SciAps
ANALYZE YOUR WORLD

Development of a Handheld LIBS Instrument for Alloy Analysis

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Overview

- Background…. Why are we doing this?
- Design goals and tradeoffs
- Subsystem selection
- Cramming it all together
- Early results

Why try to build a handheld LIBS instrument?

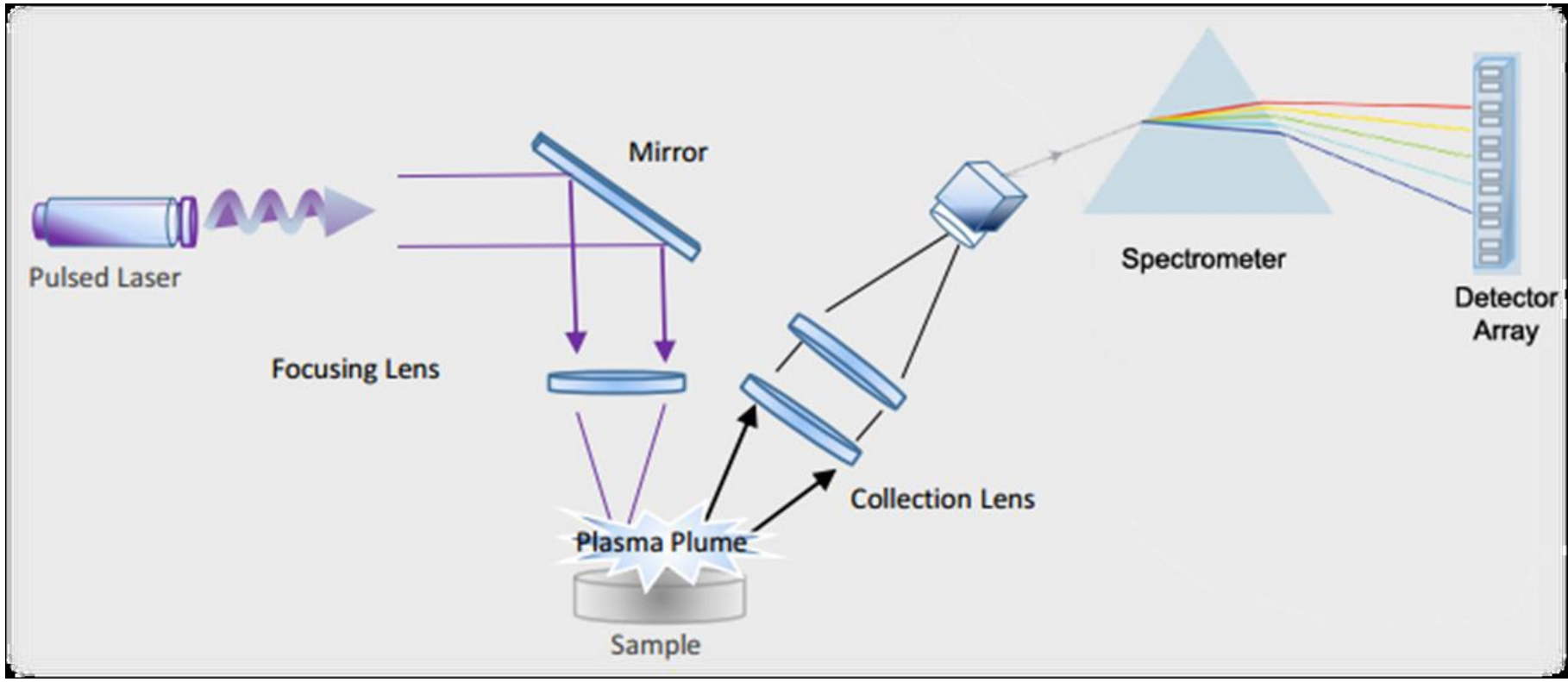
- Currently there are two technologies for Positive Materials Identification (measuring elemental chemistry of alloys).
- Handheld XRF
  - Very portable,
  - Fast, relatively easy to use
  - Good for transition metals and heavy metals
  - Cannot measure (or measures poorly) several elements Al, Mg, Si, C, Be, B, Na, Ca
  - Uses x-rays – safety and regulatory concerns
  - Analyzing welds is a challenge due to x-ray beam size
- Spark optical emission spectroscopy (OES),
  - Measures all elements including C, Al, Mg, Si, etc.
  - No x-rays
  - Not handheld, nor battery operated,
  - Large cylinders of compressed argon gas
  - Analyzing welds is difficult or impossible

The “Hope” of LIBS (Laser Induced Breakdown Spectroscopy)

- Eye-safe Laser instead of x-ray source,
- Analyzes all elements like OES,
- Handheld operation, like XRF
- Small beam (50 um) allows for targeting welds for analysis,
- Battery operated

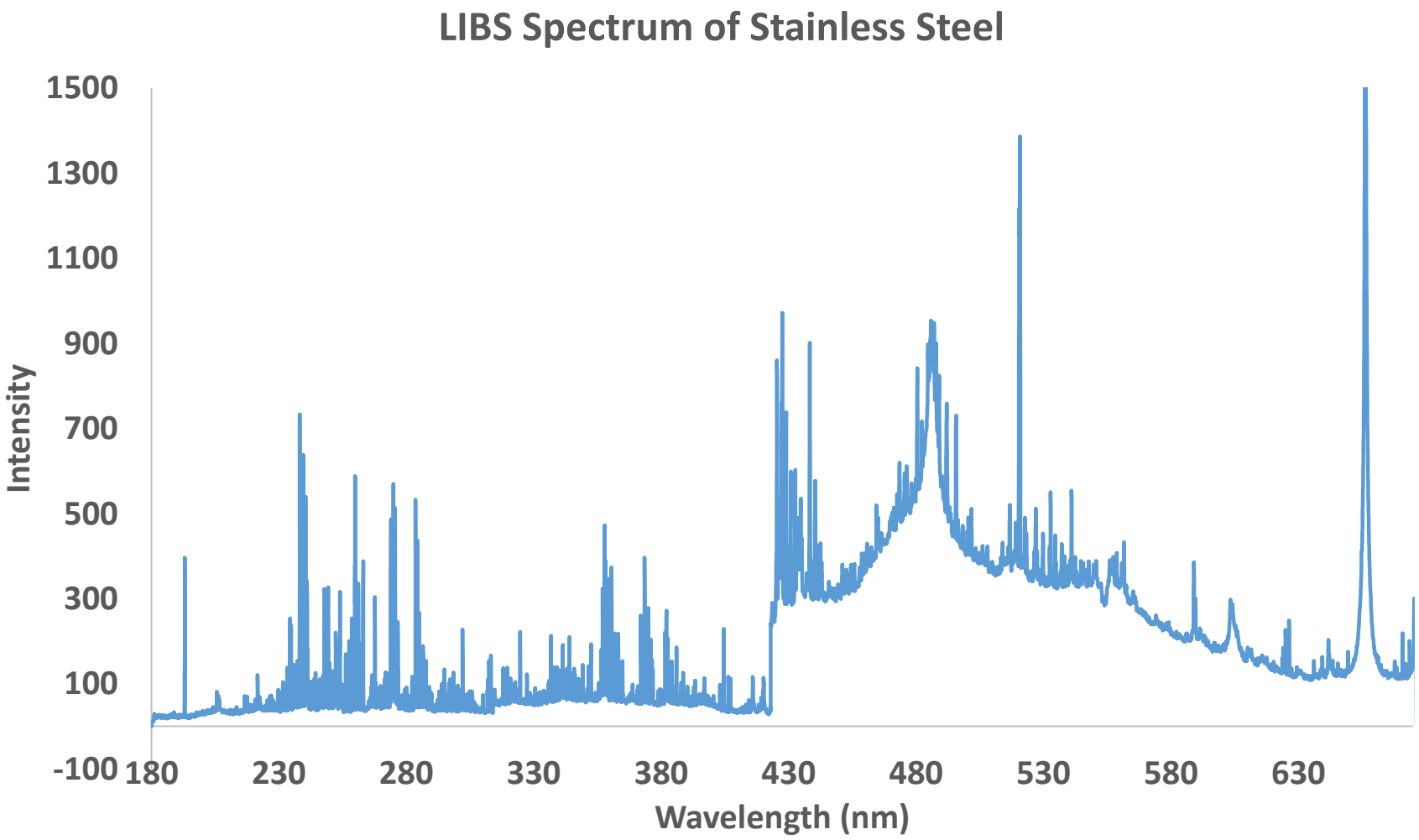
Laser Induced Breakdown Spectroscopy (LIBS!)

- **Similar to spark OES, but uses a laser to excite sample**
  - **SciAps utilizes an eyesafe Class 1M laser**
- **Our laser runs at 10 pulses/sec (10 Hz) and a single spectrum is collected for each laser pulse**
  - **Pulse energy is 4 mJ, unlike microLIBS which has pulse energy < 200 uJ**
  - **Running at a low rep rate allows for detector gating to ignore high background light that is emitted early in the plasma (continuum)**
- **Collection optics and CCD spectrometer for optical emissions**



LIBS Spectrum

- As electrons in plasma settle back to atomic orbitals, they emit characteristic photons,
- LIBS uses a diffraction grating, optics and CCD to determine wavelength of the photons to produce a spectrum,
- Some elements may only produce 1 or 2 visible peaks, while other elements may have 100's of peaks
- Good spectral resolution is important for finding interference-free peaks
- ScAps uses a stacked spectrometer design to cover the wavelength range 185-675 nm while maintaining good resolution (~0.07 nm FWHM at 200 nm)

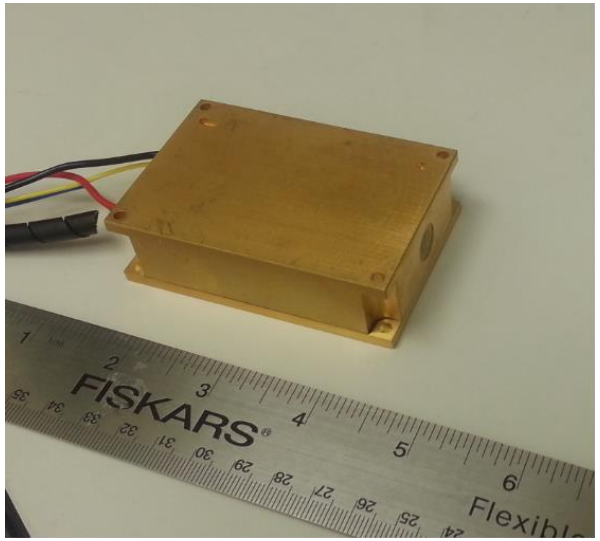


Design Challenges for a Handheld:

- High laser power per pulse,
  - Gigawatts of power density (energy/time/area),
  - 5 mJ energy, lasting 6 ns, spread over small area 2,500 um^2
  - Critical to create the plasma and produce more light. More light = better precision, lower limits of detection
- Wide range spectrometer with good resolution,
  - Need wide range for analyzing many elements,
  - Need good resolution to minimize the many interferences,
- Move the laser beam to multiple locations on the material quickly, average spectra from several laser pulses,
- High speed electronics to "gate" spectrum,
- Source of argon gas – no external tanks

Laser:

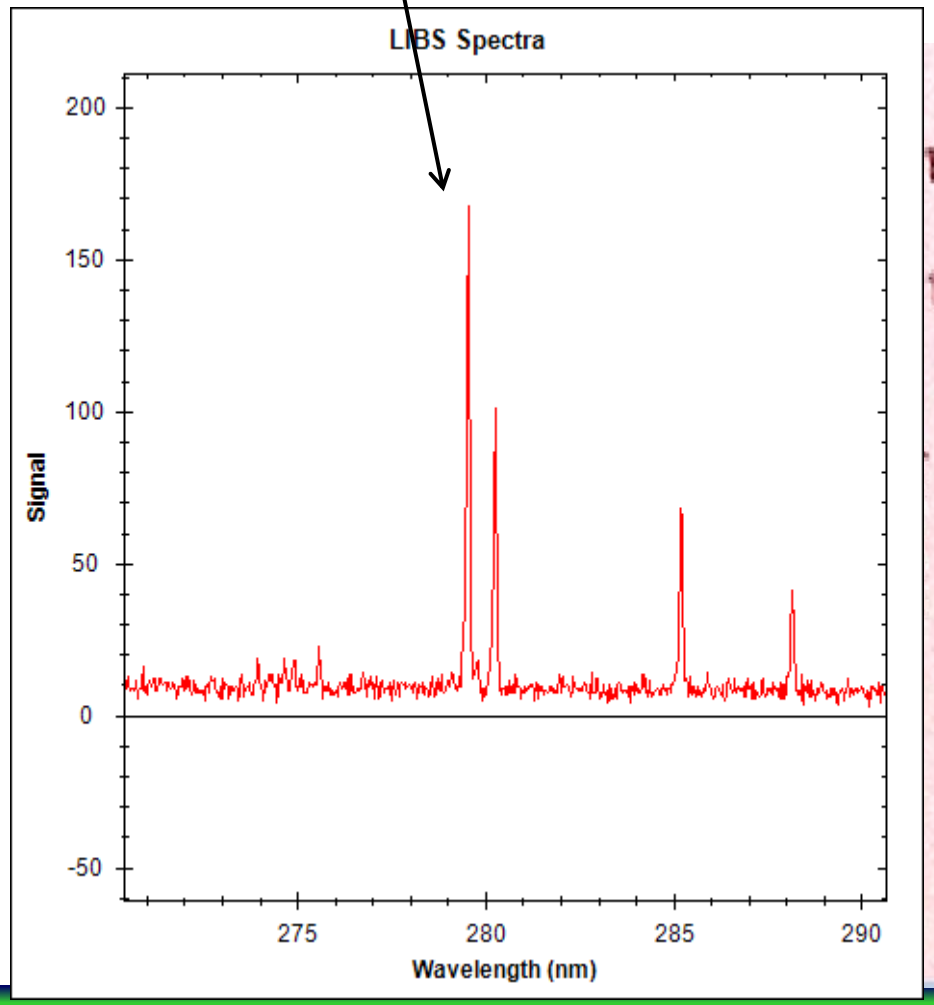
- Eye-safe, operates at 1532 nm,
- Rated Class 1M, regulated no differently than a laser pointer used for presentations,
- Developed for military for range finding on tanks and artillery,
- Laser is MilSpec 810g rated for shock, vibration.
- Originated for military applications – range finding for tanks, artillery.



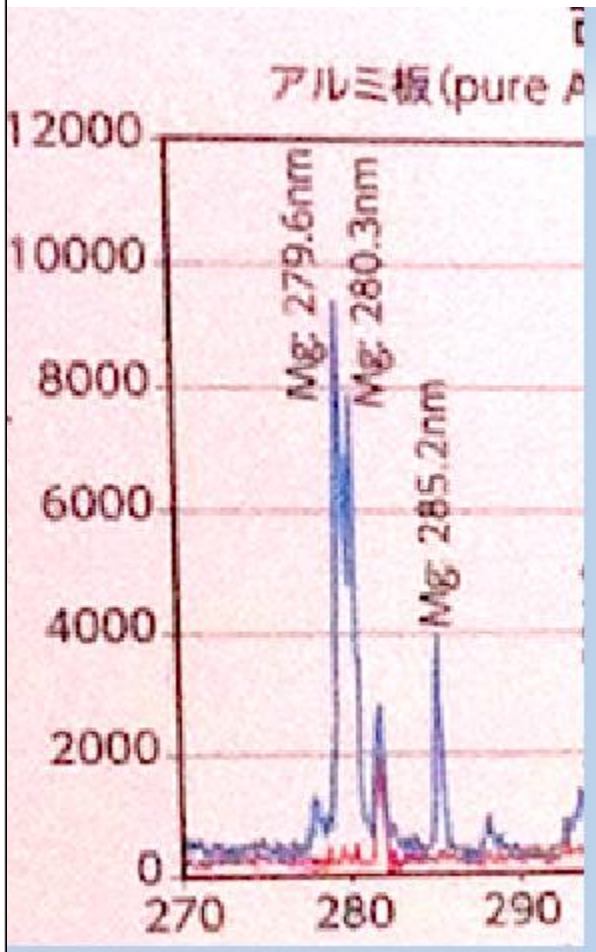
Spectrometer – Resolution Matters

- Complicated spectra, many interfering peaks (overlaps),
- Typical off the shelf small spectrometer engines offer 2000 to 3000 pixels:
- Enables high resolution over a short spectral range…. Or…
- Low resolution over a larger spectral range.

Mg lines at 279.6 nm and 280.3 nm on Z



Mg lines at 279.6 nm and 280.3 nm on a typical HH LIBS spectrometer



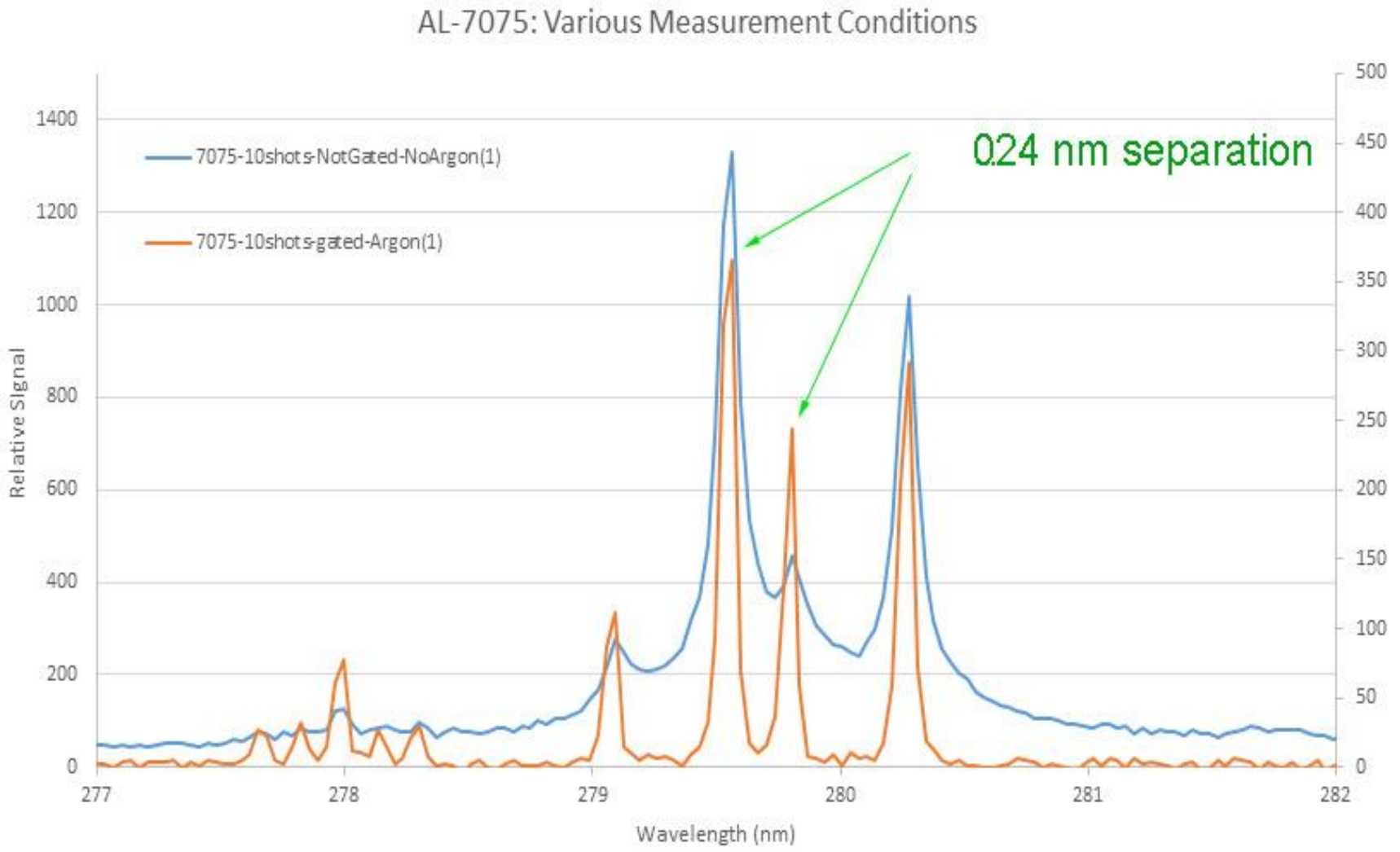
Another Key to Low Detection Limits: Gating

First usec of plasma is heat and radiation from electron collisions – no information,

After 1 us, atomic transitions dominate, producing peaks that reveal elements present,

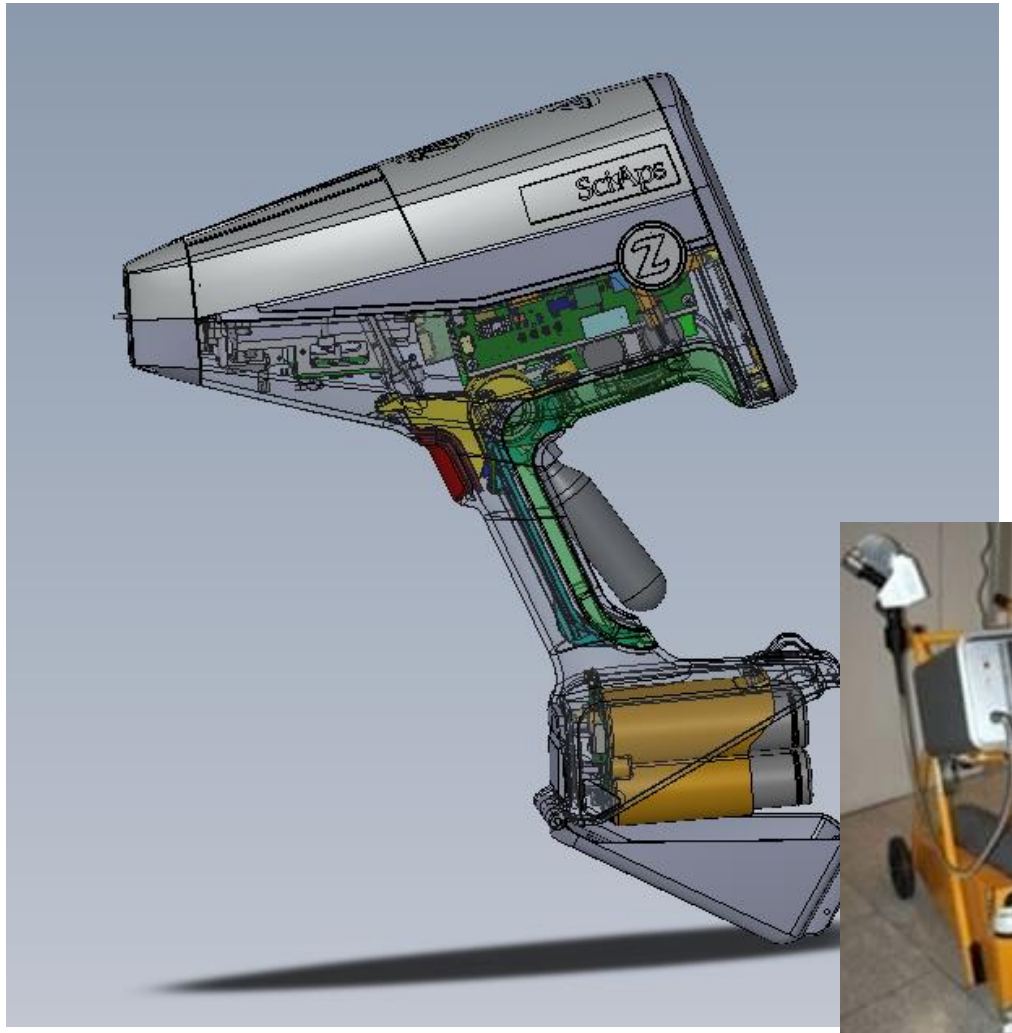
Time gate spectrometer --- wait for 1 us after laser fires, then measure the spectrum

Optimizes peak signals versus background.

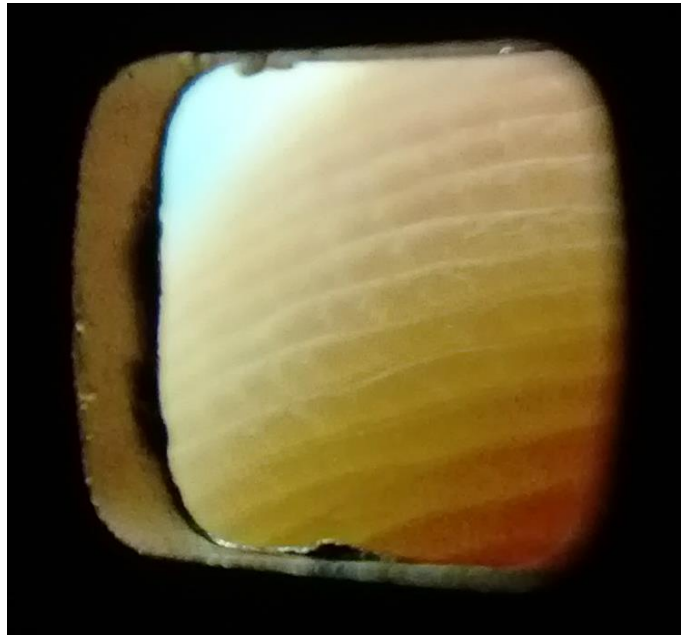


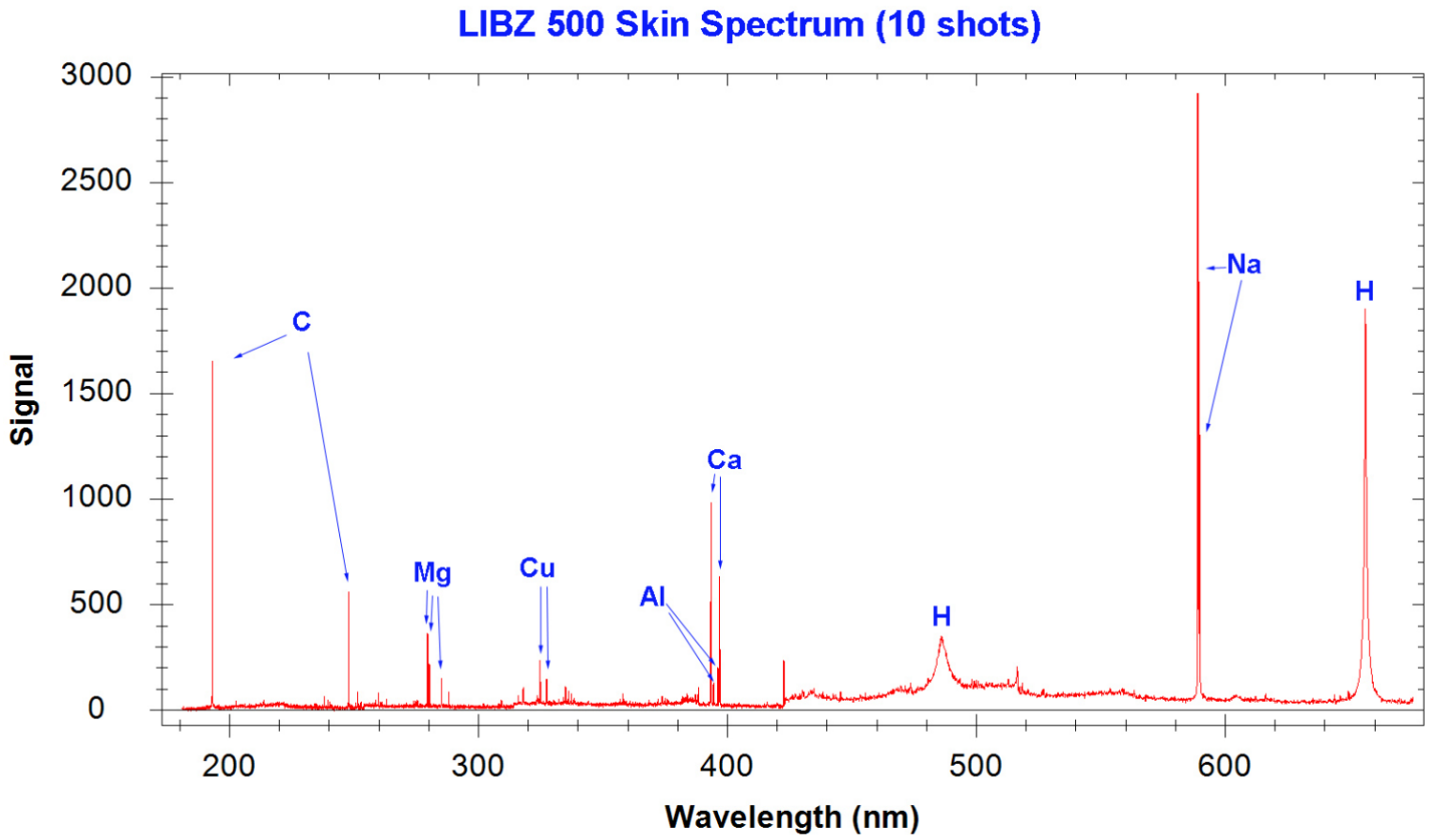
Argon Subsystem

- Argon
  - Replaceable Ar cylinder
  - Three stage regulator
  - High resolution SS pressure sensor.
  - Micro solenoid valve for precise Ar flow timing
- Why so little argon?
  - Analysis area and volume is very small (few mm^3),
  - Tests relatively fast – 5-6 s, argon turned on/off quickly.



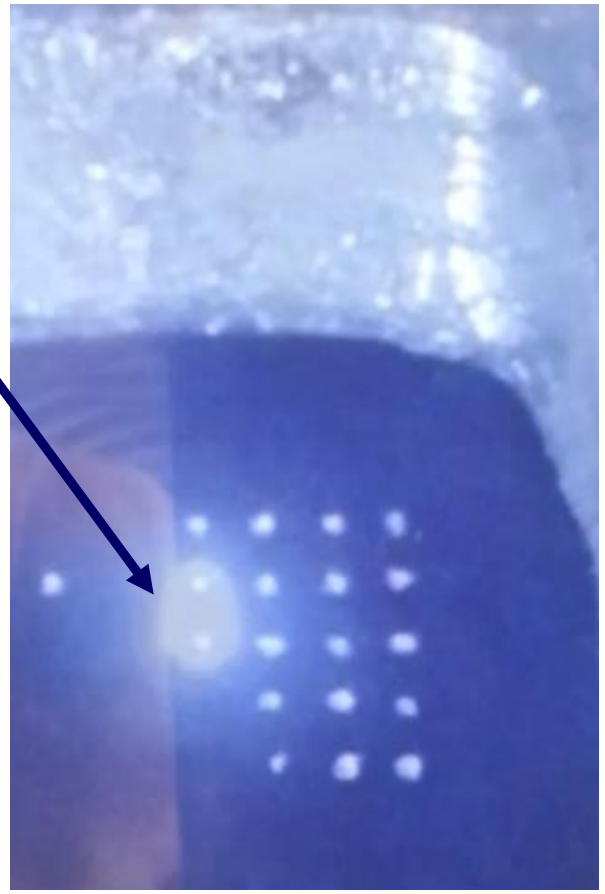
Argon purged and gated spectrum of a finger…



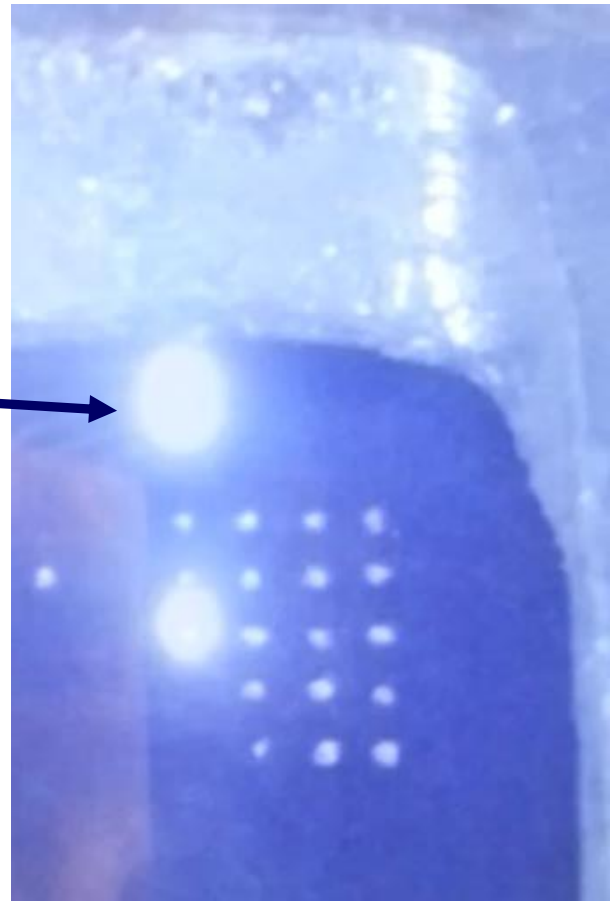


Rastering and Focus

Start of plasma on sample surface



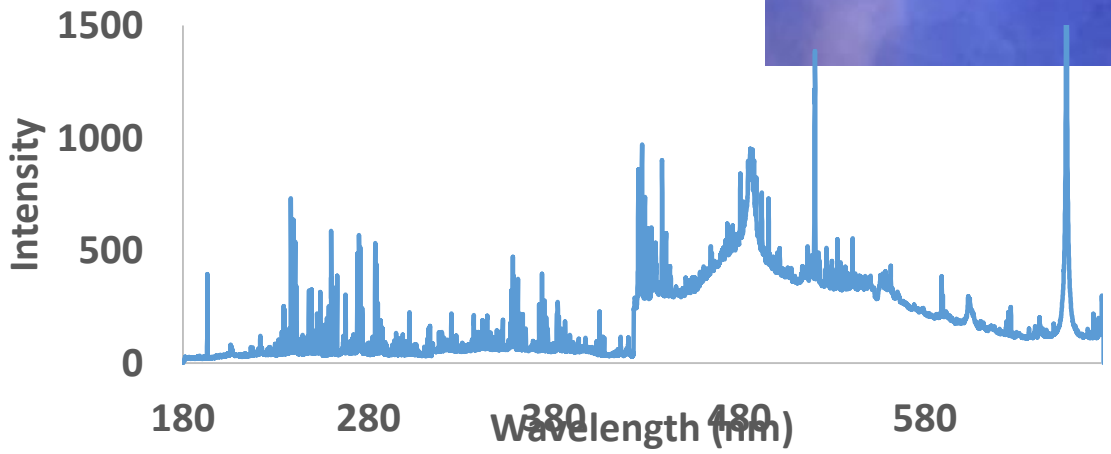
In the following video frame, a bright molten ball of metal can be seen flying away from the sample surface



UV window (a.k.a. Blast Shield) protects the optics

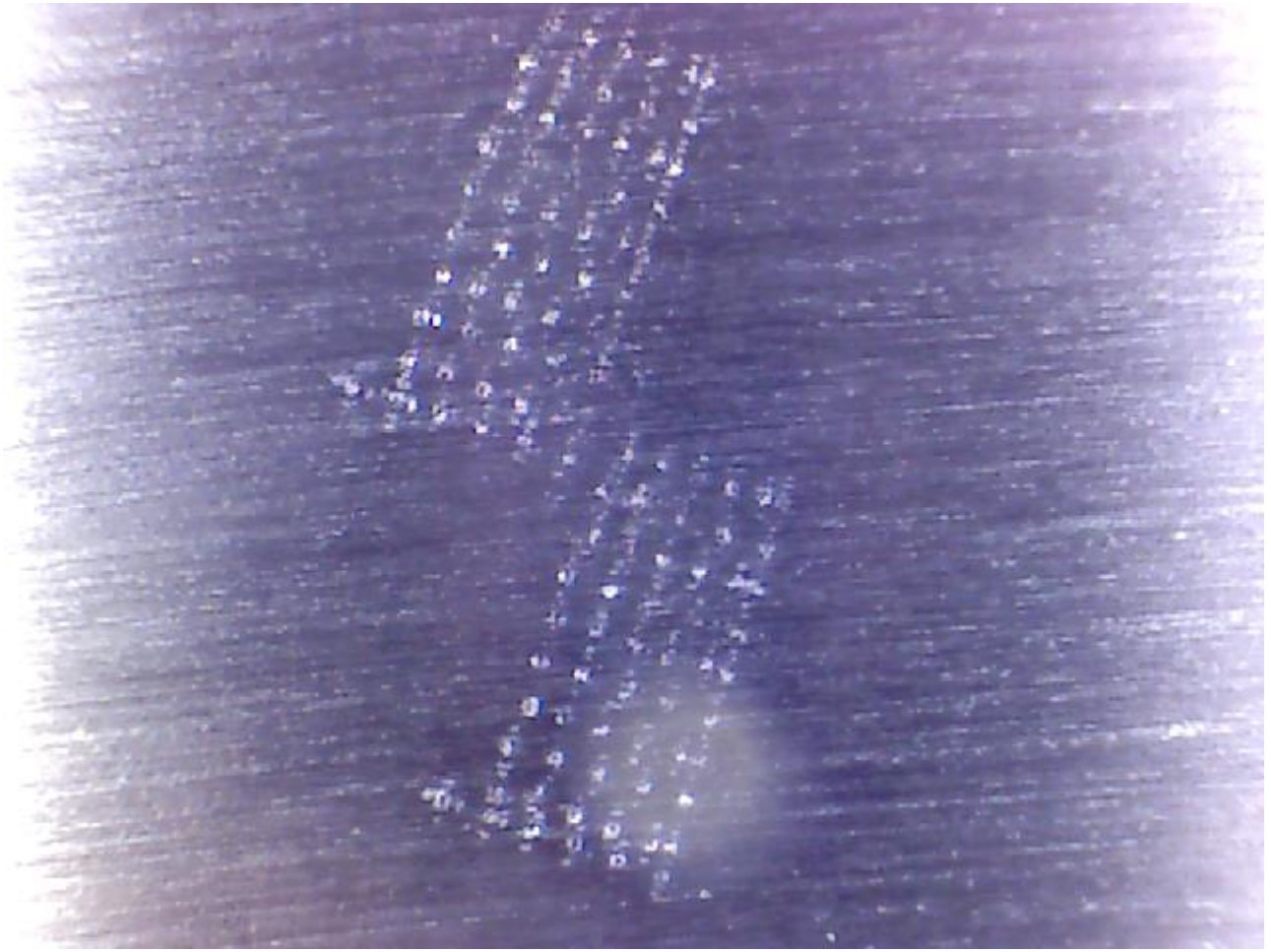
Putting it all Together

- Fire laser every 0.1 sec,
- Produce plasma on surface of sample,
- Measure spectrum at each point,
- Integrate peak intensities,
- Average the intensities,
- Move to next spot, fire laser again, etc.
- Move a distance of 250 um in 0.1 sec repeatedly

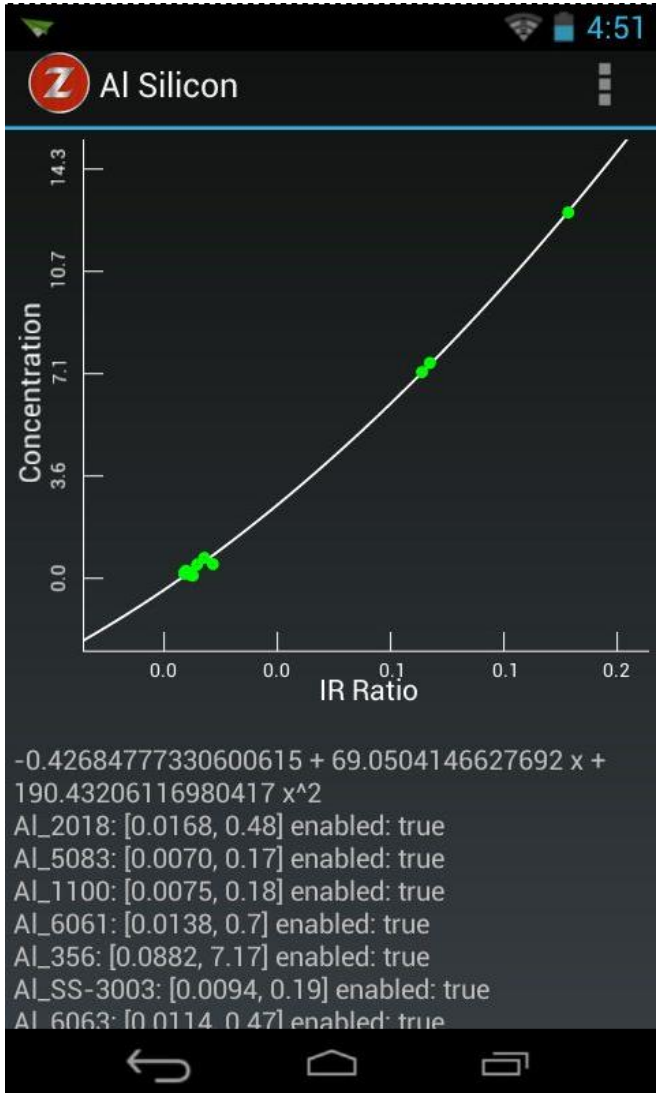


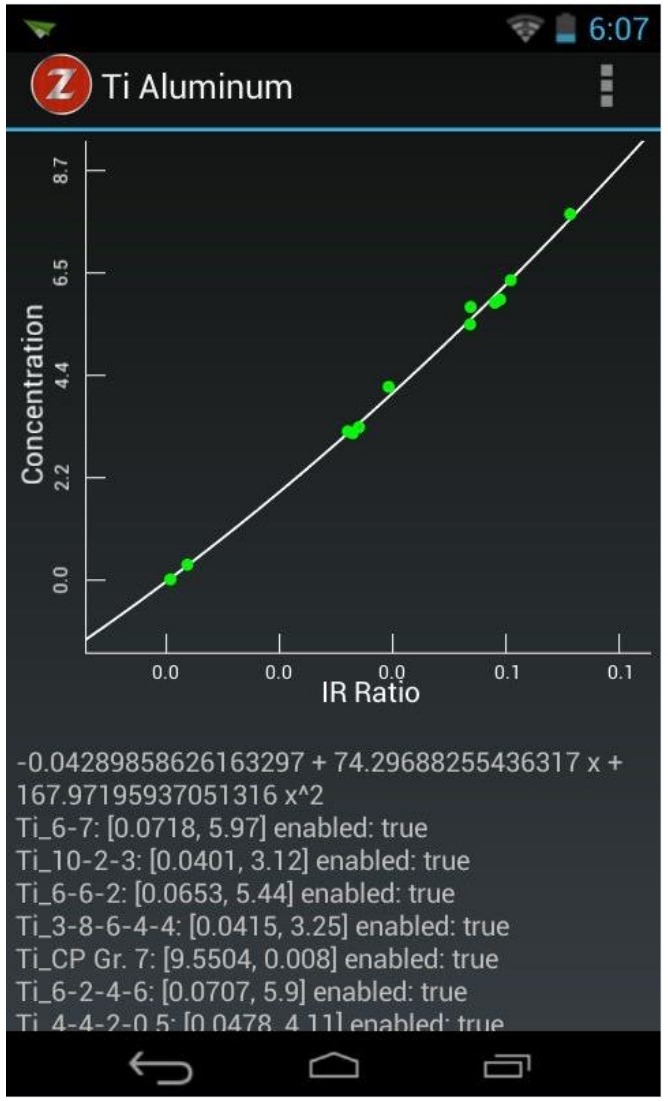
Metal Surface

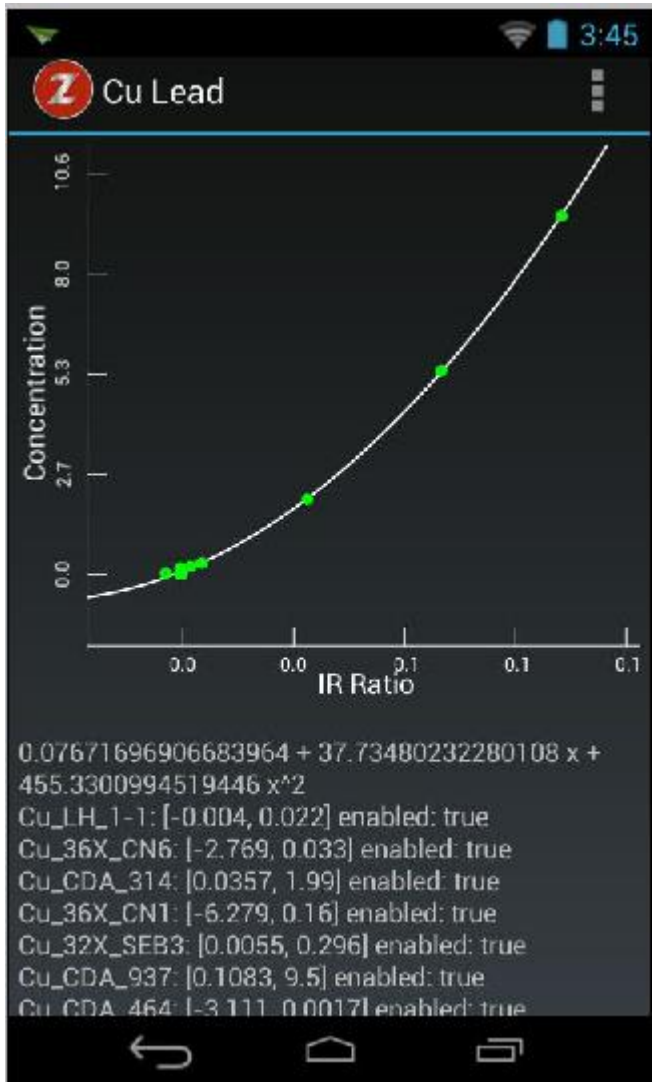
60 shot (6 sec) pattern produced on metal surface.
Magnification about 10x



Example Calibrations







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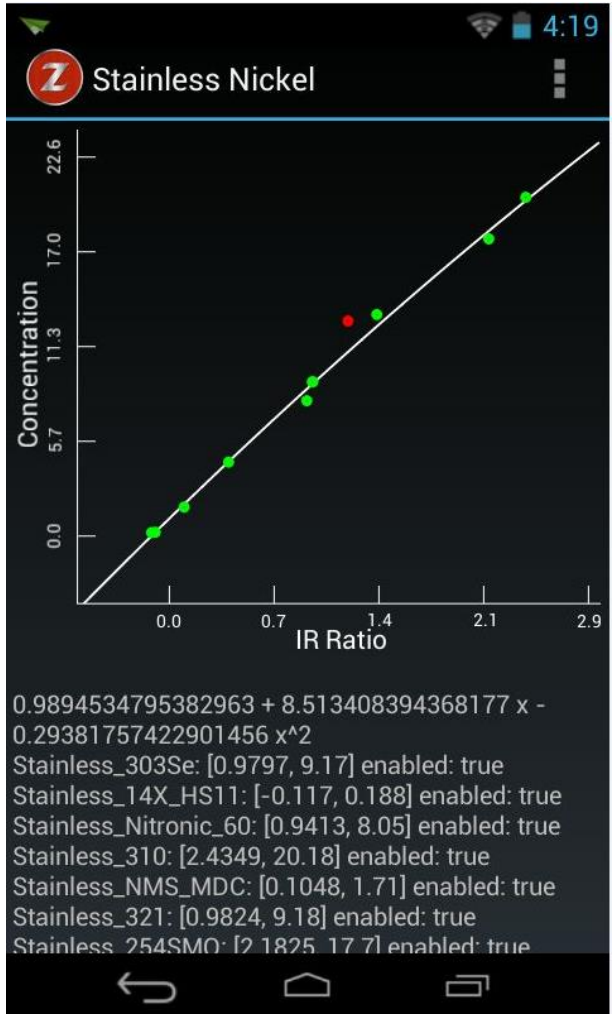
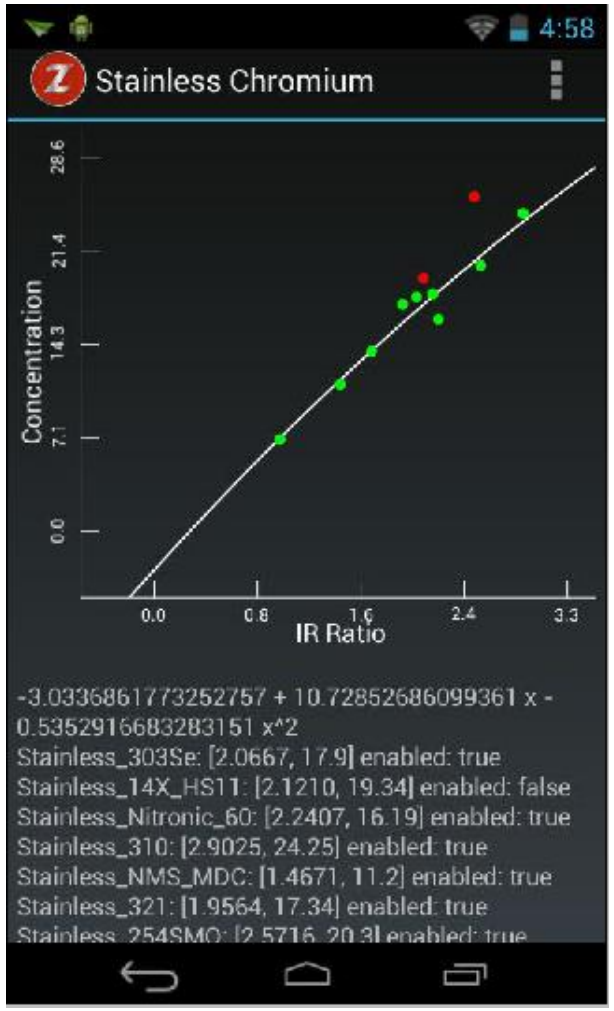

4:19
Stainless Nickel
Concentration
0.0
5.7
11.3
17.0
22.6
0.0
0.7
1.4
2.1
2.9
IR Ratio
0.9894534795382963 + 8.513408394368177 x - 0.29381757422901456 x^2
Stainless_303Se: [0.9797, 9.17] enabled: true
Stainless_14X_HS11: [-0.117, 0.188] enabled: true
Stainless_Nitronic_60: [0.9413, 8.05] enabled: true
Stainless_310: [2.4349, 20.18] enabled: true
Stainless_NMS_MDC: [0.1048, 1.71] enabled: true
Stainless_321: [0.9824, 9.18] enabled: true


4:58
Stainless Chromium
Concentration
0.0
7.1
14.3
21.4
28.6
0.0
0.8
1.6
2.4
3.3
IR Ratio
-3.0336861773252757 + 10.72852686099361 x - 0.5352916683283151 x^2
Stainless_303Se: [2.0667, 17.9] enabled: true
Stainless_14X_HS11: [2.1210, 19.34] enabled: false
Stainless_Nitronic_60: [2.2407, 16.19] enabled: true
Stainless_310: [2.9025, 24.25] enabled: true
Stainless_NMS_MDC: [1.4671, 11.2] enabled: true
Stainless_321: [1.9564, 17.34] enabled: true

Remaining Work

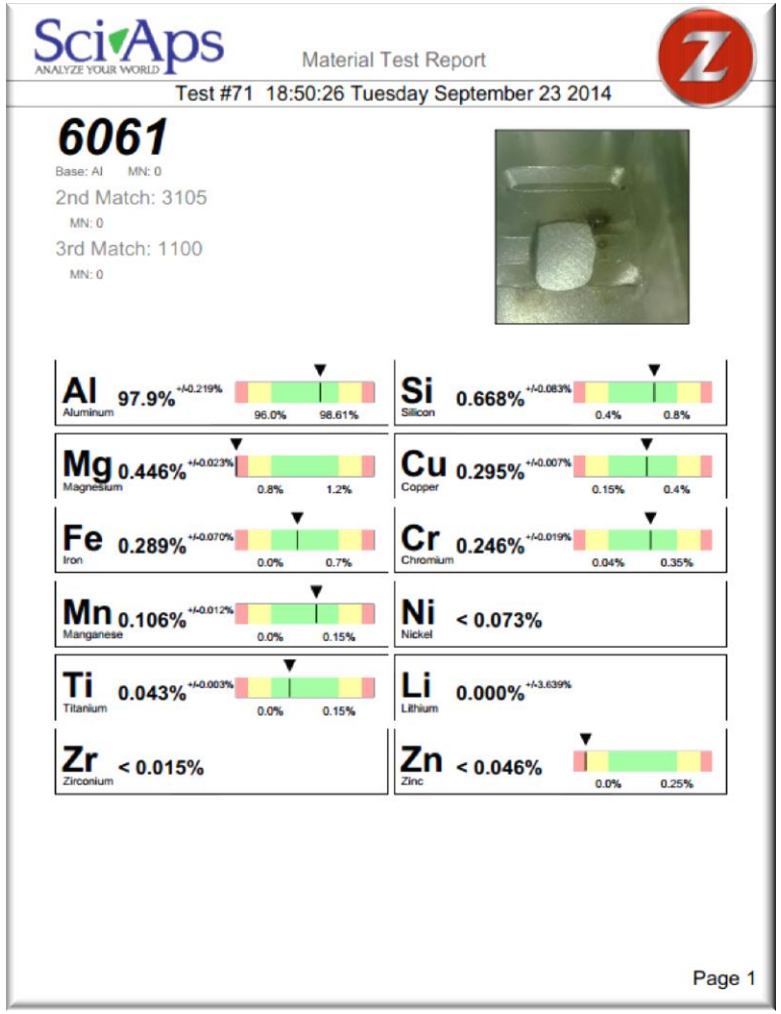
- Developing higher powered laser with better optics (10 mJ instead of 5).
  - Yields 10x more light due to improved laser quality (better focus),
- Improved limits of detection on refractory elements Nb, Mo, W, Ta especially,
- Just begun developing improved calibrations,
  - Understanding interferences, matrix effects for improved accuracy of calibrations,
- Improve carbon precision by 5X,

The End

Operating System and Connectivity

- After much head scratching we decided on the Android/Linux operating system
  - Many users are already familiar with it
  - Many built in canned features to make use of (including games!)
  - Utilize built in connectivity features:
    - “share” – reports, sample photos, (anything) via email
    - WiFi- easily connect to networks, download Apps, updates, etc.
    - Bluetooth – similar
    - GPS – location logging with sample
    - (no cellular network connection yet)

Email a Report via Android “Share”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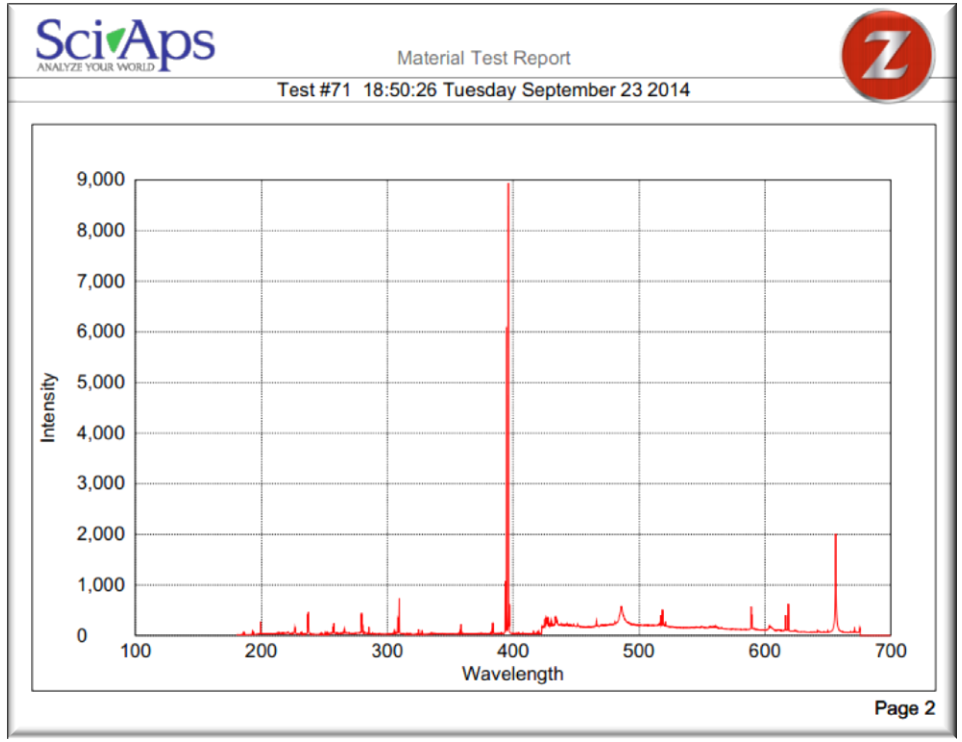
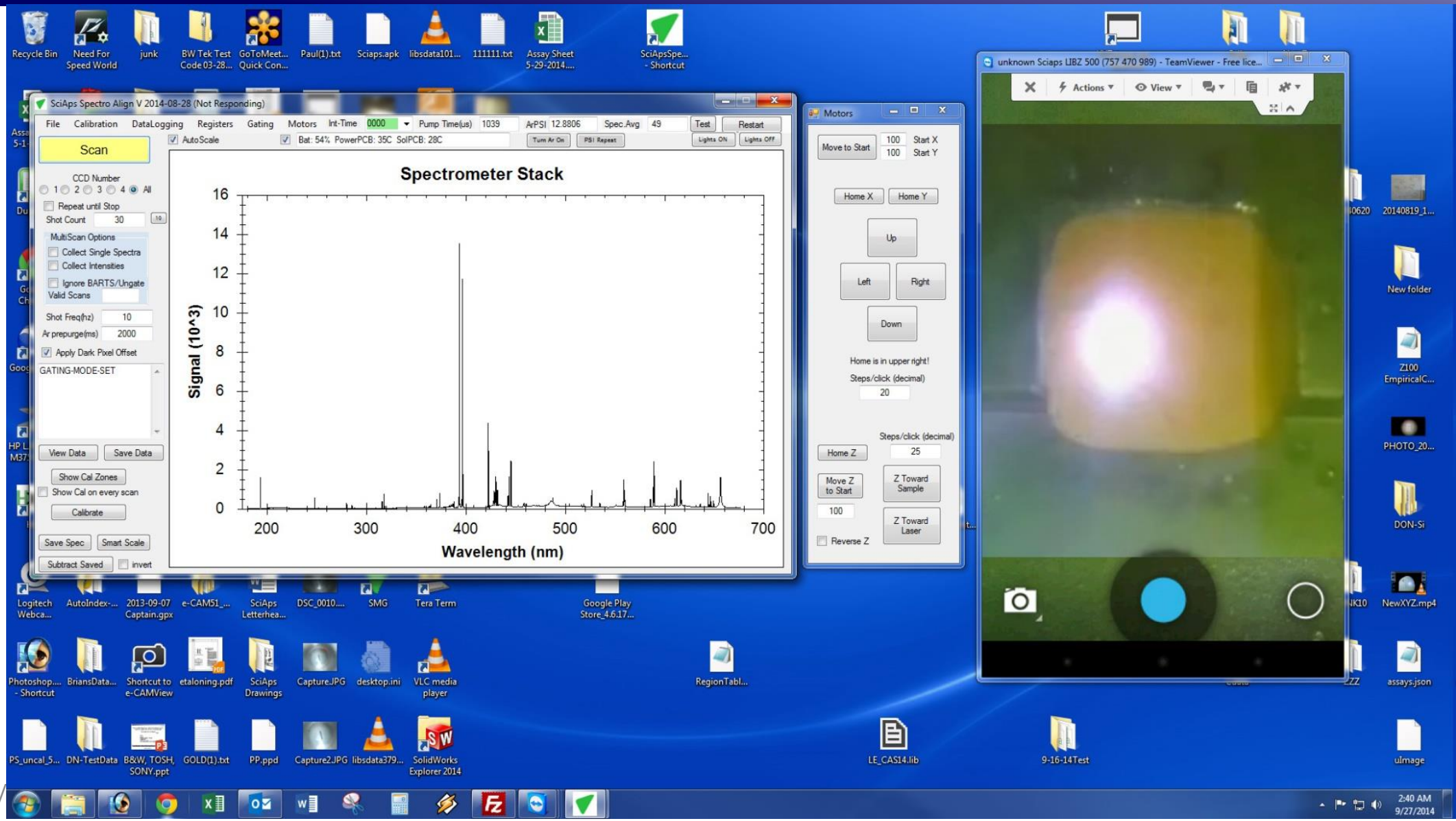
Material Test Report
Test #71 18:50:26 Tuesday September 23 2014
6061
Base: Al MN: 0
2nd Match: 3105
MN: 0
3rd Match: 1100
MN: 0
Al Aluminum 97.9% +/-0.219% 96.0% 98.61%
Si Silicon 0.668% +/-0.083% 0.4% 0.8%
Mg Magnesium 0.446% +/-0.023% 0.8% 1.2%
Cu Copper 0.295% +/-0.007% 0.15% 0.4%
Fe Iron 0.289% +/-0.070% 0.0% 0.7%
Cr Chromium 0.246% +/-0.019% 0.04% 0.35%
Mn Manganese 0.106% +/-0.012% 0.0% 0.15%
Ni Nickel < 0.073%
Ti Titanium 0.043% +/-0.003% 0.0% 0.15%
Li Lithium 0.000% +/-3.639%
Zr Zirconium < 0.015%
Zn Zinc < 0.046% 0.0% 0.25%
Page 1



Android WiFi Apps allow remote operation

Simultaneous Applications



Other stuff…..

unknown Sciaps LIBZ 500 (757 470 989) - TeamViewer - Free lice...
Actions
View
TI Sensor Test...
FM Radio
Downloads
LIBZFactoryMo...
AirDroid
LIBZ Calibrate
Quick Alloy Mo...
Empirical Mode
GeoChem Mode
Alloy
Alloy Results
QuickSupport
ES File Explorer
Beam
Angry Birds
Pool Billiards Pro
OruxMaps

- **Summary**
  - **A versatile handheld LIBS has been developed**
  - **Most standard bench-top instrumentation features have been incorporated**
    - **(variable gating, argon purge, rastering, cleaning/sample pulse selection,…)**
  - **Many applications currently in development (and will continue!)**

Thanks for your attention