- **Pyrotechnics:** Color range from 460nm-630nm (BGR) classic formulations (CuCl-, Ba-, Sr-), alternatives. Also smokes/flares.

- **Explosions:** TNT (neat), Tritonal, Bulgarian TBX, melt-castable eutectics with and without Al

Example: Explosions WP19-F4-1392

Anaerobic

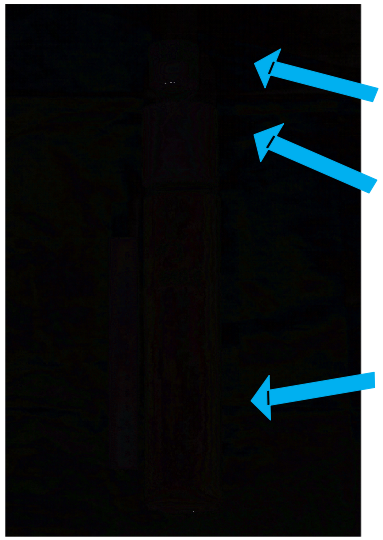
0 µs

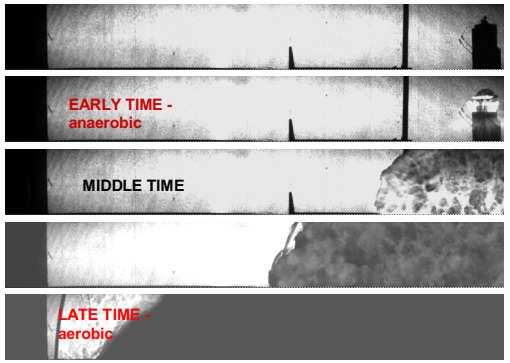


45 µs

Aerobic

30 cm





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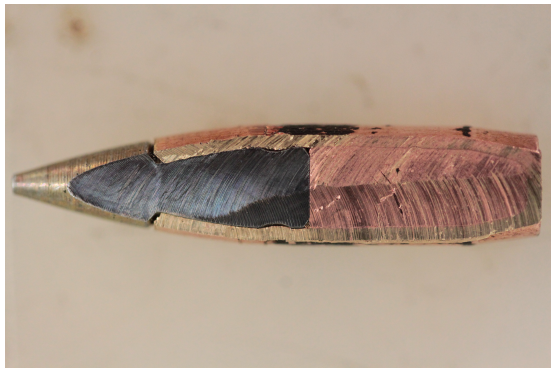
Example: Gun Firings WP19-F4-1392

M4 carbine



M855A1 projectile
Cu jacketed, steel/Cu projectile

Combine simulation with experiment

Simulations:
CFD-based simulation incorporating chemical kinetics

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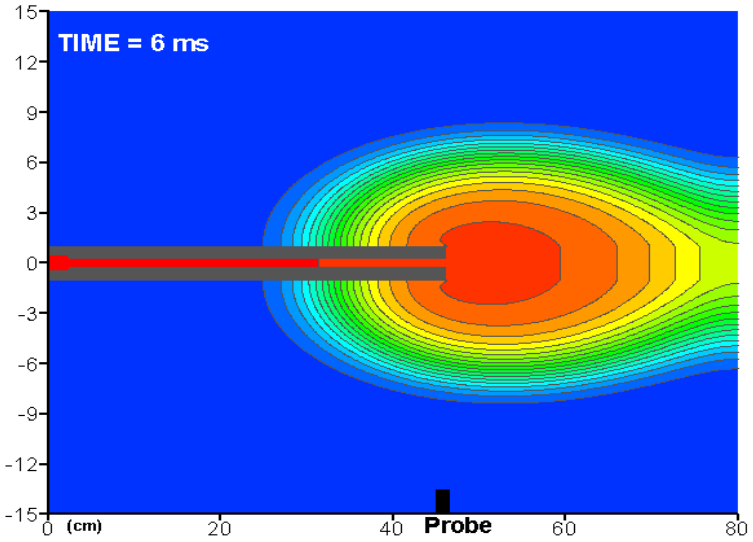
Equilibrium thermochemistry for anaerobic chemistry (fast).

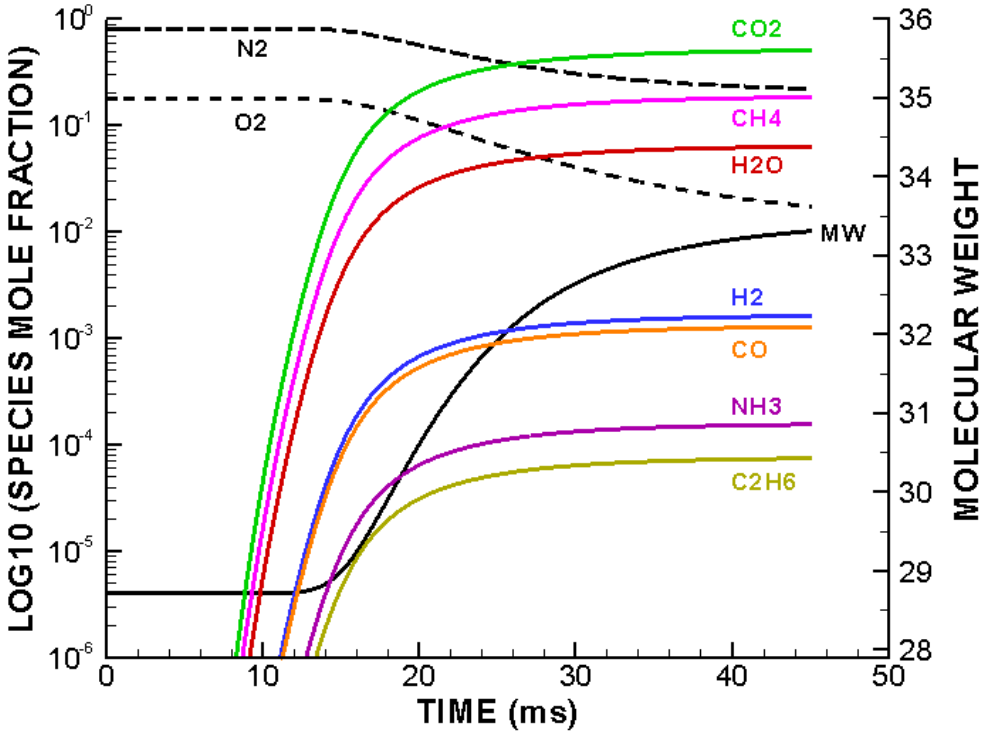
Predicted species at EPA probe location

CO_2 (blue to red:0 to 0.6)

At muzzle exit

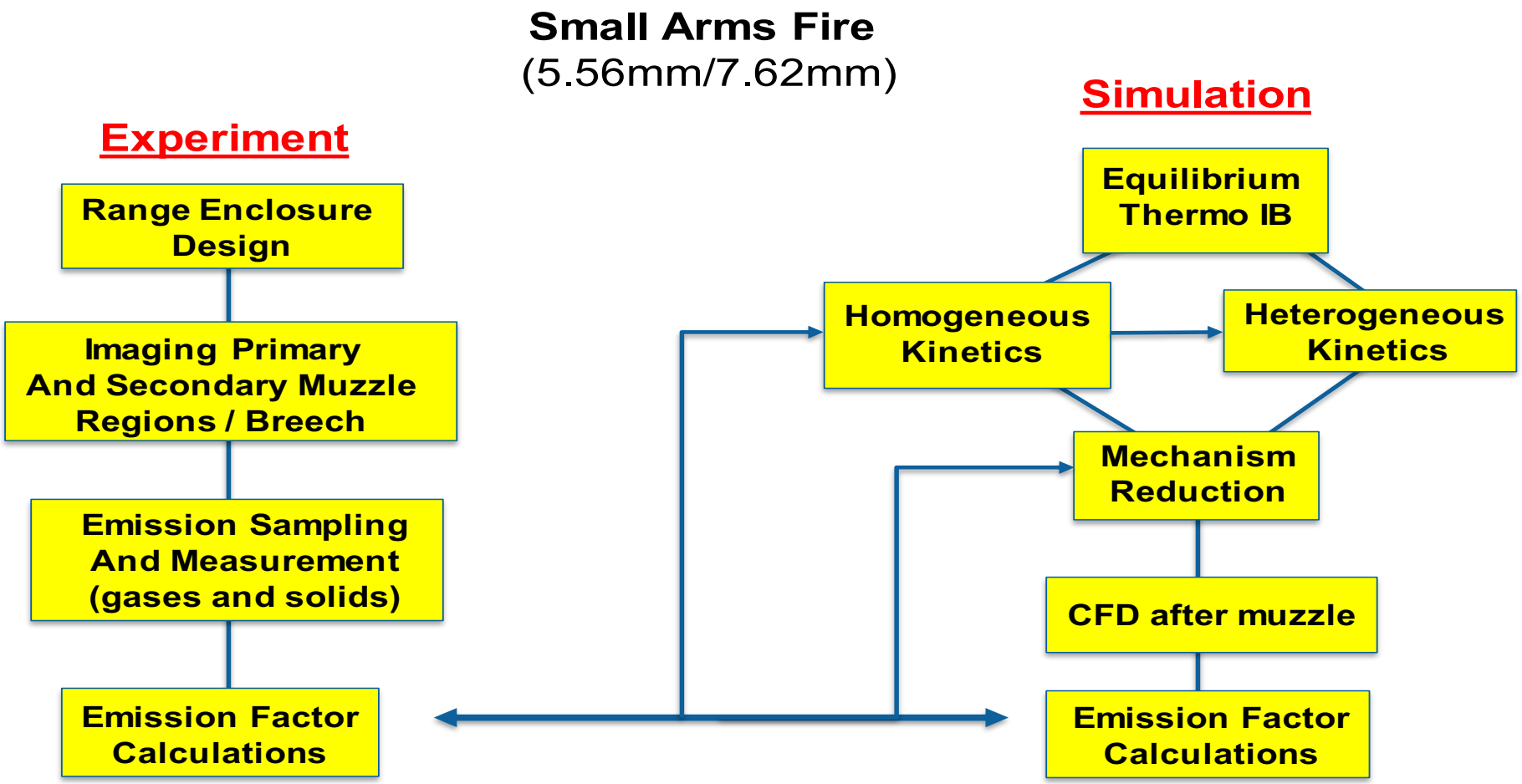


Fluid dynamics to simulate expansion of products after muzzle (aerobic chemistry).



Simultaneous chemical kinetics to follow product chemistry as sensor is encountered (heterogeneous).

WP19-F4-1392 Approach: Small Arms Fire



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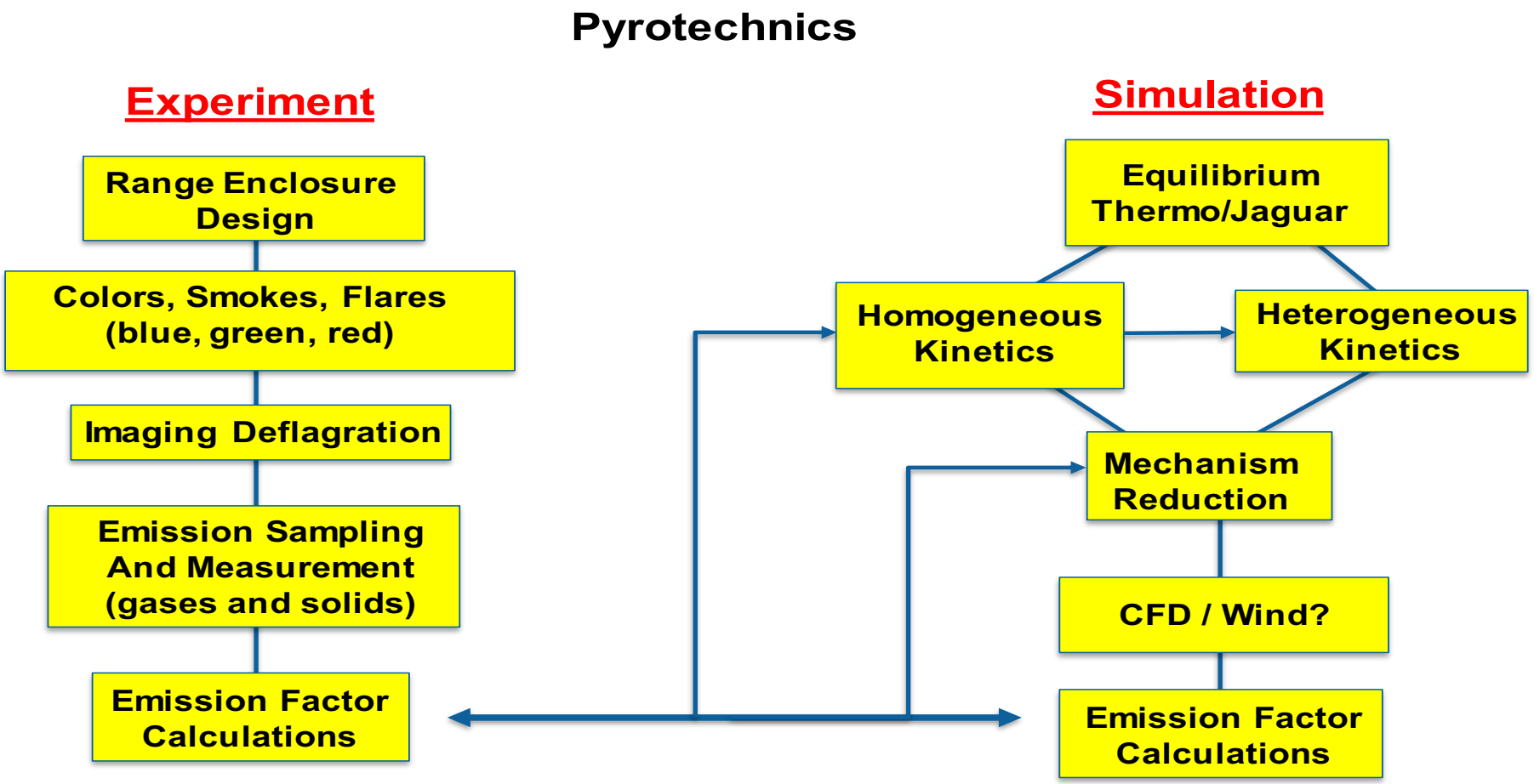
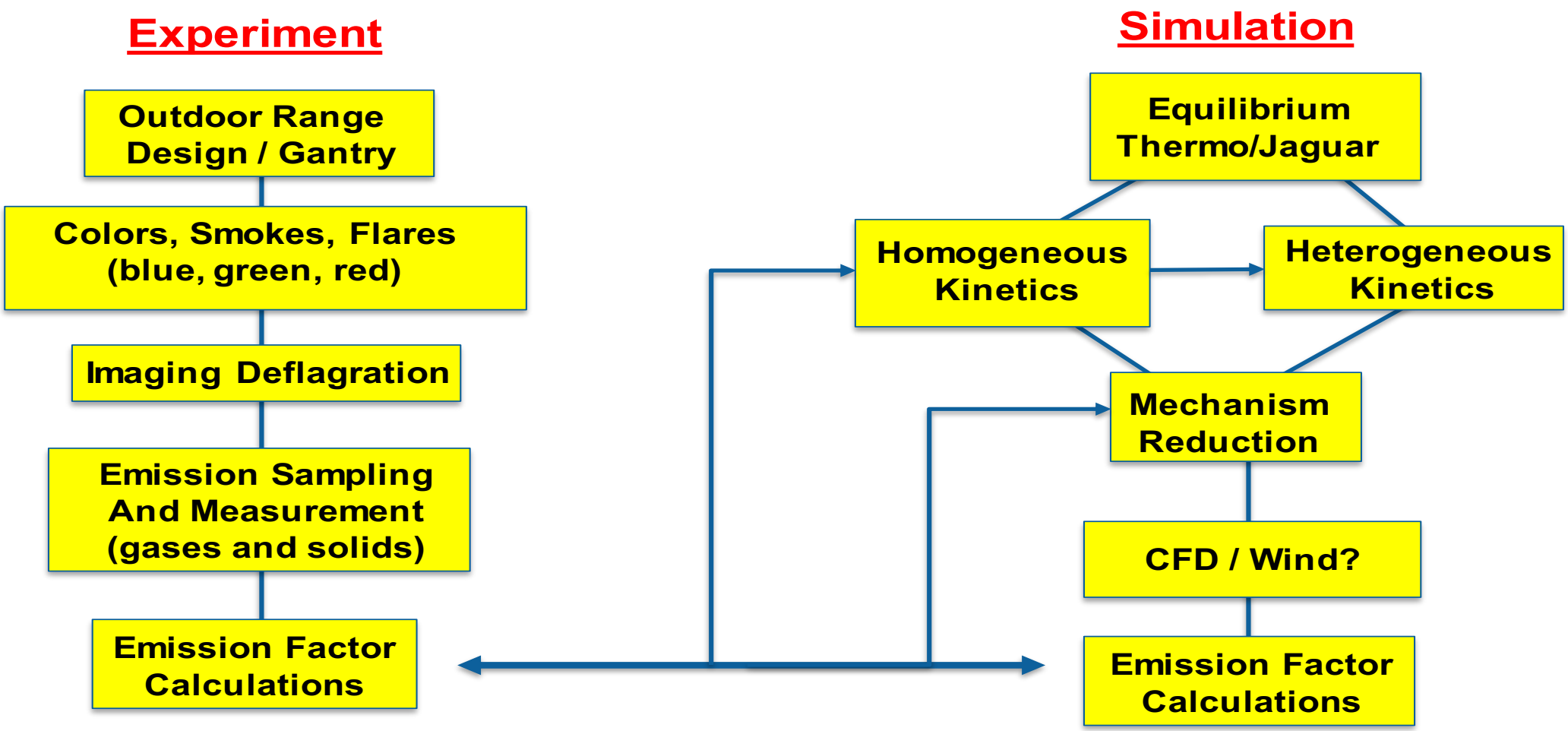
WP19-F4-1392 Approach: Pyrotechnics



WP19-F4-1392 Approach: Metal-containing Explosives

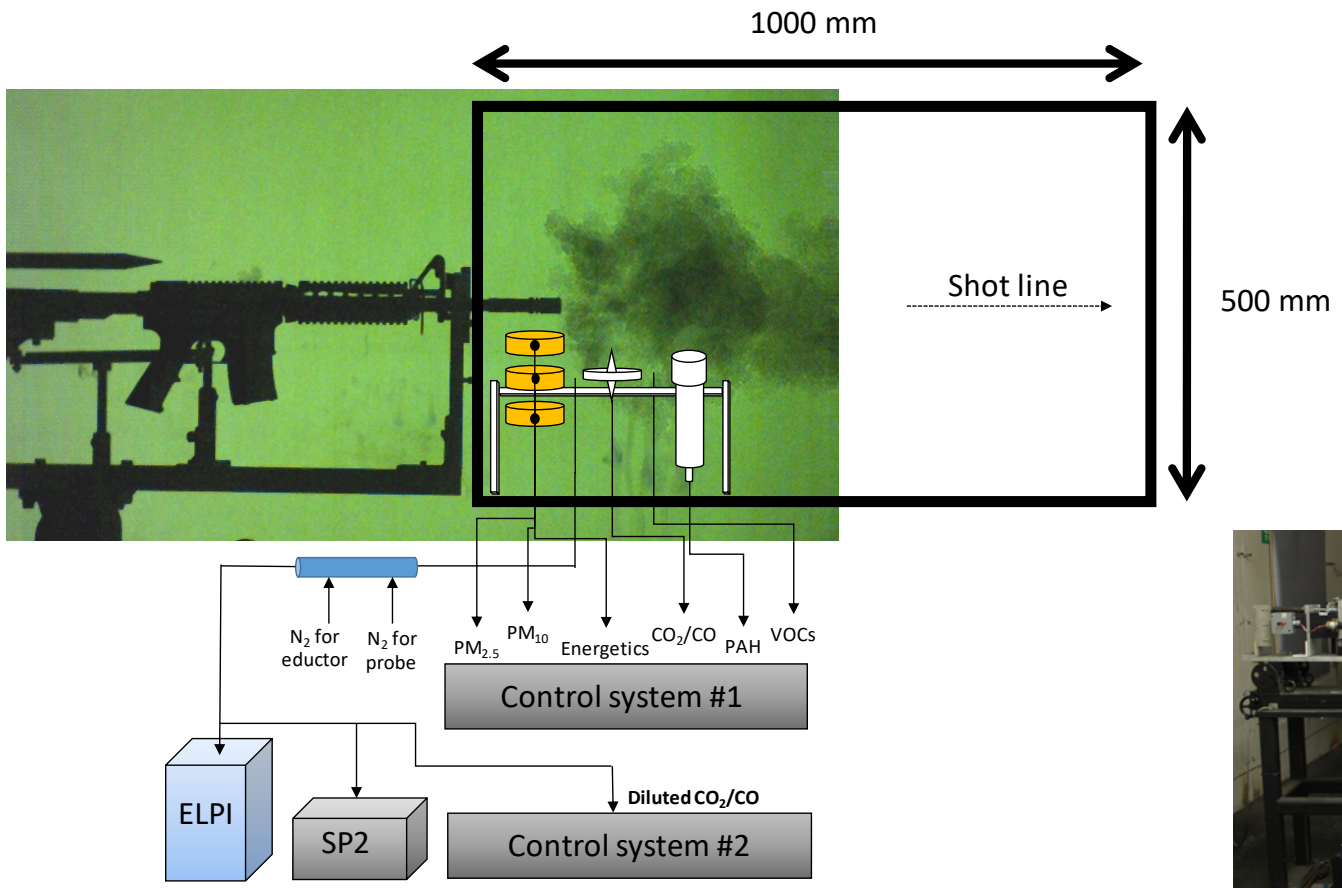


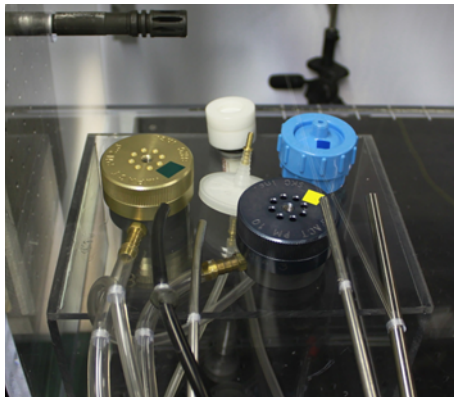
Experiments
EPA Instrumentation – WP19-F4-1392

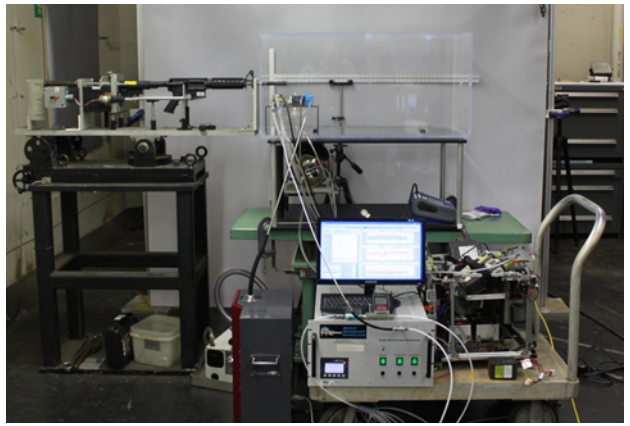
Remotely controlled chemical analysis sampling suite developed by EPA for aircraft, drone and aerostat deployment

- **Continuous data logging**
- **CO_2 measured using NDIR spectrograph**
- **CO measured using electrochemical gas sensor**
- **PM2.5 and PM10 sampled via SKC impactors (47 mm Teflon filters)**
- **PM greater than 10 um collected on oiled impaction disks**
- **Metals analyzed from particles using ED-XRF spectrometry**
- **B analyzed by ICP spectrometry**
- **VOC collected using SUMMA cannisters, analyzed via GC/MS**
- **Energetics/aromatics (including nitroaromatics) analyzed by HPLC**
- **Particle size distribution measured using a low pressure impactor (ELPI)**
- **Soot particle size measured photometrically by incandescence**
- **HCN, NH3 analyzed by FTIR spectrometry**

Gun Firings Sampling – Methods WP19-F4-1392







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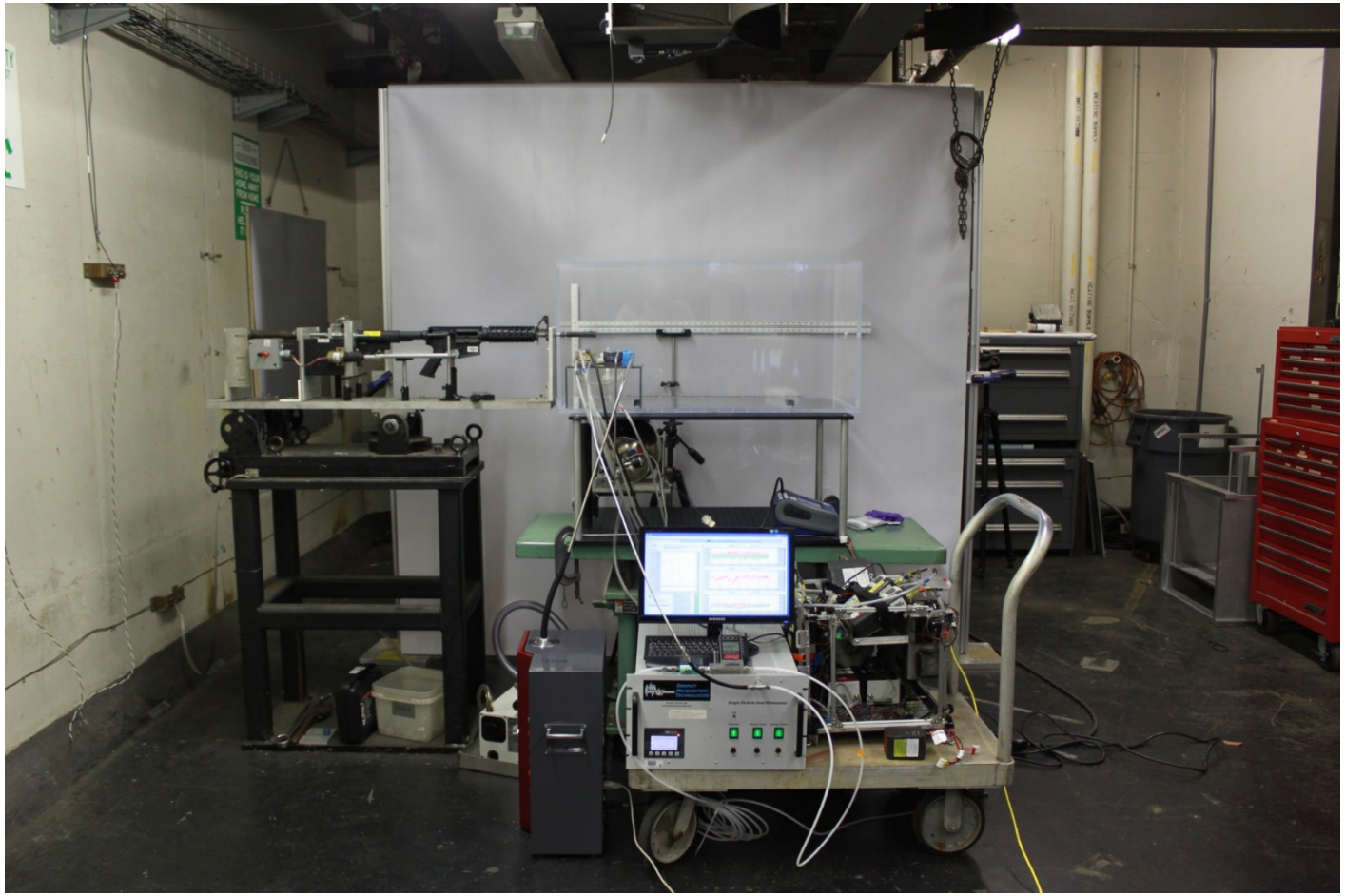
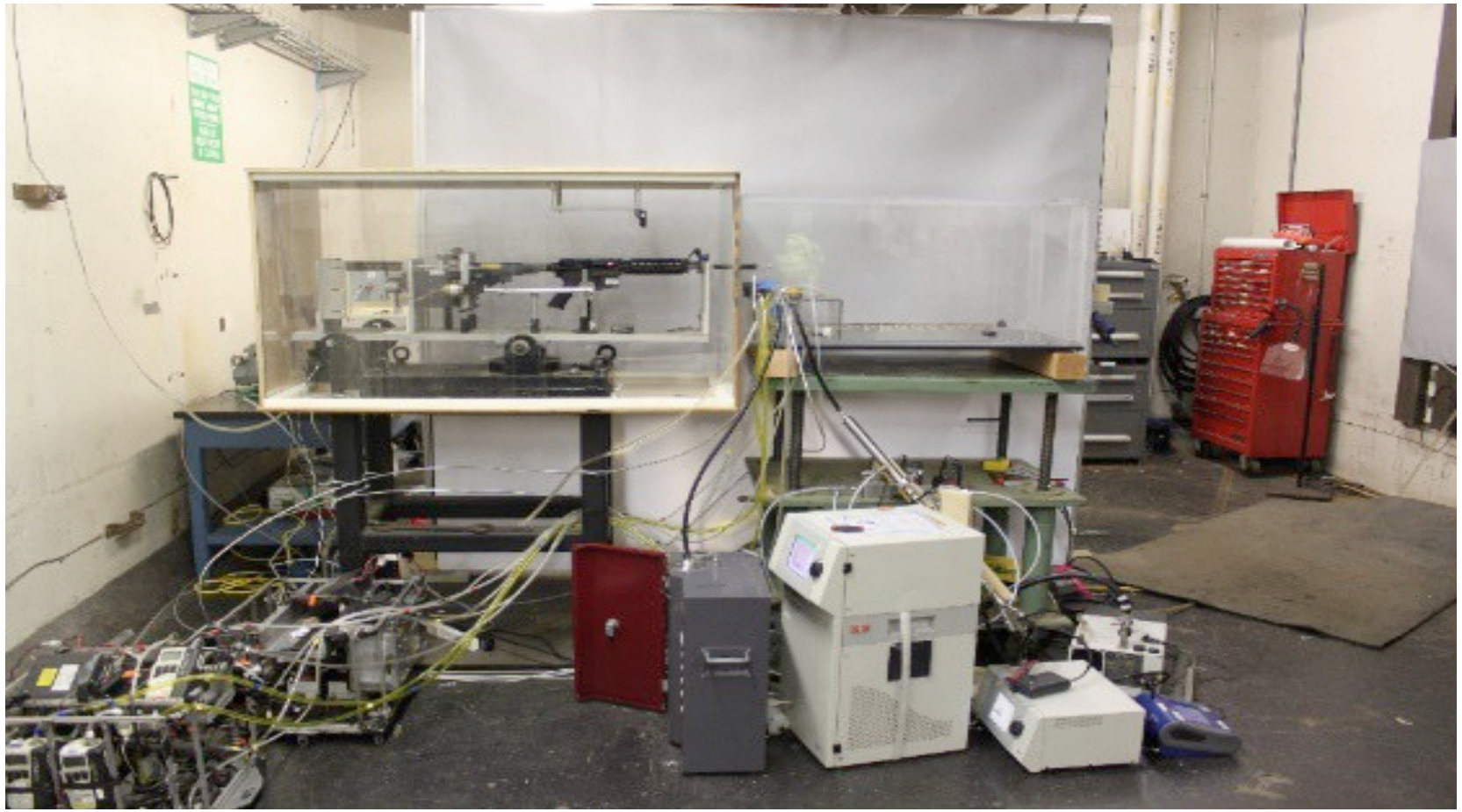
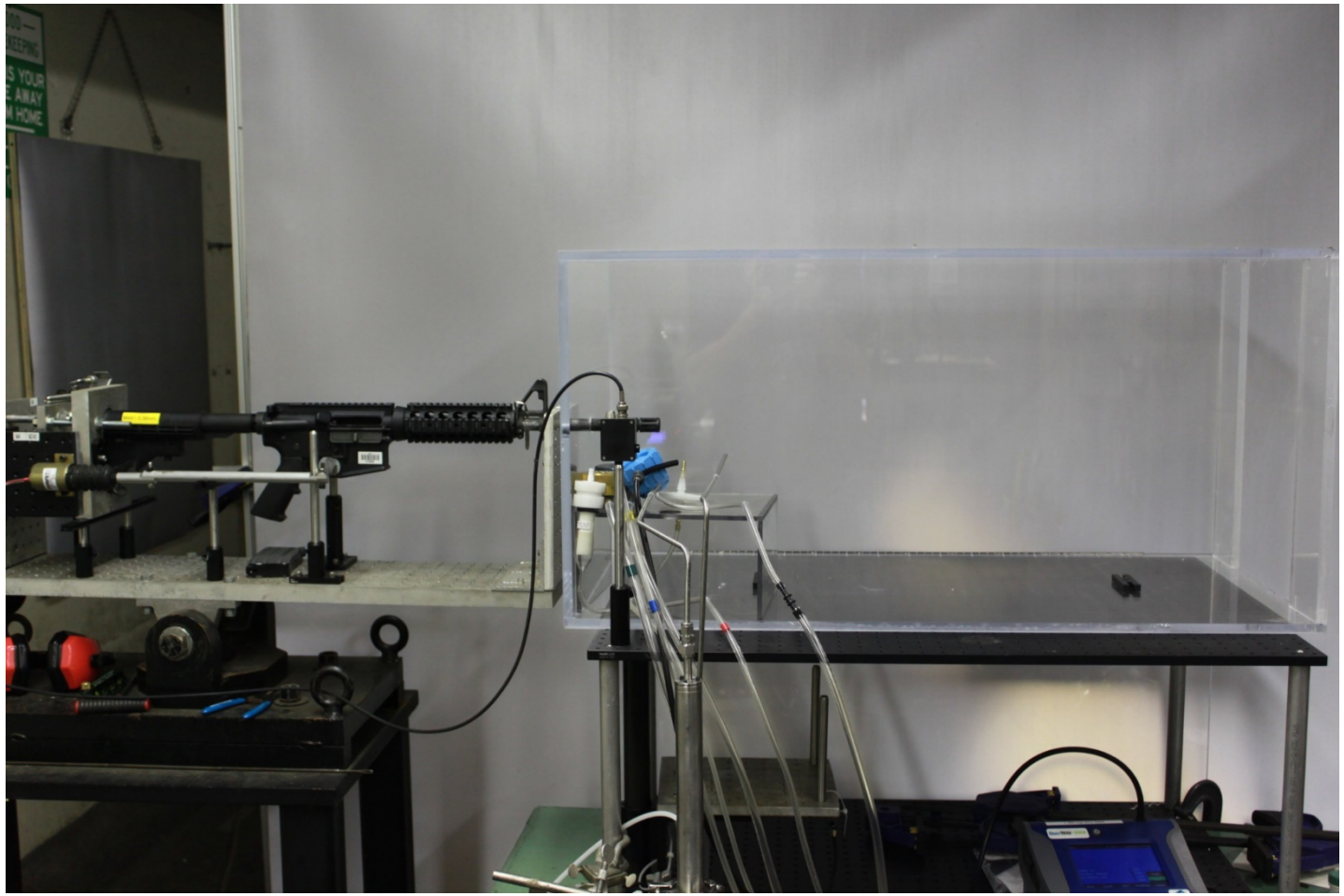
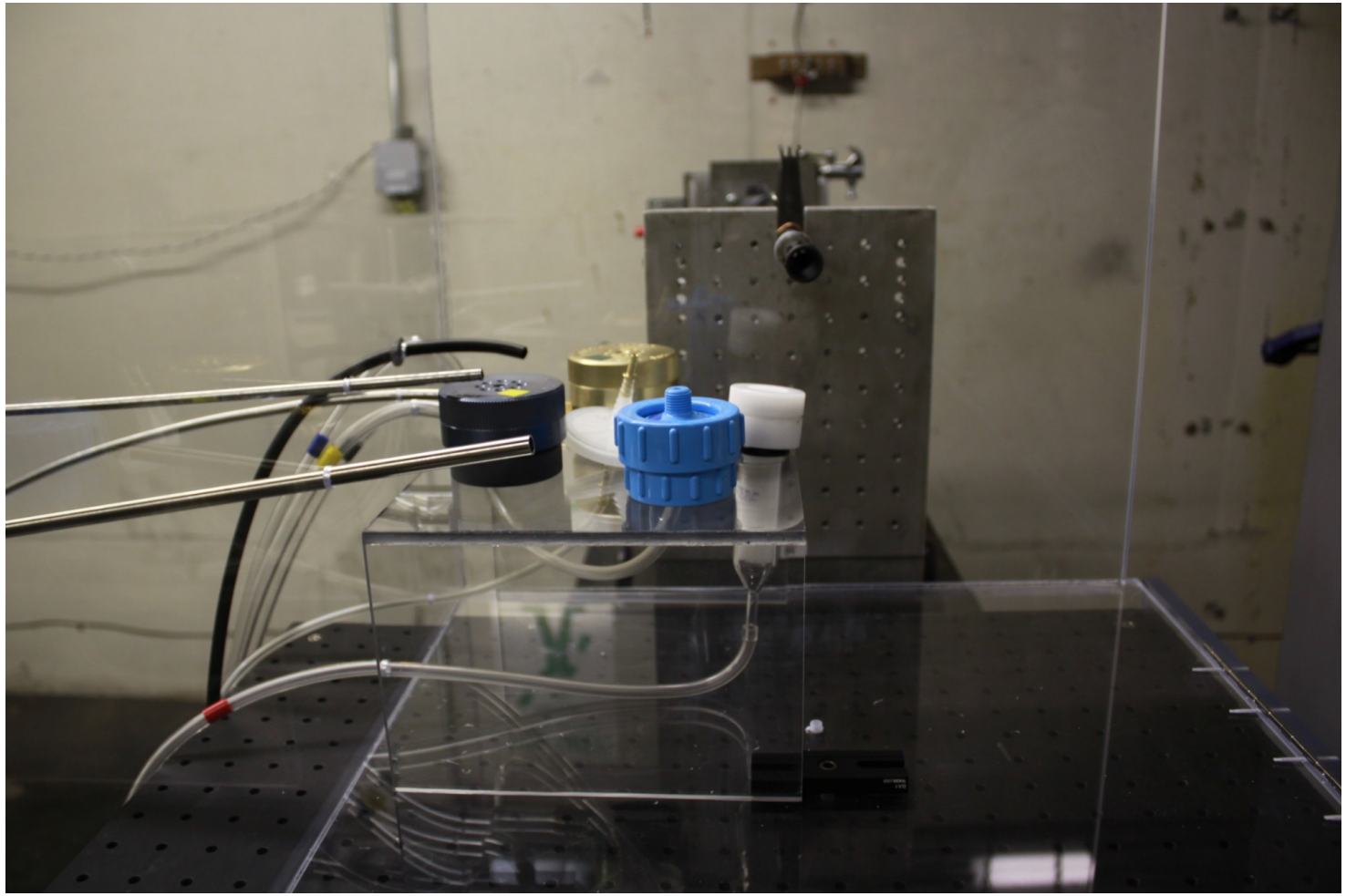


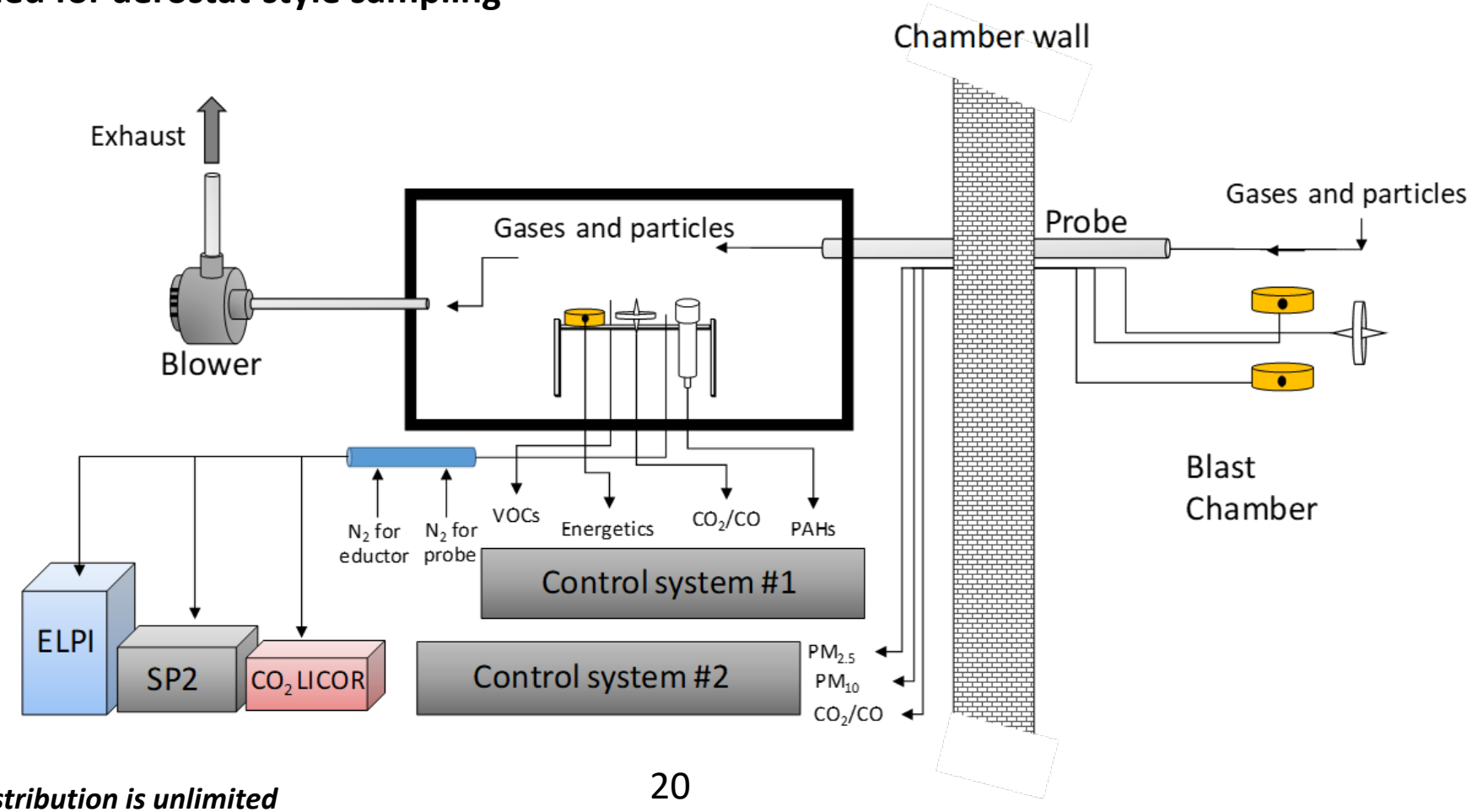




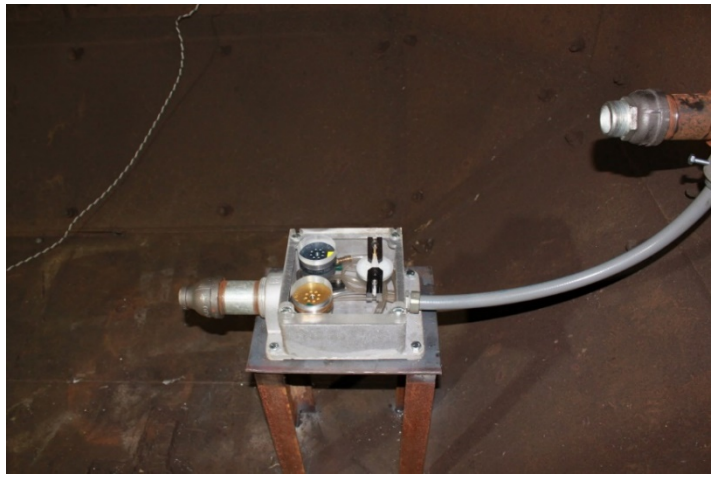


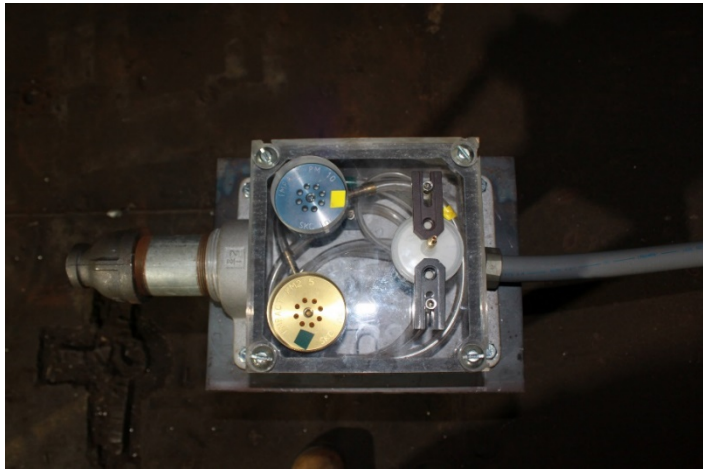
Example: Explosives Sampling – Methods

To be modified for aerostat-style sampling



Explosives Sampling – Methods





EF-17A Aberdeen Proving Ground

2018

2010

EF-17A blast facility on-line FY19

Explosive / Pyrotechnic Sampling

EF-17A blast facility on-line June 2019

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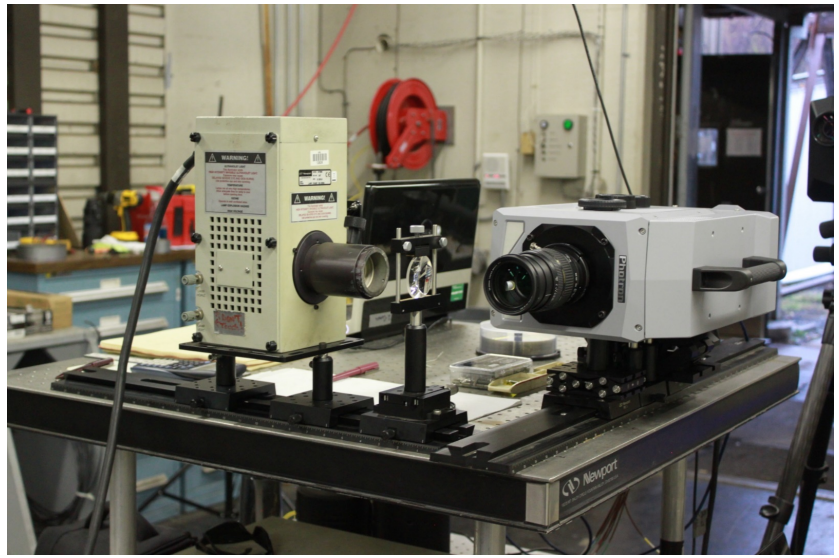
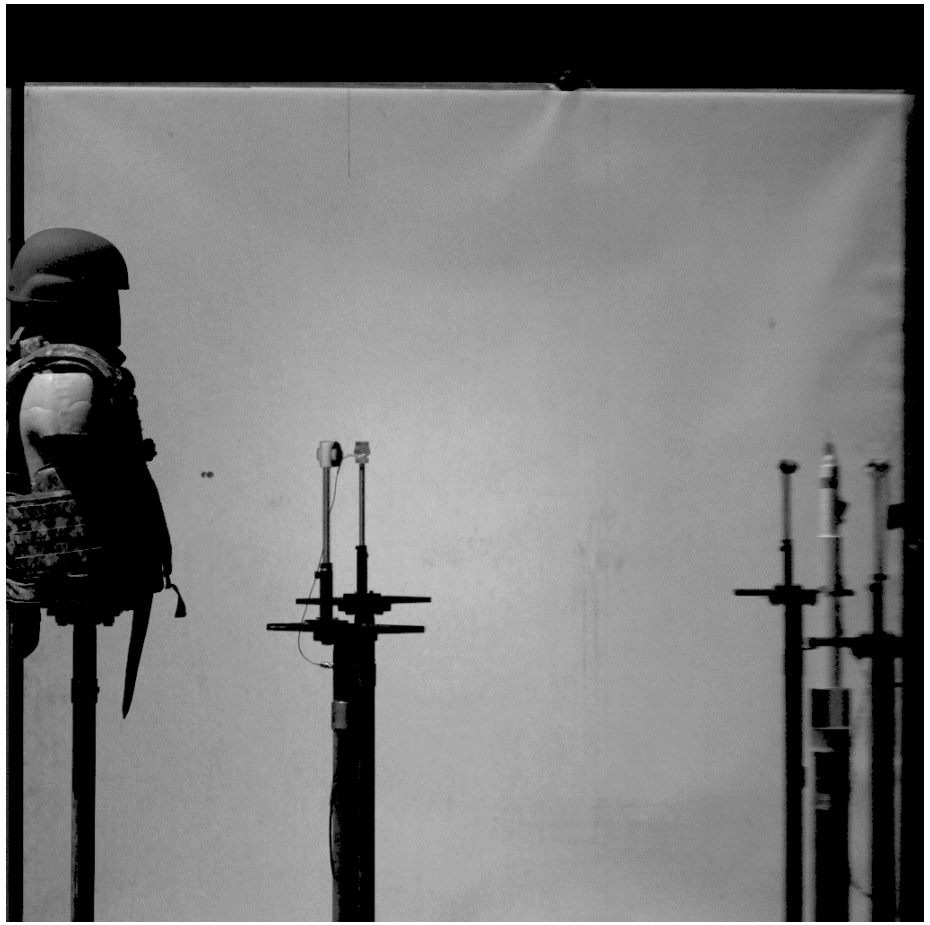
ARL Facilities WP19-F4-1392

- Measurement of state variables (T&P)
- Instrumented gun room
- Instrumented blast chamber (20 kg NEW limit)
- Gun room and blast chamber are contiguous (connecting port)
- Arc-lamp/Laser-based Edgerton Shadowgraphy system in gun room
- High-speed high definition imaging in blast chamber
- High speed imaging spectroscopy and pyrometry in gun room and blast chamber
- Pressure measurement via piezoelectric transducers
- Remote automated firing in gun room and blast chambers
- Argon-candle illumination in blast chamber
- Outdoor arena-style range with arc-lamp Edgerton shadowgraphy

Pressure Imaging - Edgerton Shadowgraphy





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Temperature Imaging
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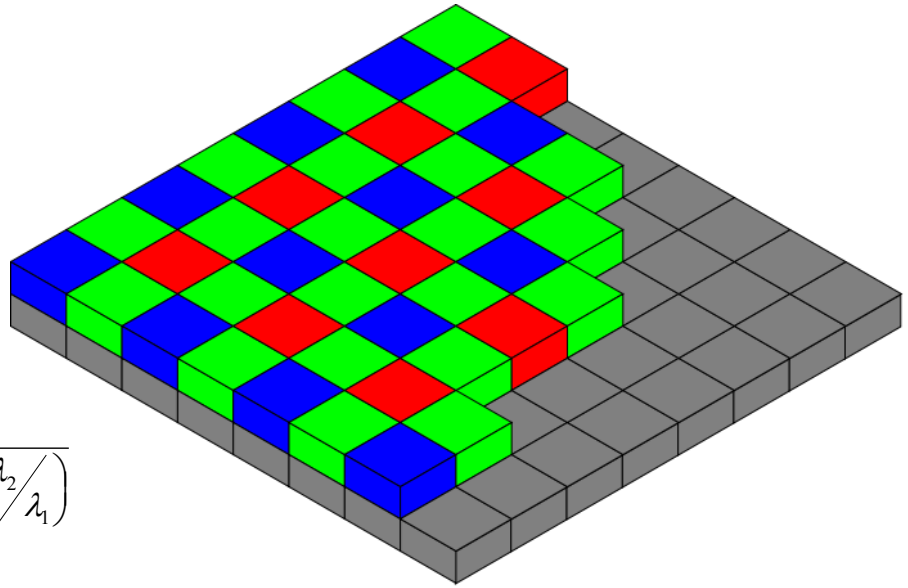
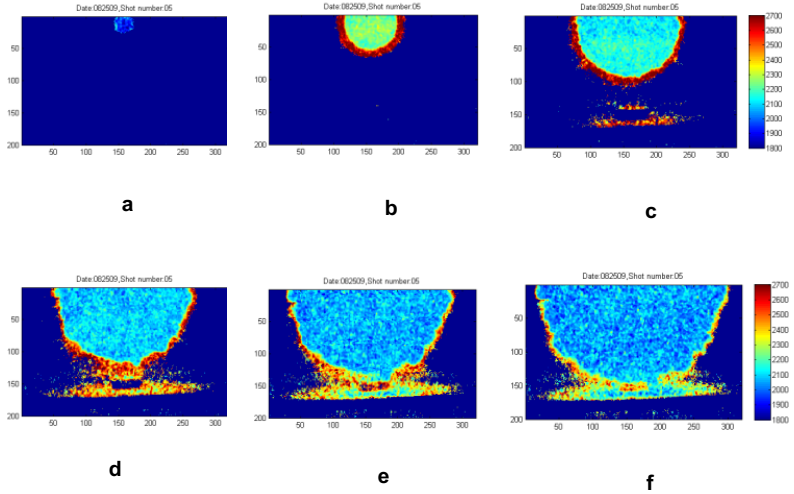
Reduced Bandwidth Imaging Pyrometry

Planck's Law

$$T = \frac{C_2}{\ln\left(\frac{I_1}{I_2}\right) - \ln\left(\frac{E_1}{E_2}\right) - 5\ln\left(\frac{\lambda_2}{\lambda_1}\right)}$$

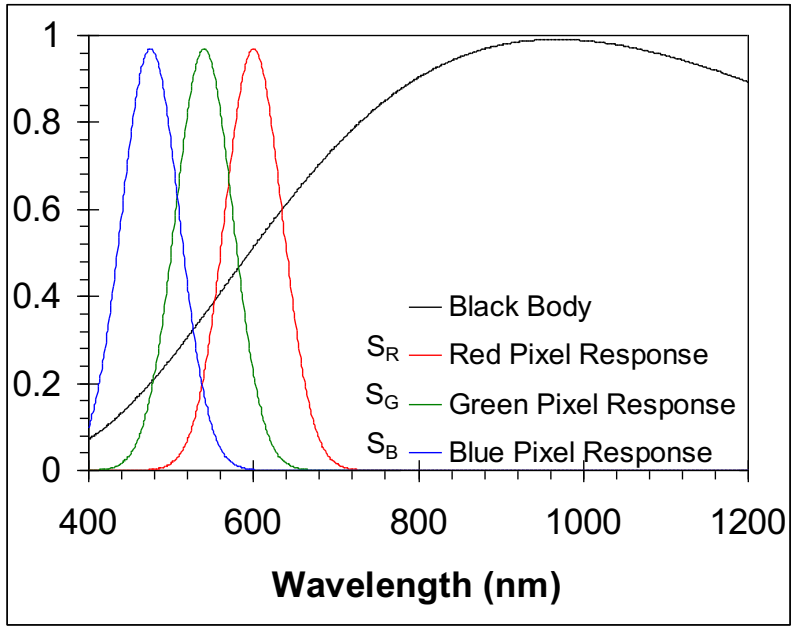




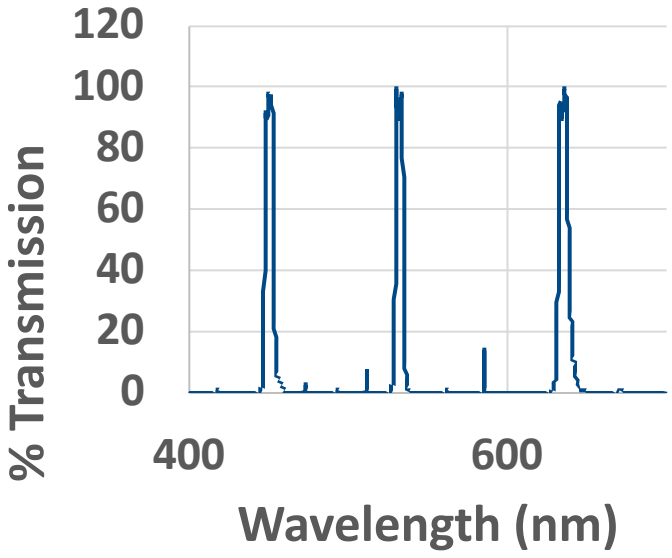
Full Color CCD Blast Imaging

225 g C-4 0.25m above steel platform

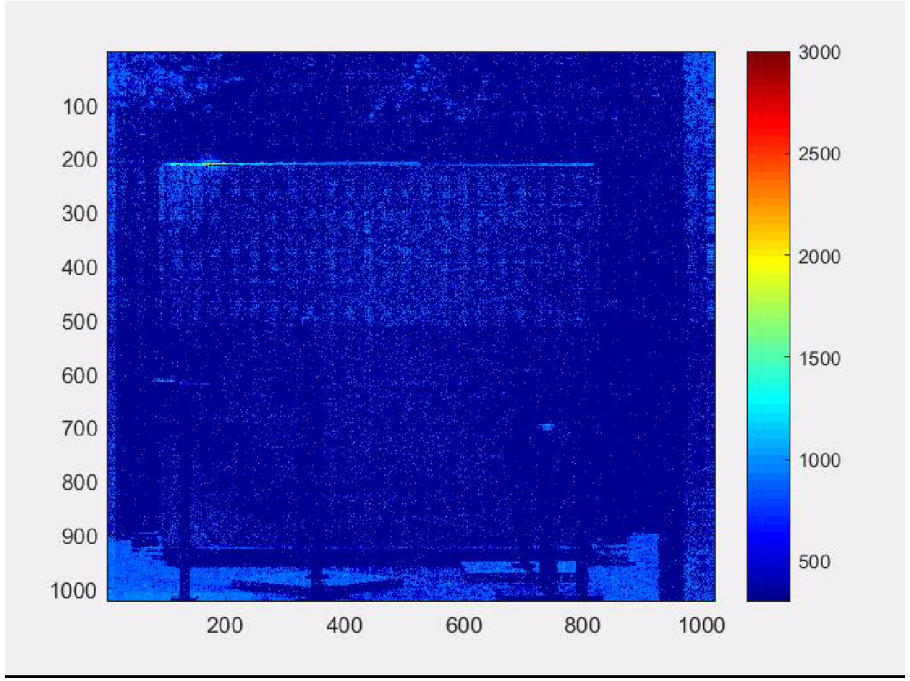
Reduced Bandwidth Imaging Pyrometry



Color camera response



3-color notch filter



Reduced bandwidth imaging pyrometer

Summary: Three Field Campaigns

- Comprehensive effort on gun fire emissions, pyrotechnics, and open detonation built on methods demonstrated in the SEED project
- Inclusion of CFD + finite rate chemical kinetics for species predictions
- Metal mass balances, exposure calculations, range deposition
- Models with metal oxidation and particle burning
- Energetics, pyrotechnics formulated at ARL
- Chamber and open range testing of gun firing
- New, open detonation range for explosives and pyrotechnics
- EPA OB, OD, and Static Firing (rockets) open area sampling methods
- Testing and verification of OBODM
- Field sampling methods to include optical pyrometry, high dynamic range imaging, Edgerton shadowgraphy.

Schedule and Outputs

Task	Month 0-6	Month 6-12	Month 12-18	Month 18-24	Month 24-30	Month 30-36
M4 Carbine testing, at ARL		1				
Pyrotechnics testing, at ARL			2	1,3		
Open detonations, at ARL						
Field data processing and analysis						1,4
Final Report						5

- SERDP Symposium poster presentation.
- Paper on carbine emissions and range exposure scenarios.
- Paper on a reduced combustion mechanism including particle combustion.
- Paper on pyrotechnics emission factors.
- Paper comparing field and laboratory detonation results, and paper on incorporation of Jaguar code for the metallized explosives.
- Final report

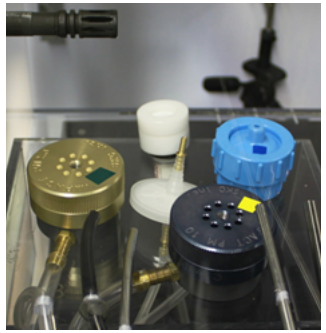
Transition Plan

- **Results incorporated into EPA publications.**
- **Results incorporated into safety protocol at DoD ranges.**
- **Postdoc addition-training / training of professional staff in explosive science / training of explosive technicians.**
- **Incorporation/improvement of heterogeneous kinetics to DoD/DoE explosives estimators (CHEETAH/Jaguar).**
- **Reports / Publications / Symposia**

Questions?

EPA Toxicological Assessment

$PM_{2.5}$ samples will be collected from the experiments and brought to EPA for toxicological assessment. Standard protocols will be followed for comparison with other combustions sources (diesel engines, wildfires, etc.)



$PM_{2.5}$ COLLECTION

PM EXTRACTION

Gun Firing, Detonation, Obscurants PM2.5

Toxicity Analysis

***In Vivo* Test**

OROPHARYNGEL ASPIRATION

WILDFIRE PM (100 µg)

MOUSE

BALF Analysis

- **Lung injury**
- **Lung inflammation**
- **Cardiac function**

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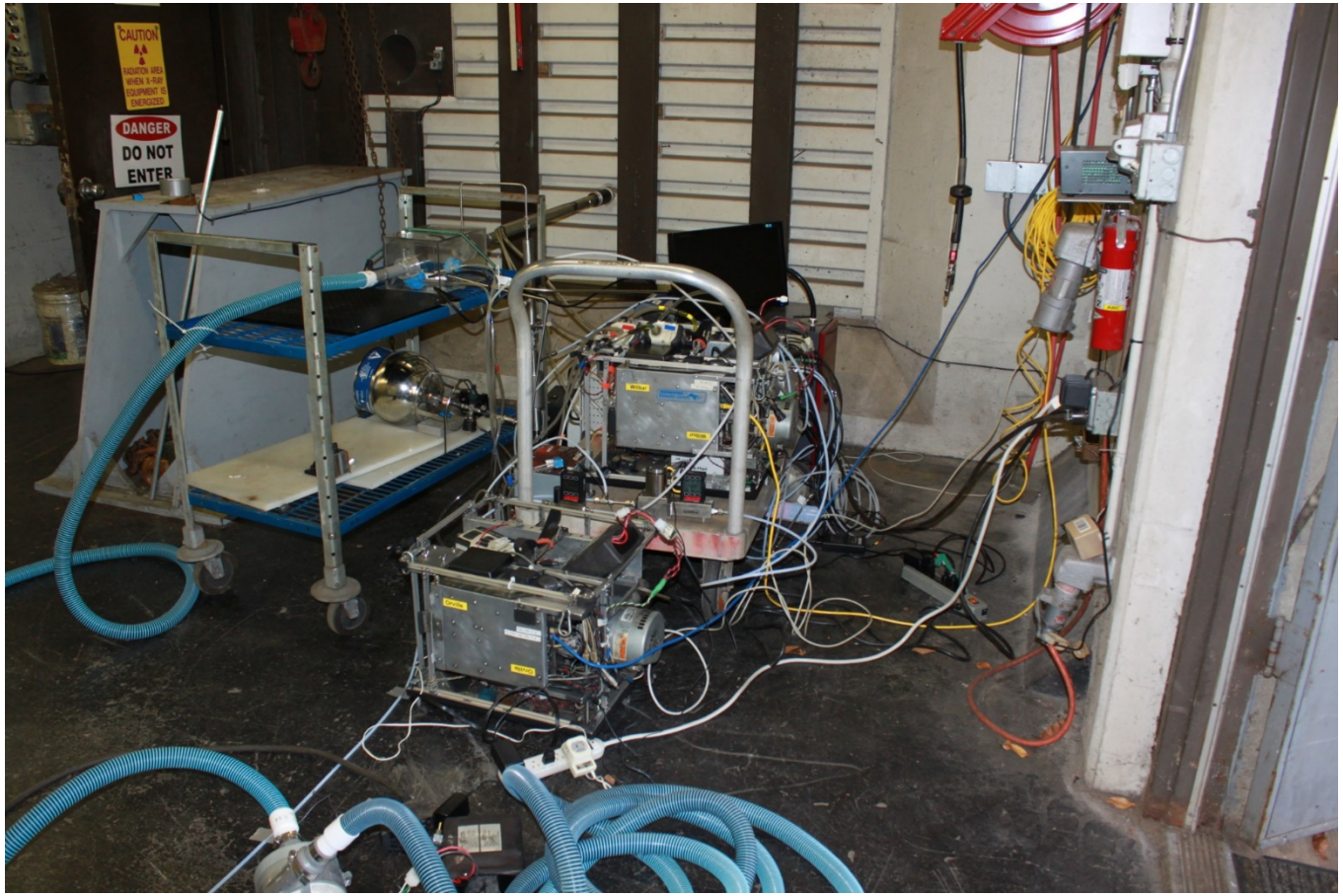
CAUTION
DANGER
DO NOT
ENTER

Conclusions from SEED effort

- Measured MCE for TNT enclosed detonations near 98%.
- Laboratory EF differ from field values (possible soil entrainment).
- Addition of Mg:B to the TNT formulations increases the $PM_{2.5}$ emission by factor of 8.
- Lead (Pb) detected likely from blast chamber walls (no lead in the explosive train).
- Sensitivity of VOC sampling - detection of PMMA - TNT cylinder centering device.
- MCE simulation using CHEETAH plus CHEMKIN in reasonable agreement with measurement (0.865 predicted vs 0.98 measured).
- Use of blast chamber affected results (shock reflections).

Recommendations

- Indoor vs. outdoor results comparison to verify residual carry over and wall effects.
- Ground-deposited residuals should be sampled concurrently with air emissions.
- Compositional analyses of the formulations should be determined prior to testing.
- Finite rate kinetics (+ heterogeneous) should be incorporated into CFD in follow on.
- Temperature measurements should be included in follow on effort