



U.S. Army Research, Development and
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Laser-induced plasma chemistry of the explosive RDX with various metals

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TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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Motivation

Understand chemistry between metal nanoparticles and molecular explosives

Develop more efficient explosives

LIBS

Nanoparticle production followed by laser-induced plasma chemistry

Time-resolved emission spectra

Laser Parameters

Laser pulse energy dependence

Single vs. double pulse

Substrate characterization

Matrix effects

Effect of impurities on chemistry

Experiments

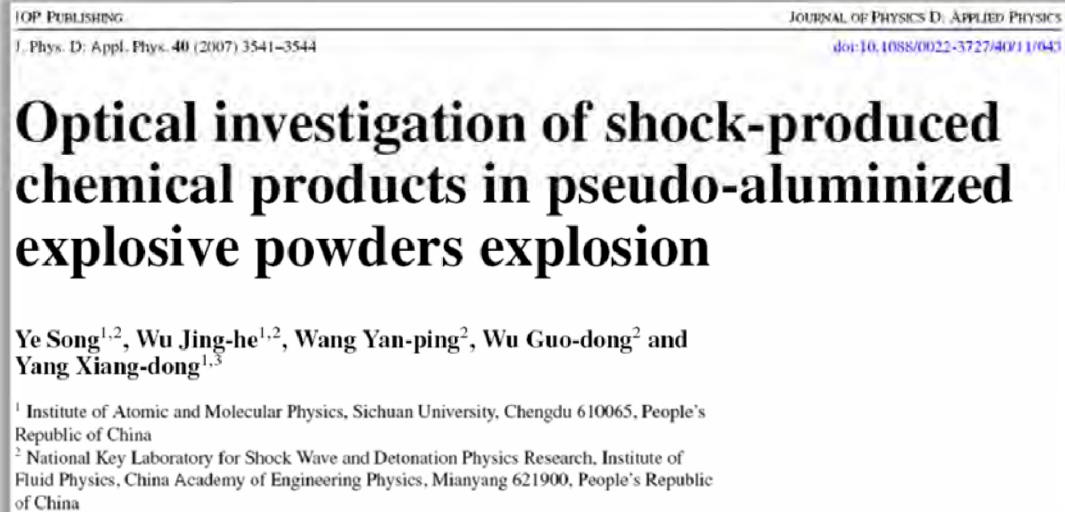
Double pulse (air/argon)

Aluminum powder additives

RDX discrimination

RDX residue on various metals

Effects of substrate on discrimination



Investigated formation of carbon in aluminized-RDX shock tube initiation

Production of AlO and C decreases rocket propellant performance

- XRD confirmed presence of C and Al₂O₃ in blast residue

Observed that ↑ micron-Al results in ↑ C₂ emission

- AlO and C₂ emission collected with two 2-nm resolution monochrometers/PMTs

Our idea was to use Al nanoparticles rather than conventional micron-sized Al and look at the emission from additional atomic and molecular species, all on a much smaller scale

- In the past decade, laser ablation has increasingly been used to produce metallic nanoparticles
 - the size and distribution of the nanoparticles can be controlled by:
 - sequential laser pulses, varying repetition rates
 - laser fluence, wavelength and pulse width
 - carrier gas (air, argon, nitrogen, etc.)

J. Laser Micro. Nanoengineer., 3(2), 100-105 (2008).

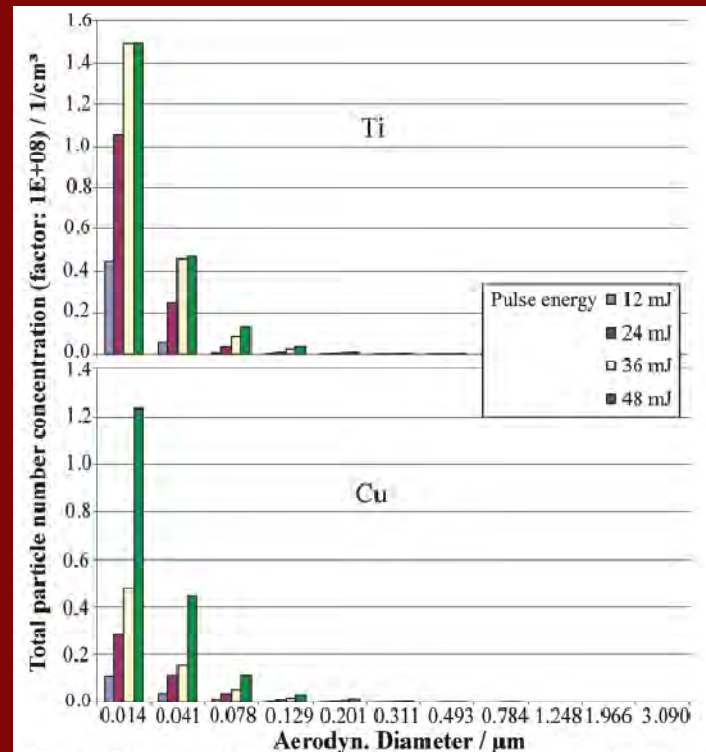


Fig. 3 Influence of the pulse energy on the particle size distribution of metal nanoparticles (carrier gas: N_2 , gas pressure inside the chamber: 200kPa, pressure of the particle flow rate: 75kPa)

Key advantages of LIBS over the technique used by Song et al.:

Little or no sample preparation is needed

- no need to cast explosive formulations
- any type of material can be ablated with the laser as long as the laser energy > breakdown threshold

The properties of the laser (pulse energy, wavelength, pulse duration) can be tuned to control the size of the particles formed

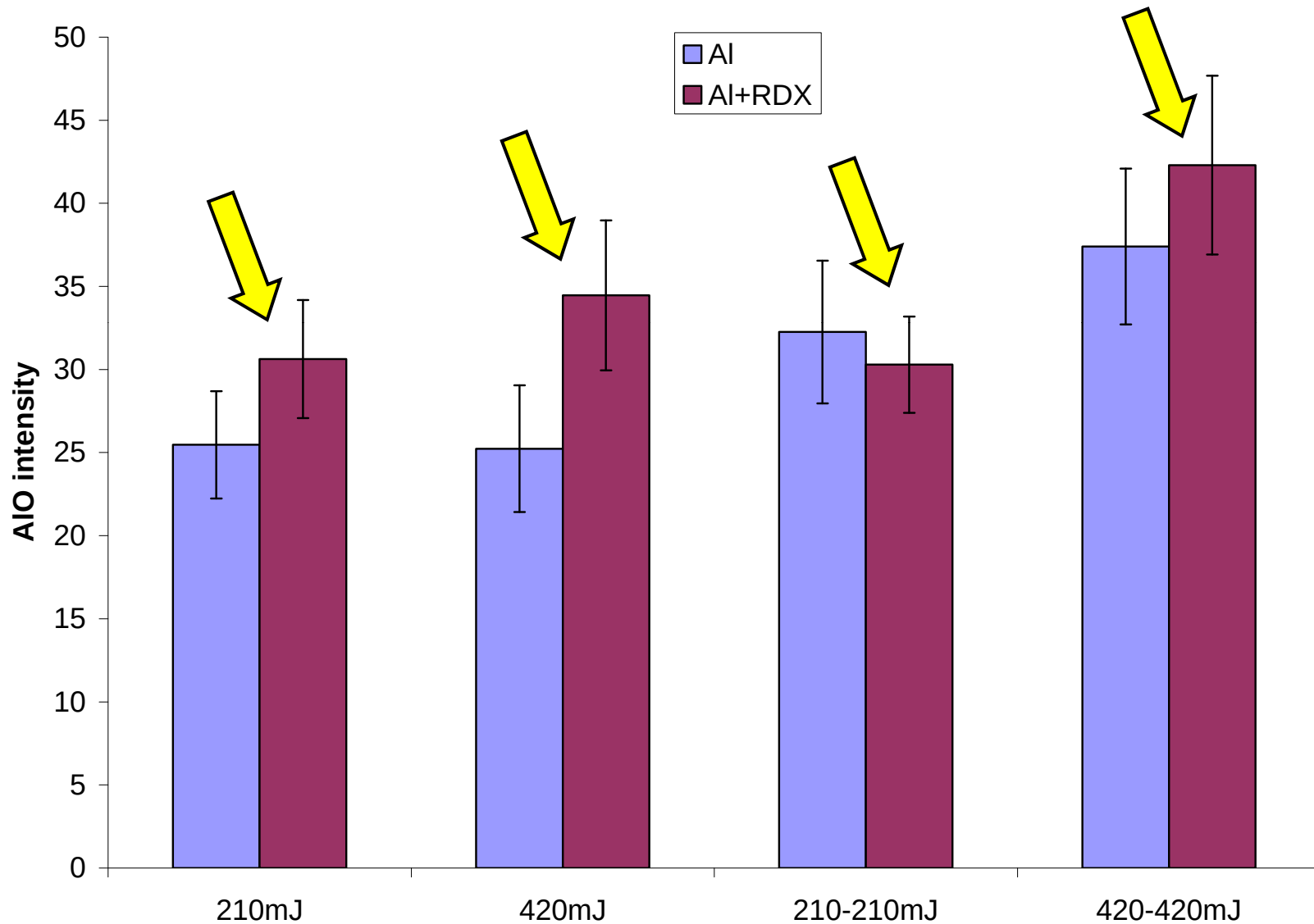
- laser-generated nanoparticle formation

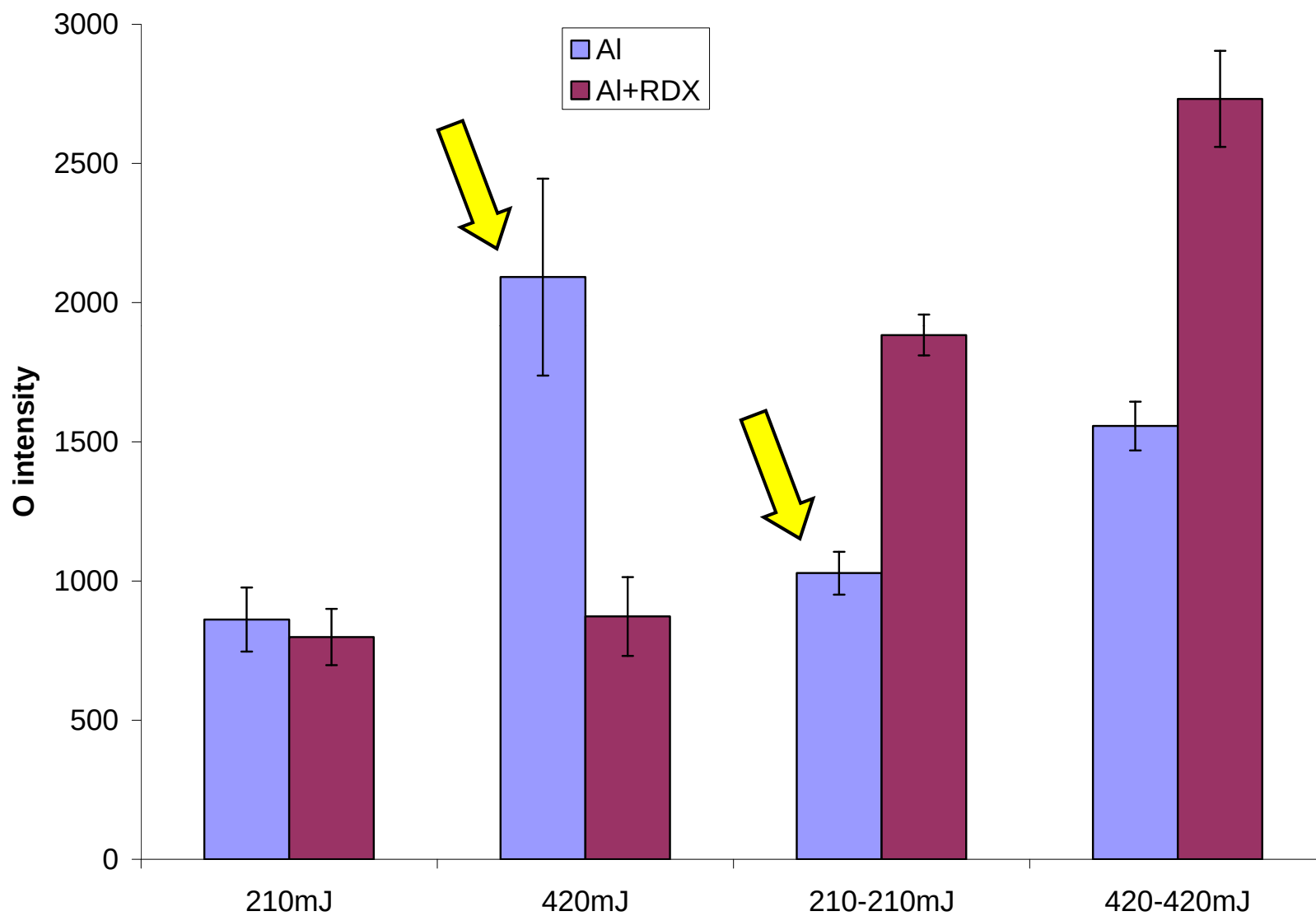
The intermediate chemical reactions of RDX and Al can be studied on a smaller scale

- no shock tube needed

Ability to track relative concentrations of a large number of atomic and molecular species simultaneously

- $C + C \rightarrow C_2$
- $C + O_2 \rightarrow CO + O$, $CO + O \rightarrow CO_2$, $Al + CO_2 \rightarrow AlO + CO$
- also H, N, CN







Survey of Substrates



Question: do trace impurities in the metal substrate affect the plasma chemistry?

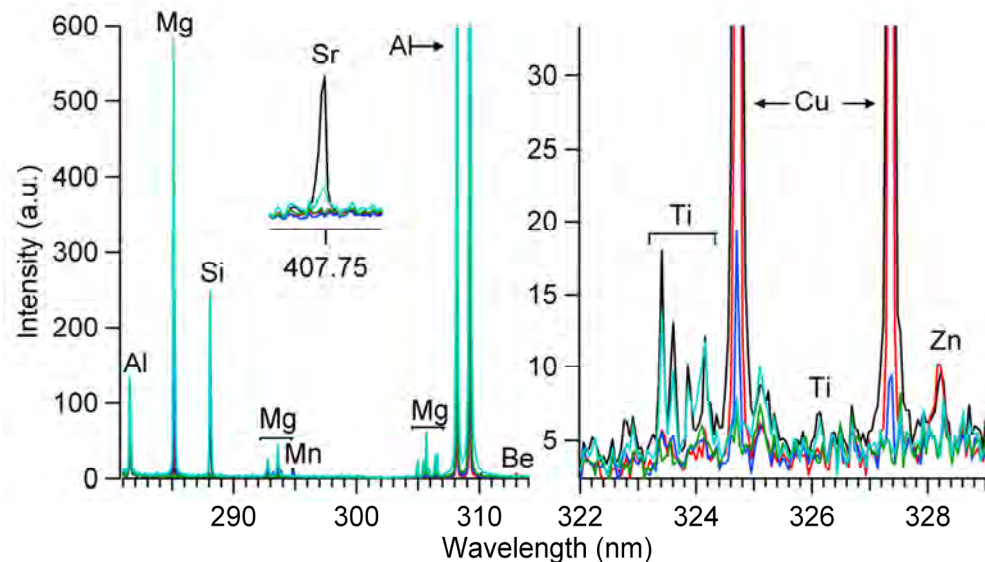
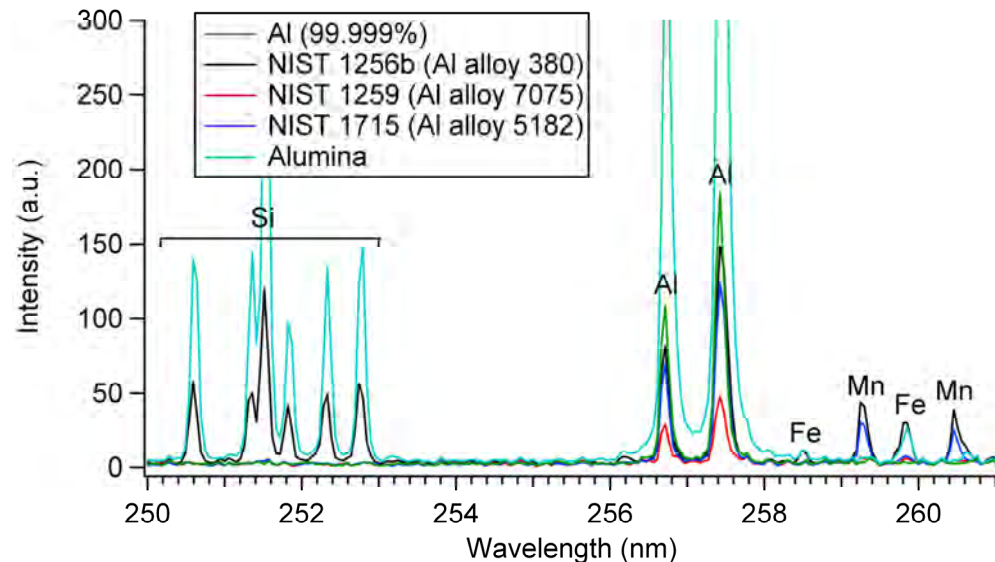
Spectra of 68 metal substrates were acquired

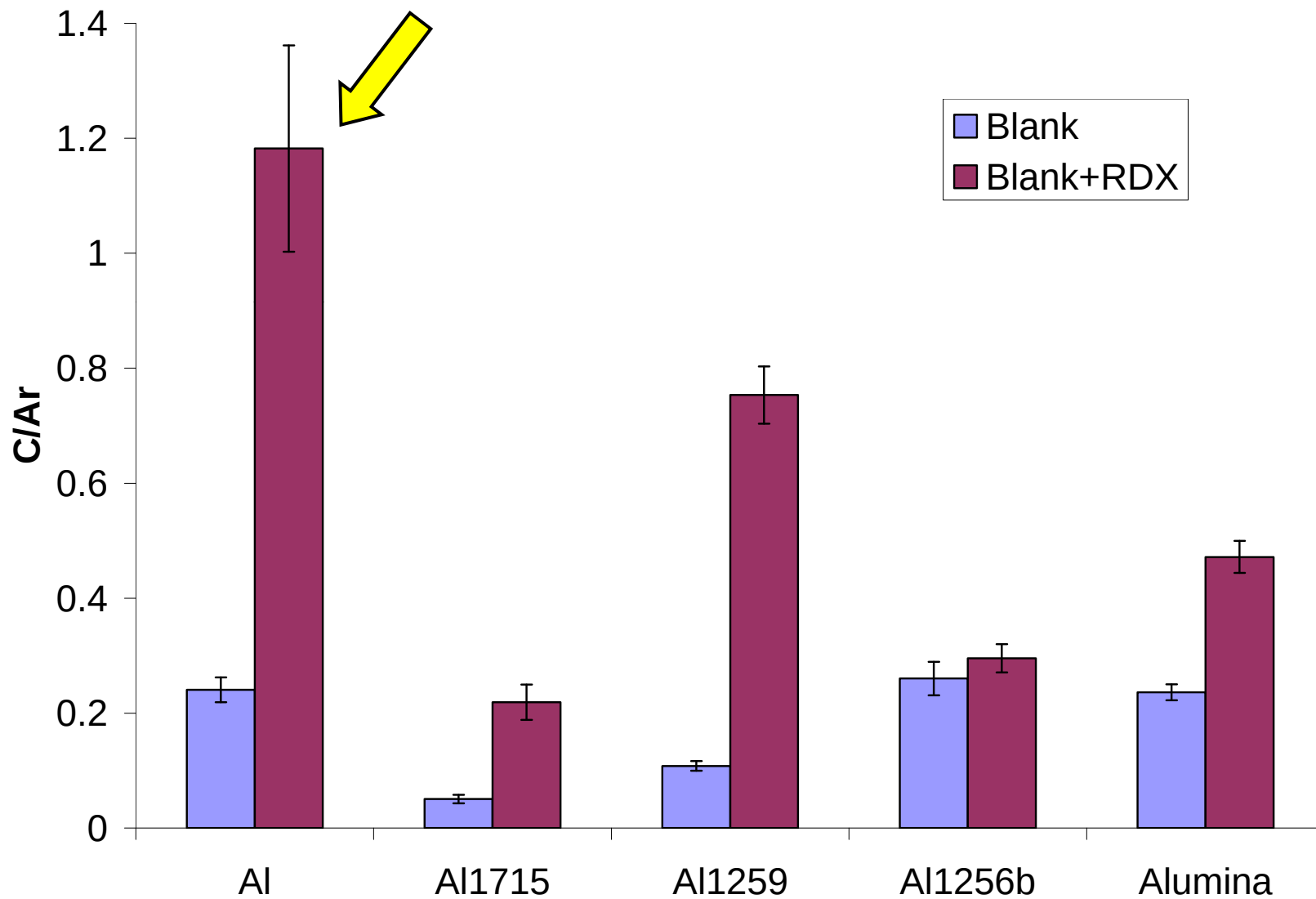
Samples surveyed included:

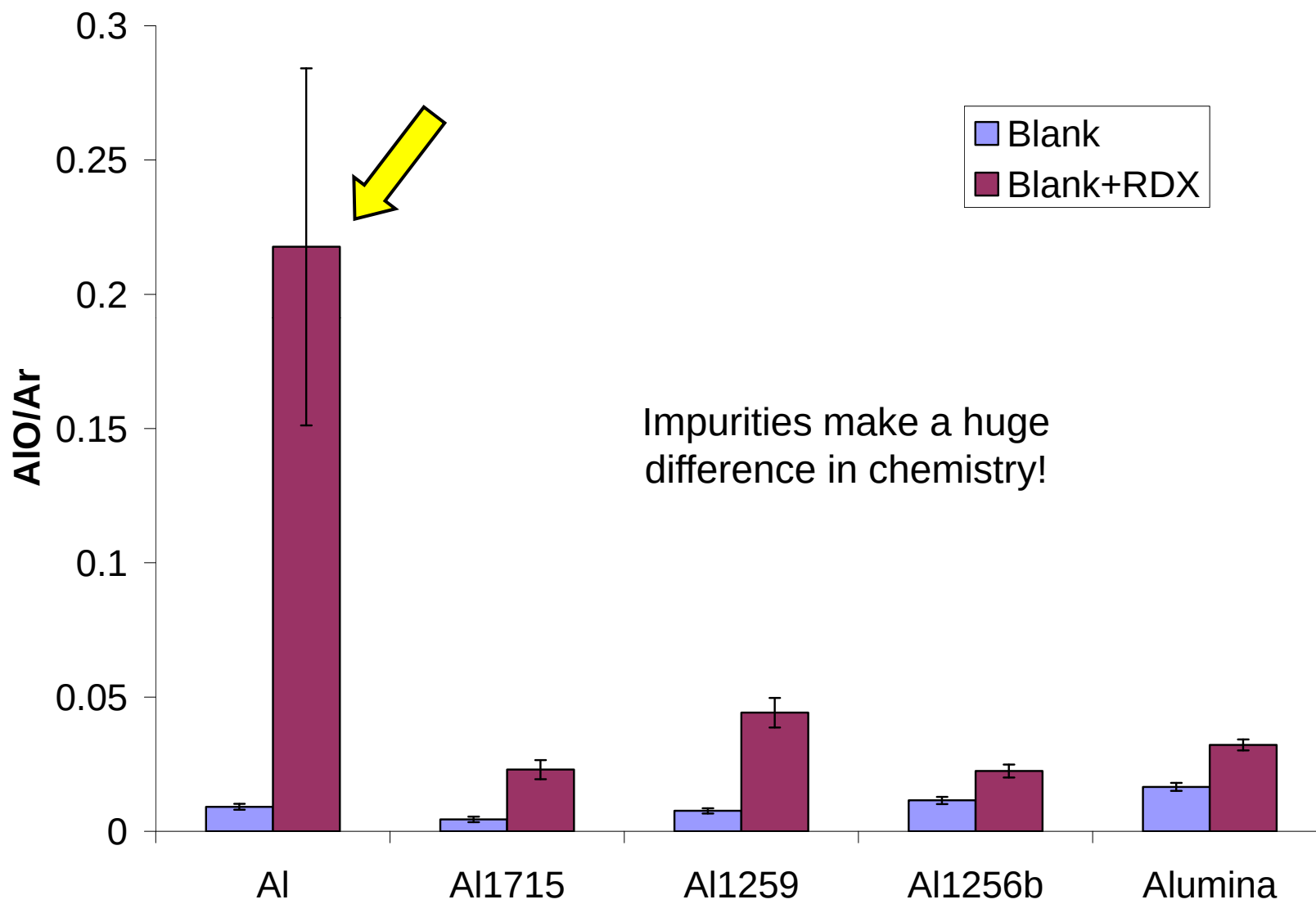
- high-purity aluminum (99.999%), copper (99.999%), nickel (99.98%), tin (99.998%) and titanium (99.998%)
- numerous metal alloys including brass, lead and steel

Differences in the spectra were observed based on trace element additives and impurities

- **Alumina (Al_2O_3)**
- **NIST 1256b (82.99%)**
 - 9.362% Si (obs.), 3.478% Cu (obs.), 1.011% Zn (obs.)
 - <1% Fe, Mn, Ni, Sn, Sr, Ti (obs.)
 - <0.1% Cr, Mg, Pb, V (not obs.)
- **NIST 1259 (89.76%)**
 - 5.44% Zn (obs.), 2.48% Mg (obs.), 1.60% Cu (obs.), 0.025% Be (obs.)
 - <0.2% Cr, Fe, Mn, Ni, Si (not obs.)
- **NIST 1715 (94.58%)**
 - 4.474% Mg (obs.), 0.3753% Mn (obs.)
 - <0.1% Cr, Cu, Fe, Ni, Pb, Si, Sr, Ti, V, Zn (not obs.)
- **Aluminum (99.999%)**









Double pulse experiments

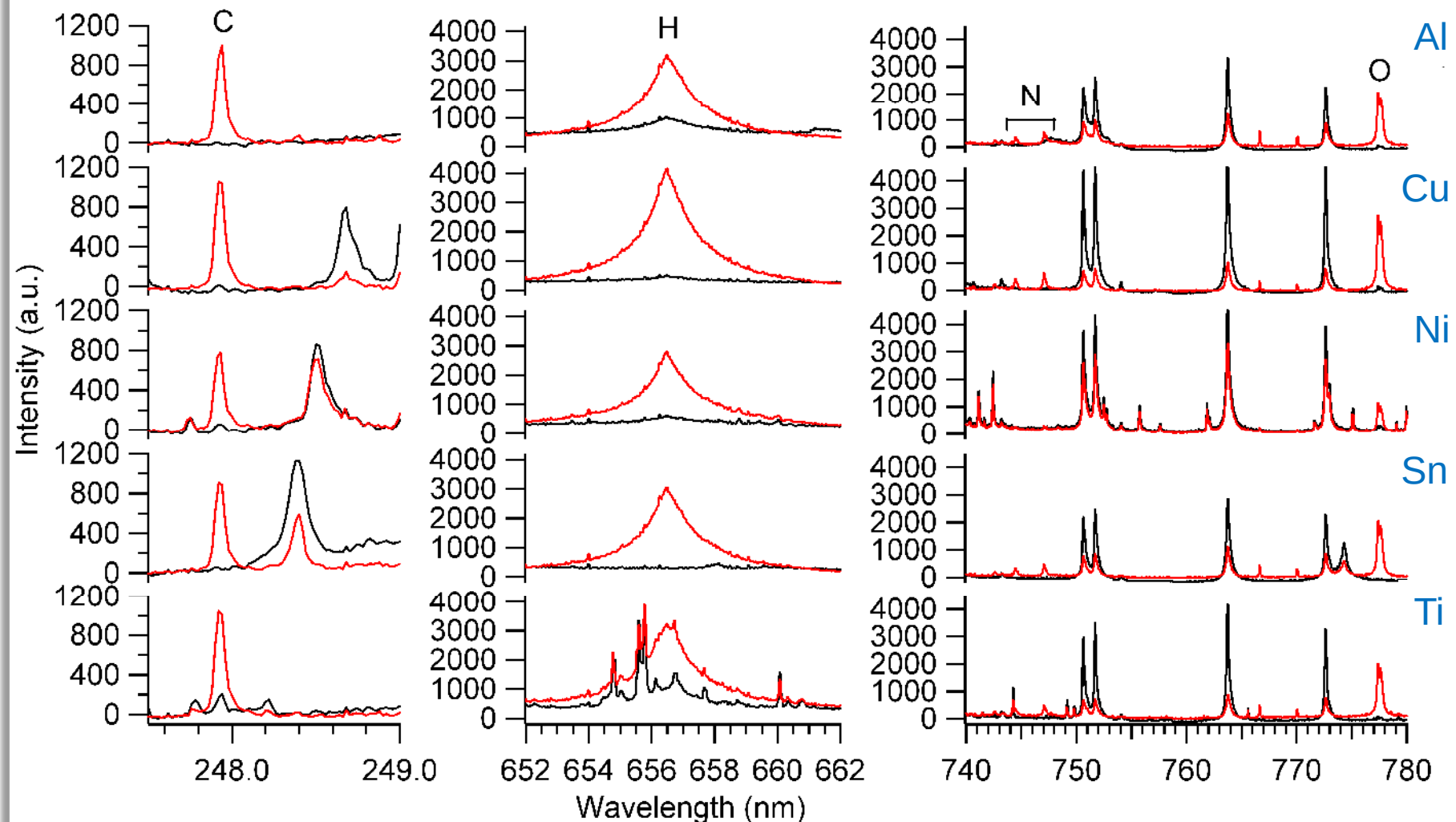


Double-pulse spectra acquired using a Continuum Surelite two-laser system w/echelle spectrograph (EMU-65 with an EMCCD camera)

- 420 mJ per laser, $\Delta t=2\mu\text{s}$, $t_{\text{delay}}=1.0\mu\text{s}$, $t_{\text{gate}}=50\mu\text{s}$

Spectra of 5 substrates with and without RDX residue were obtained in air and under an argon flow

- Al (99.999%), Cu (99.999%), Ni (99.98%), Sn (99.998%), and Ti (99.7%)





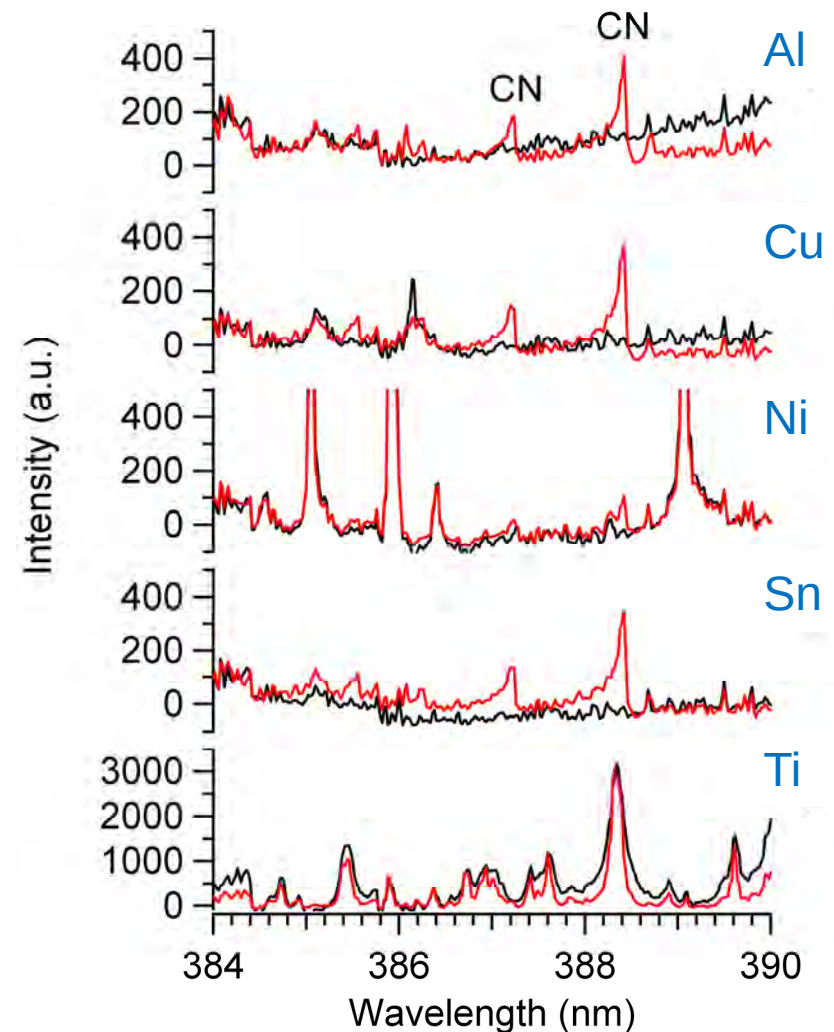
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Double pulse spectra (argon)



V.I. Babushok, F.C. DeLucia, P.J. Dagdigian, J.L. Gottfried et al., Kinetic modeling study of the laser-induced plasma plume of cyclotrimethylenetrinitramine (RDX), *Spectrochim. Acta, Part B*, **62B**, 1321-1328 (2007).

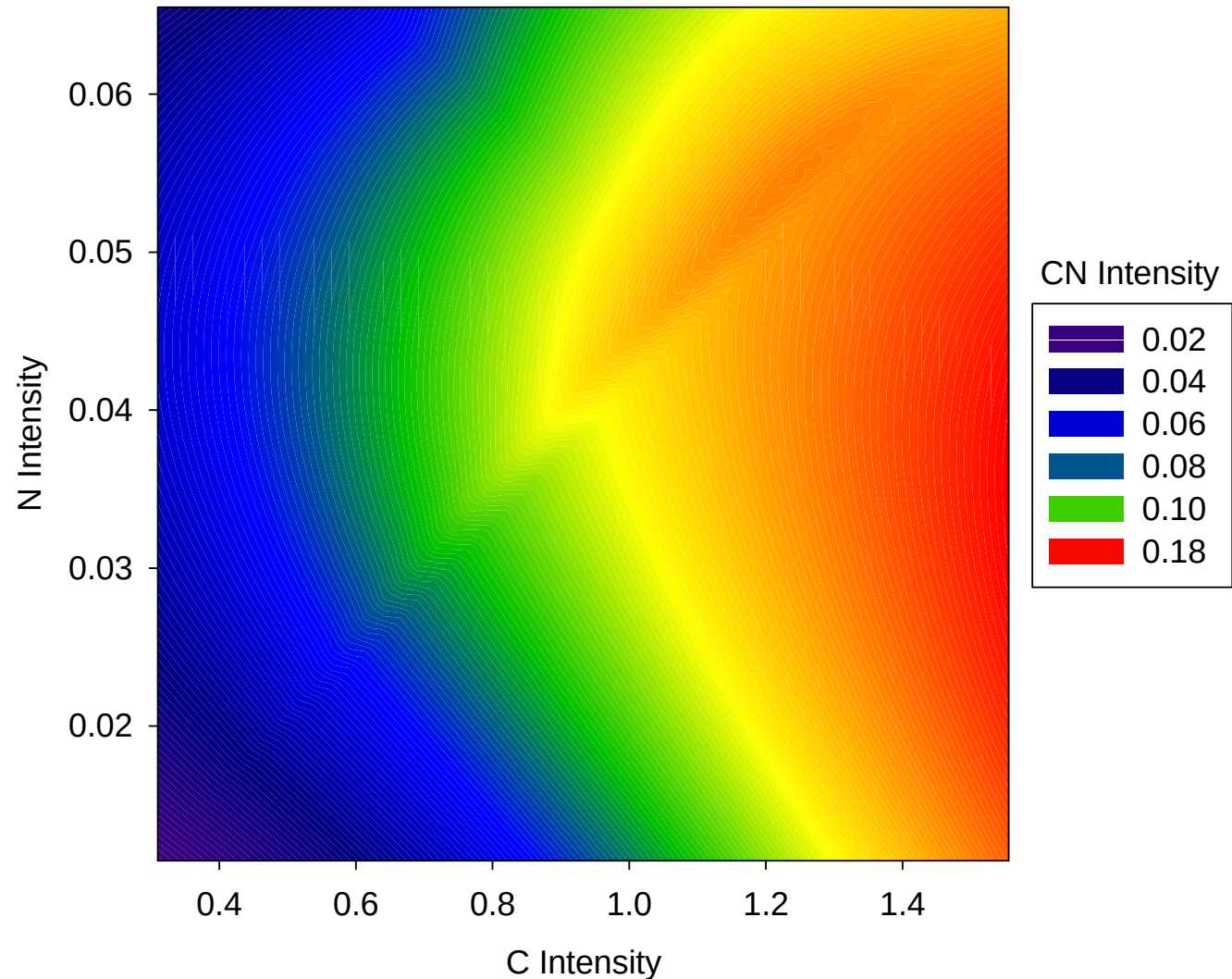
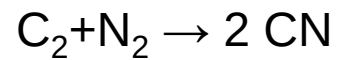
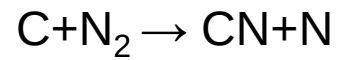
- the nitrogen must come from the explosive when under argon
- therefore the CN formation is indicative of the chemical reactions the RDX undergoes in the plasma





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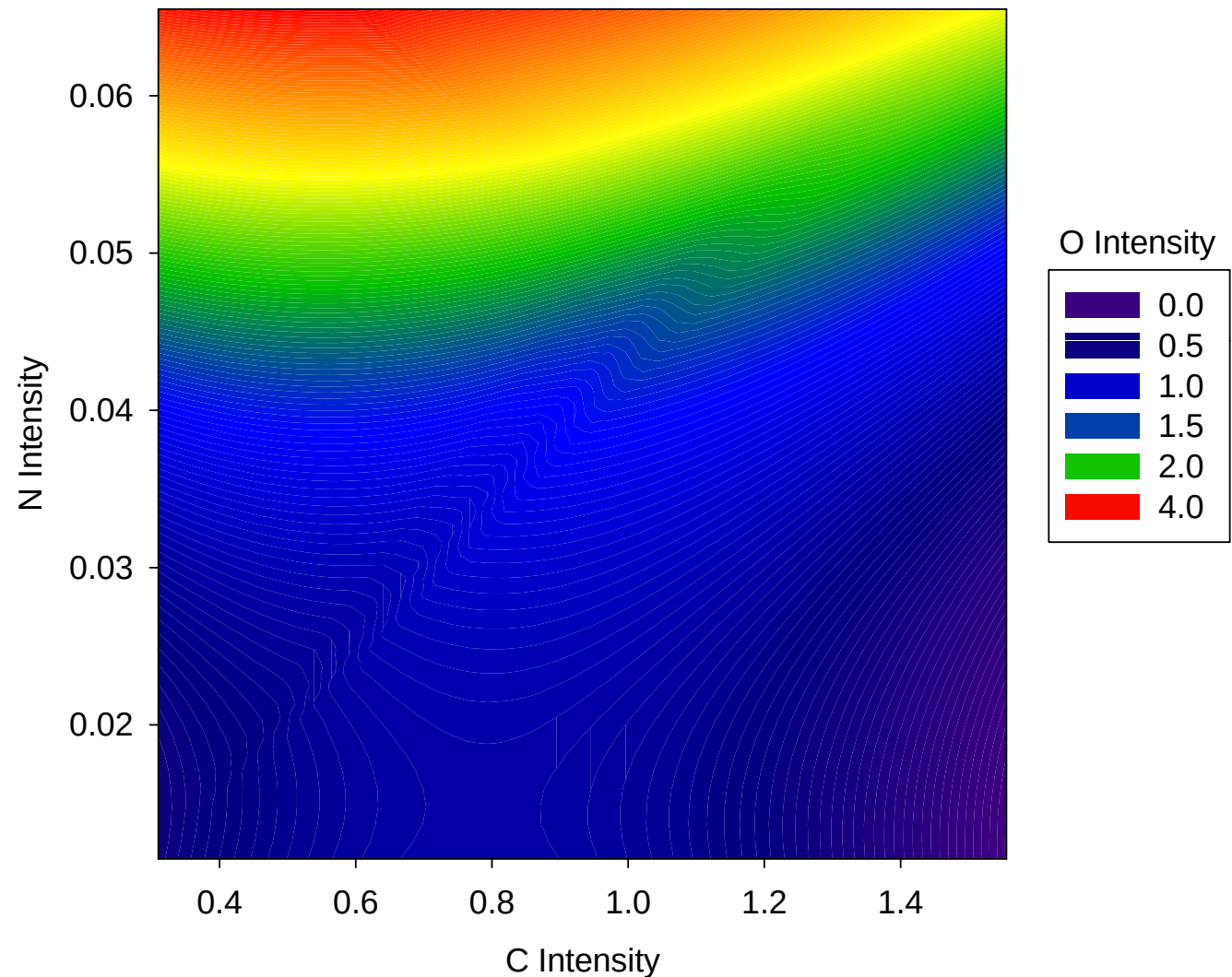
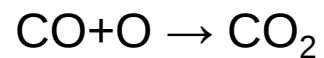
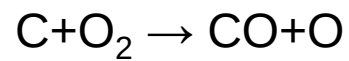
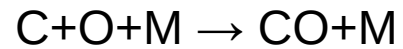
Double pulse results (argon)





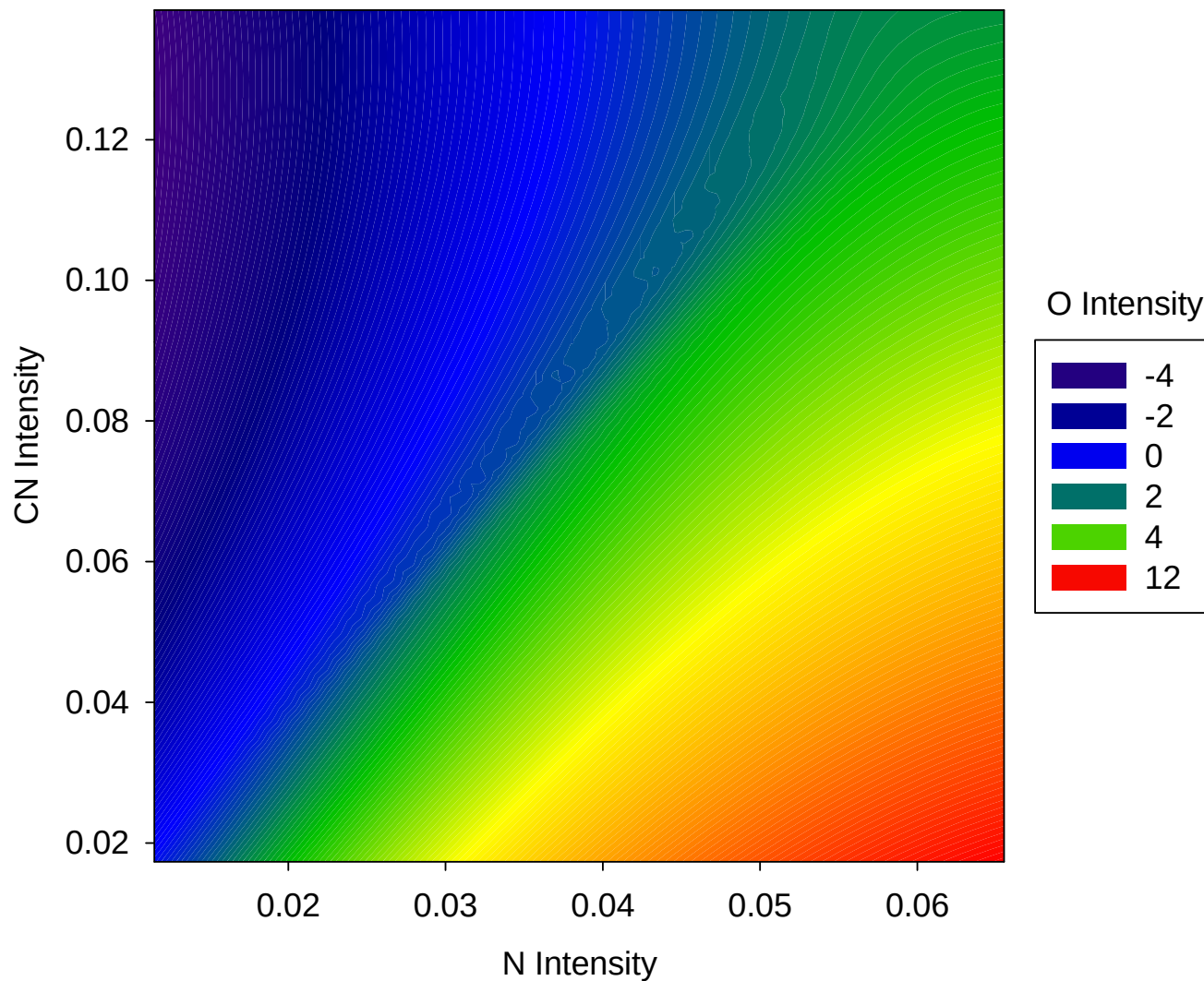
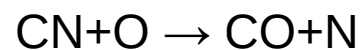
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Double pulse results (argon)





Double pulse results (argon)





Aluminum powder additive

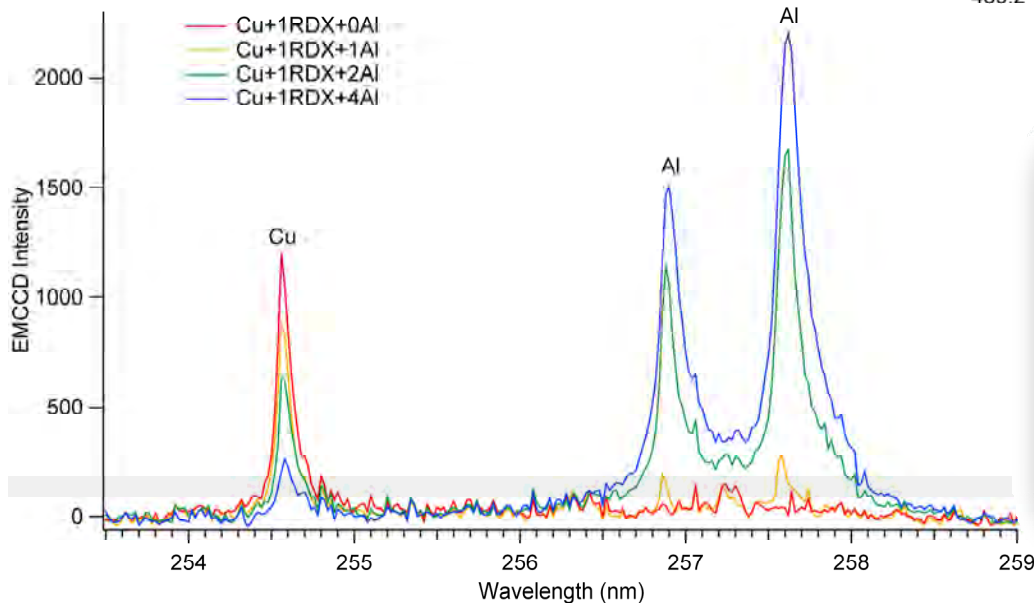
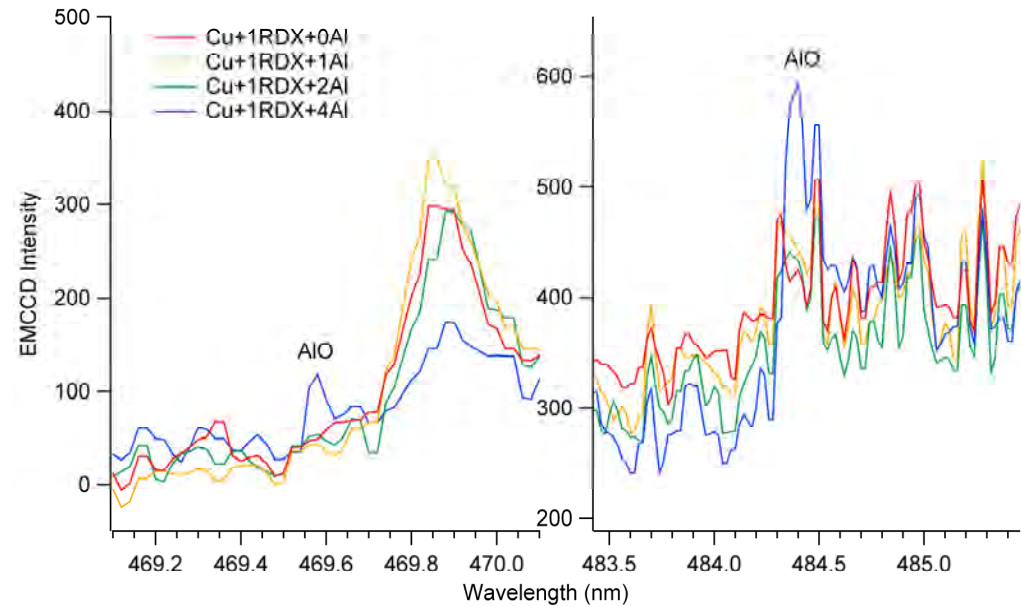
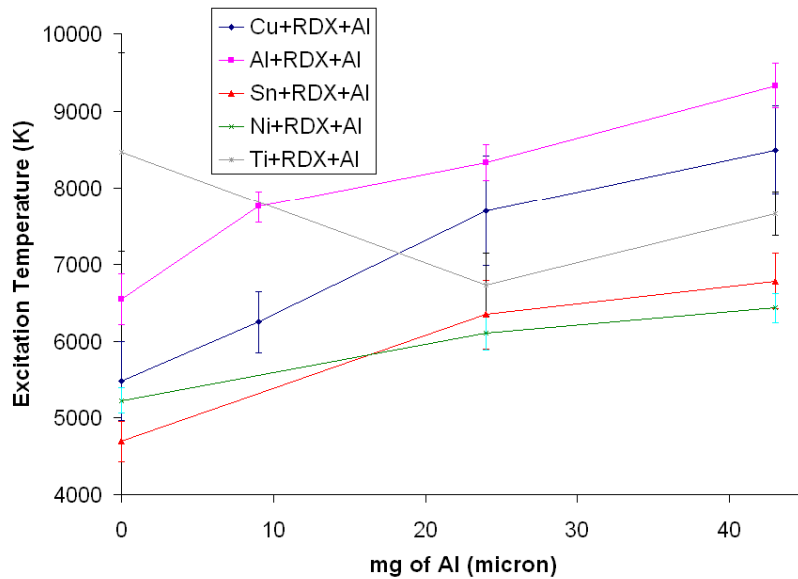


<75 μm Al powder mixed with RDX in varying concentrations

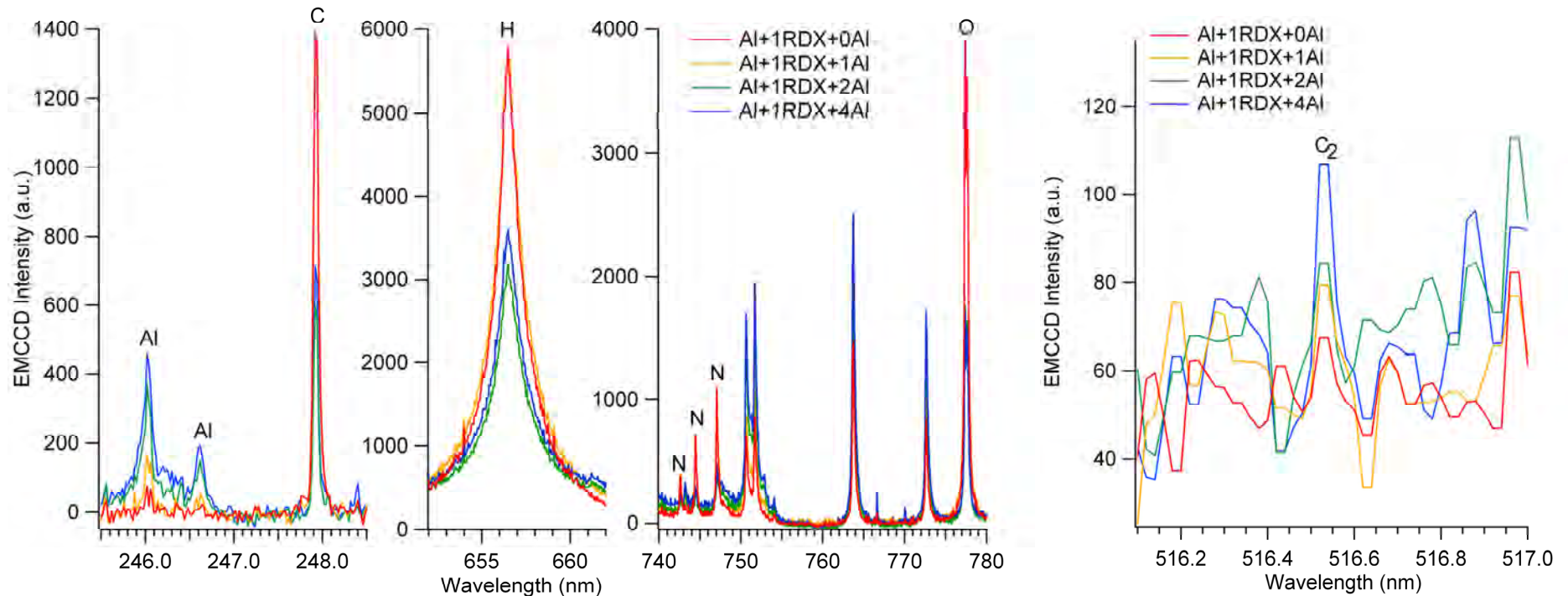
- 1:0, 1:1, 1:2, and 1:4 RDX to Al mixtures
- substrates: Al, Cu, Ni, Sn, and Ti
- double pulse laser system under argon

RDX/Al mixtures were crushed onto the substrate surfaces

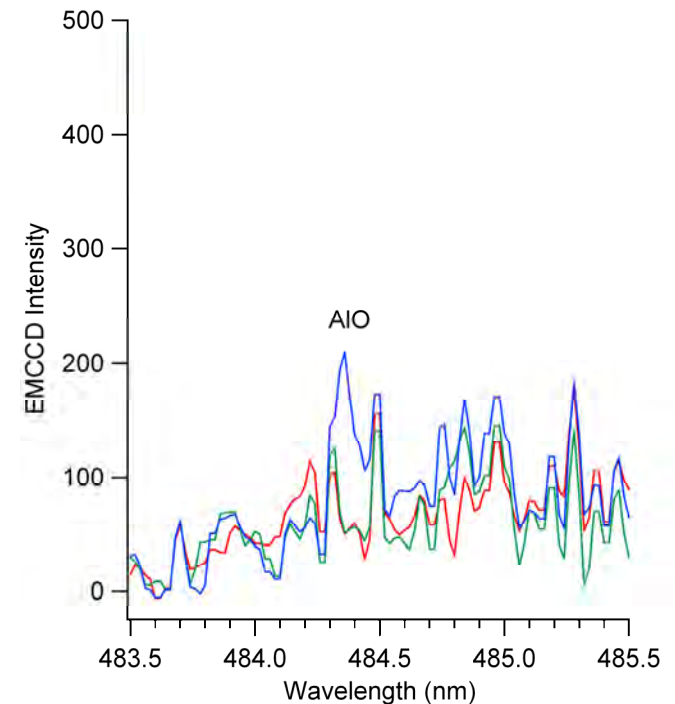
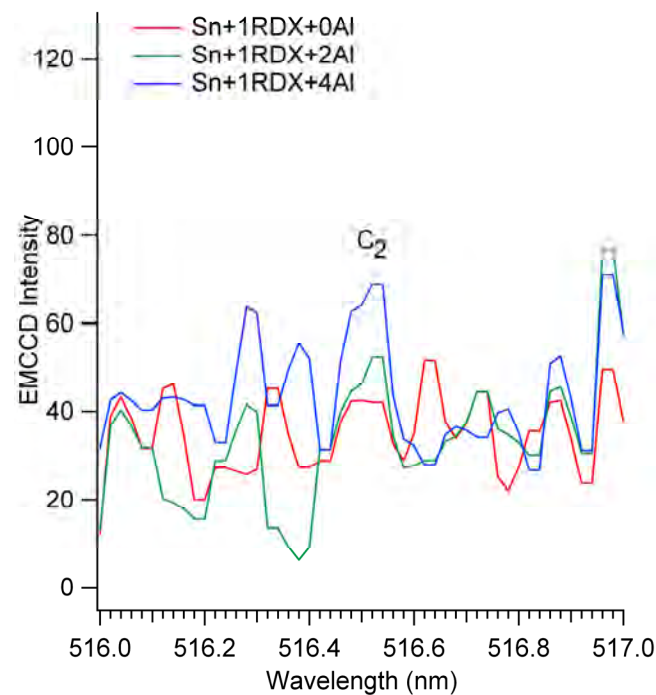
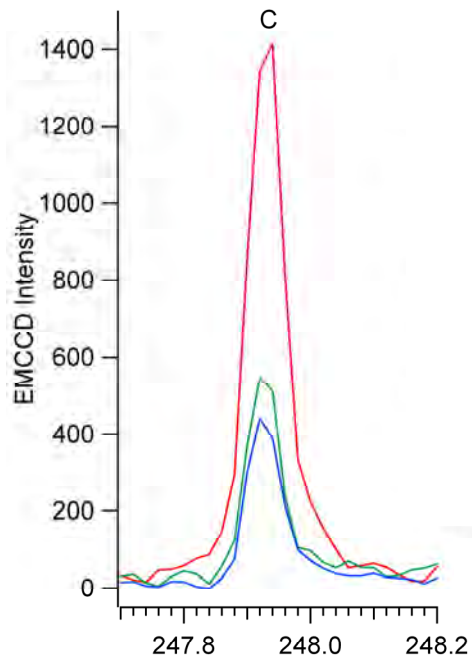
- each laser shot would blow off a significant amount of material
- 15 spectra of each sample were acquired



- increasing the Al:
 - $\uparrow T_{exc}$
 - $\downarrow$ substrate emission
 - $\uparrow$ Al emission
 - $\uparrow$ AlO emission



- increasing the Al:
 - ↓ C, H, N, O and CN emission (less RDX sampled?)
 - ↑ C₂ emission (O being scavenged by the Al, less CO and CO₂)



- same optical emission trends observed on all 5 substrates (Al, Cu, Ni, Sn, and Ti)
- ↑ C₂ and AlO confirms observations of Song et al.!
- decrease in atomic C is new information



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Classification of RDX on metals



PLS-DA model: 11 classes of pure metals with and without RDX

- RDX+(Al, Cu, Ni, Sn, Ti, Au, Mg, Zn, In, Ag) = 1 class
- Al, Cu, Ni, Sn, Ti, Au, Mg, Zn, In, Ag
- 20 latent variables

Test samples: additional spectra from each sample type

- 400 spectra in test set

Test samples: spectra acquired on metal alloys not in model

- 160 spectra in aluminum alloy test set
- 280 spectra in other metal alloy test set



Classification of RDX on metals



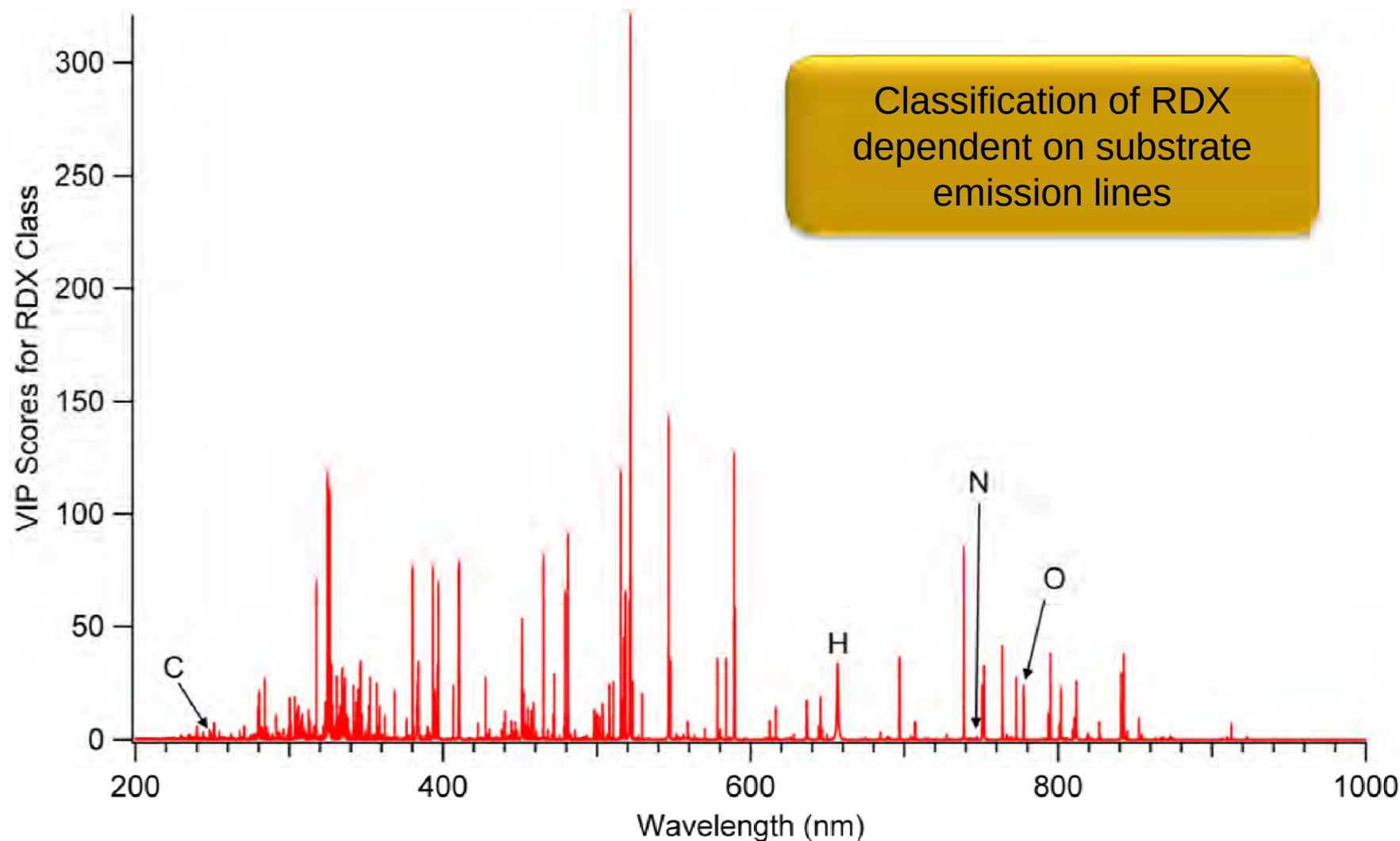
92.5% true positives, 2.5% false positives

	RDX	Ag	Al	Au	Cu	In	Mg	Ni	Sn	Ti	Zn
Al+RDX (35)	34	0	5	0	0	0	0	0	0	0	0
Cu+RDX (35)	35	0	0	0	1	0	0	0	0	0	0
Ni+RDX (35)	28	0	0	0	0	0	0	33	0	0	0
Sn+RDX (35)	31	0	0	1	0	0	3	0	0	0	0
Ti+RDX (35)	35	0	0	0	0	0	0	4	0	1	0
Au+RDX (5)	4	0	0	3	0	0	0	0	0	0	0
Mg+RDX (5)	5	0	0	0	0	0	4	0	0	0	0
Zn+RDX (5)	5	0	0	0	0	0	0	0	0	0	1
Ag+RDX (5)	5	0	0	0	0	0	0	0	0	0	0
In+RDX (5)	3	0	0	0	0	3	0	0	0	0	0
Ag (5)	0	5	0	0	0	0	0	0	0	0	0
Al (35)	0	0	35	0	0	0	0	0	0	0	0
Au (5)	0	0	0	5	0	0	0	0	0	0	0
Cu (35)	0	0	0	0	35	0	0	0	0	0	0
In (5)	2	0	0	0	0	4	0	0	0	0	0
Mg (5)	1	0	0	0	0	0	5	0	0	0	0
Ni (35)	2	0	0	0	0	0	0	34	0	0	0
Sn (35)	0	1	0	0	0	0	0	0	35	0	0
Ti (35)	0	0	0	0	0	0	0	0	0	35	0
Zn (5)	0	0	0	0	0	0	0	0	0	0	5



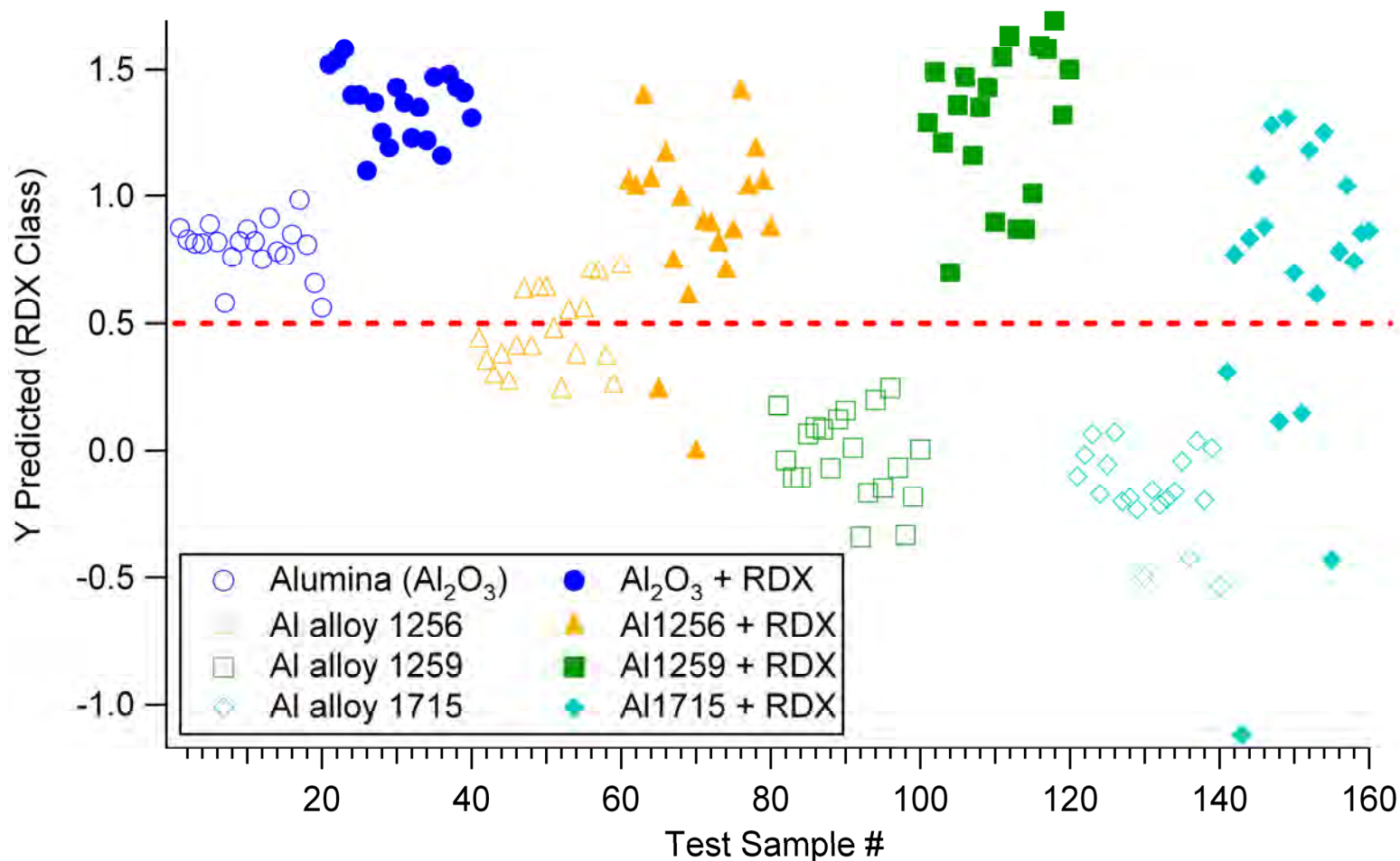
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Classification of RDX on metals



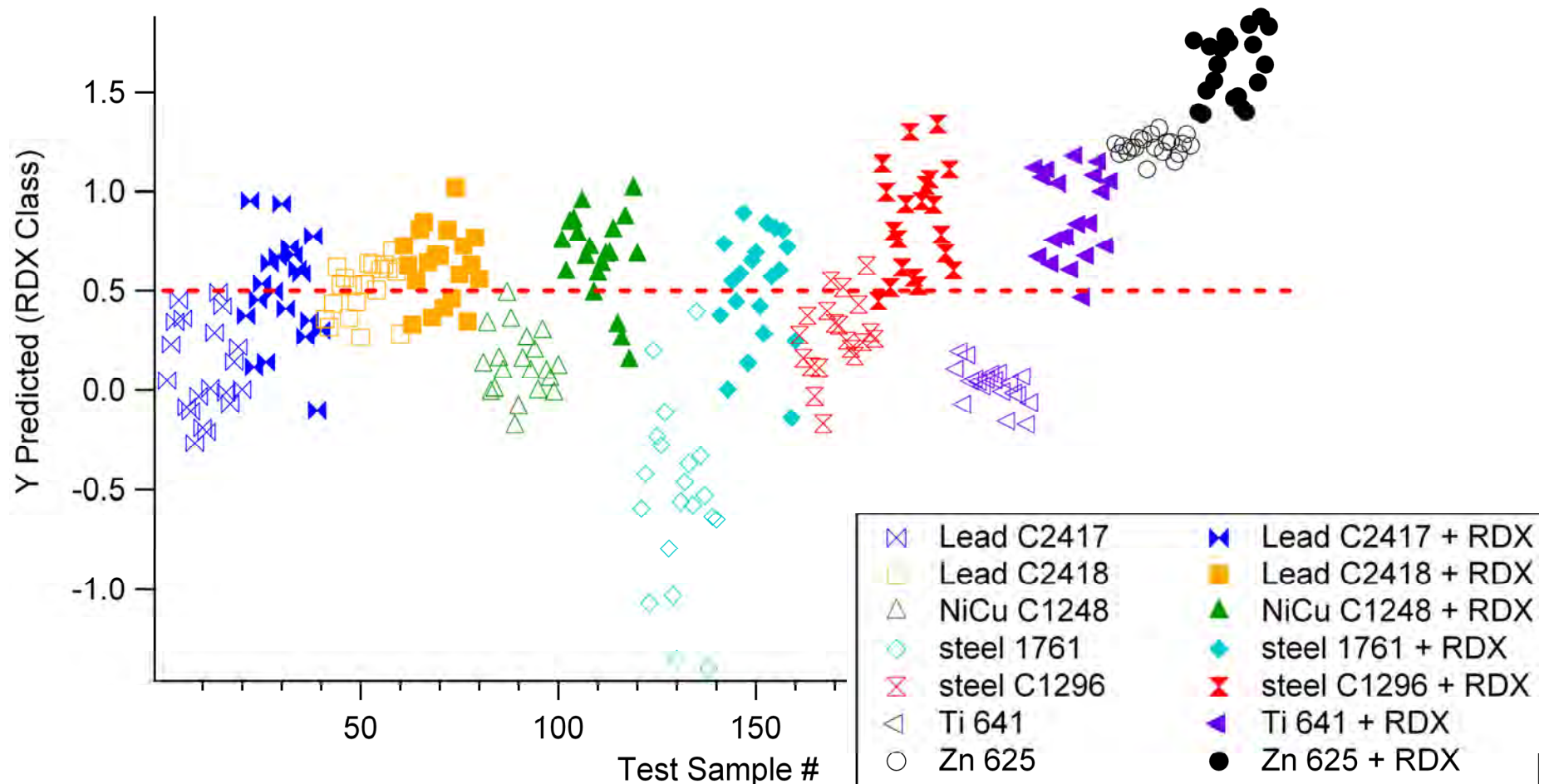


Classification of RDX on Al alloys (not in model)





Classification of RDX on other alloys (not in model)



Time-resolved, broadband emission of chemical species involved in the reaction of RDX and Al were observed

Confirmed observations of Song et al. using the new experimental methodology

- plasma chemistry vs. shock tube detonation

Compared pure metal vs. alloys

- trace metals do affect chemistry, so broadband emission detection is extremely important

Demonstrated that laser pulse energy affects chemistry

- related to size of laser ablated particles

Despite differences in the plasma chemistry, RDX residue on different metal substrates can be correctly classified with PLS-DA