The Realization of a New Solid-State Spectrometer for Glow Discharge Optical Emission

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Outline

- Challenges of GD instrument design
- GD characteristics that must be considered
- Impact of these characteristics on GD instrument design
- An evaluation of three important design challenges:
  - the data acquisition requirements for bulk and CDP
  - the photon flux and the most appropriate approach for collection light in GDS
  - use of the full spectra to produce more robust analytical results
- The Realization of this work in the newly designed GDS900
- Conclusion

Introduction

Designing and building an analytical instrument requires that we:

- understand **what** we desire to measure
- understand the **capabilities and limitations** of our chosen technique and the instrumental components
- evaluate most, if not all, of the appropriate **design alternatives**
- use a knowledge based approach when considering these alternatives to best understand the various **trade-offs**

Glow Discharge
Instrument Design

The "What" of
GDS Optical Emission Analysis

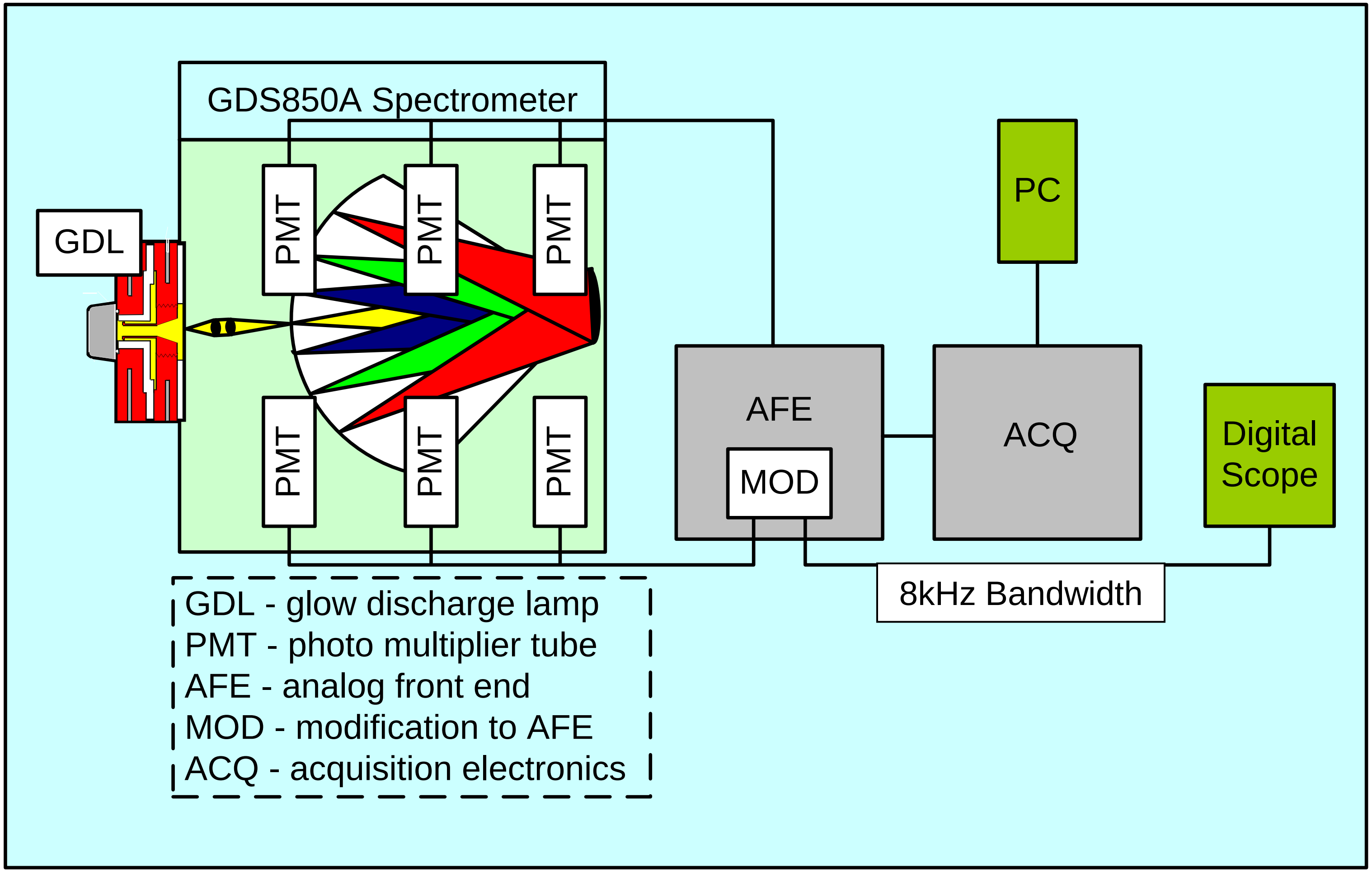
- Bulk analysis for all "emission active" elements – which includes some 70 elements
- "In depth" analysis for these same elements
- Both conductive and non-conductive matrices and layer materials that may be comprised of both
- Thermally labile materials
- This list includes a huge array of applications, sample types and material form factors. The potential range of applications for GDS is staggering and much broader than experienced by either Spark or ICP optical emission.
- Designing appropriate instrumentation to analyze this vast array of applications and materials is not a simple task for the instrument designer.

The Challenges for the Instrument Designer

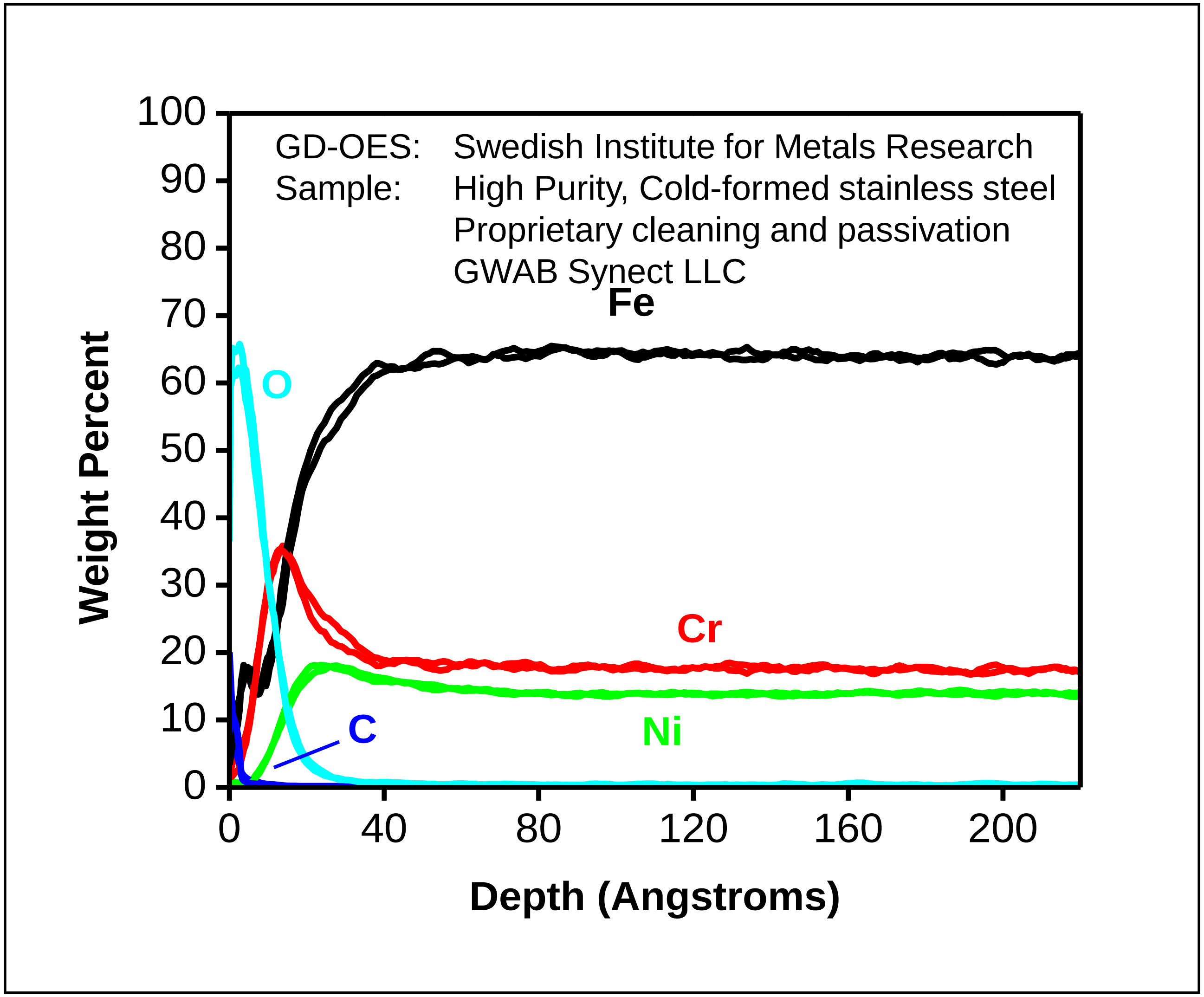
- Fundamental aspects of GD that may impact the instrumental design:
  - photon fluxes (Signal intensity)
  - photon energies (spectral wavelength range)
  - source temporal stability
  - source spatial homogeneity
  - signal temporal bandwidth (e.g. layered samples)
- Specifically we will consider the instrumental requirements for:
  - **data acquisition in surface and near surface analysis**
  - **data collection requirements for bulk analysis**
  - **collecting and focusing light into the spectrometer**
  - **leveraging the information content of the full spectra to provide better analysis**

Temporal Behavior of the GDS Plasma in CDP and Bulk Analysis

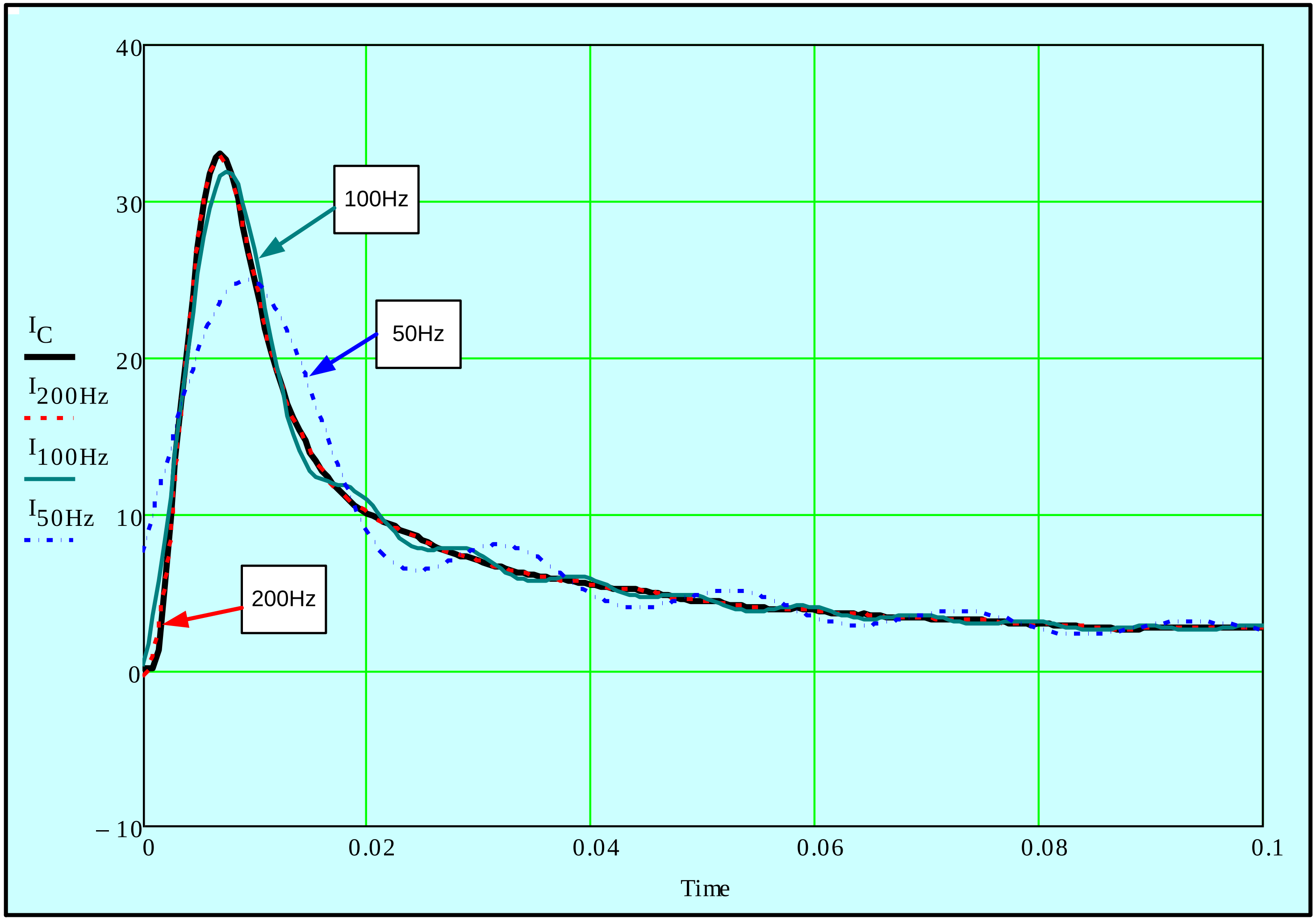
Acquisition System for Frequency Measurements

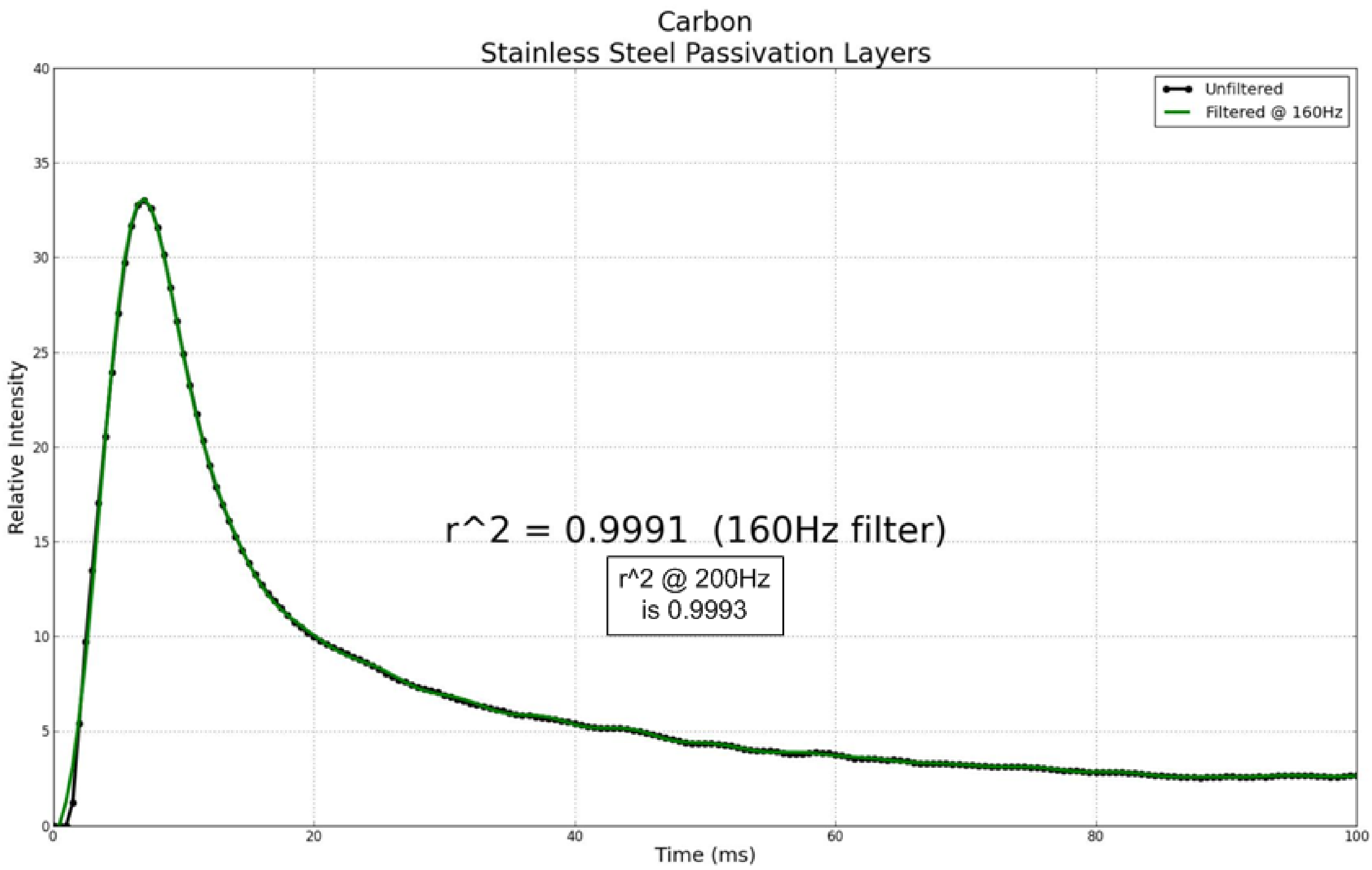


Passivated Stainless Steel DC-GD-OES

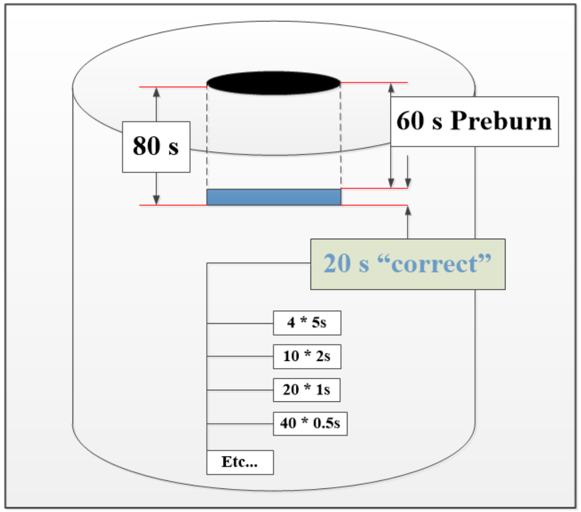


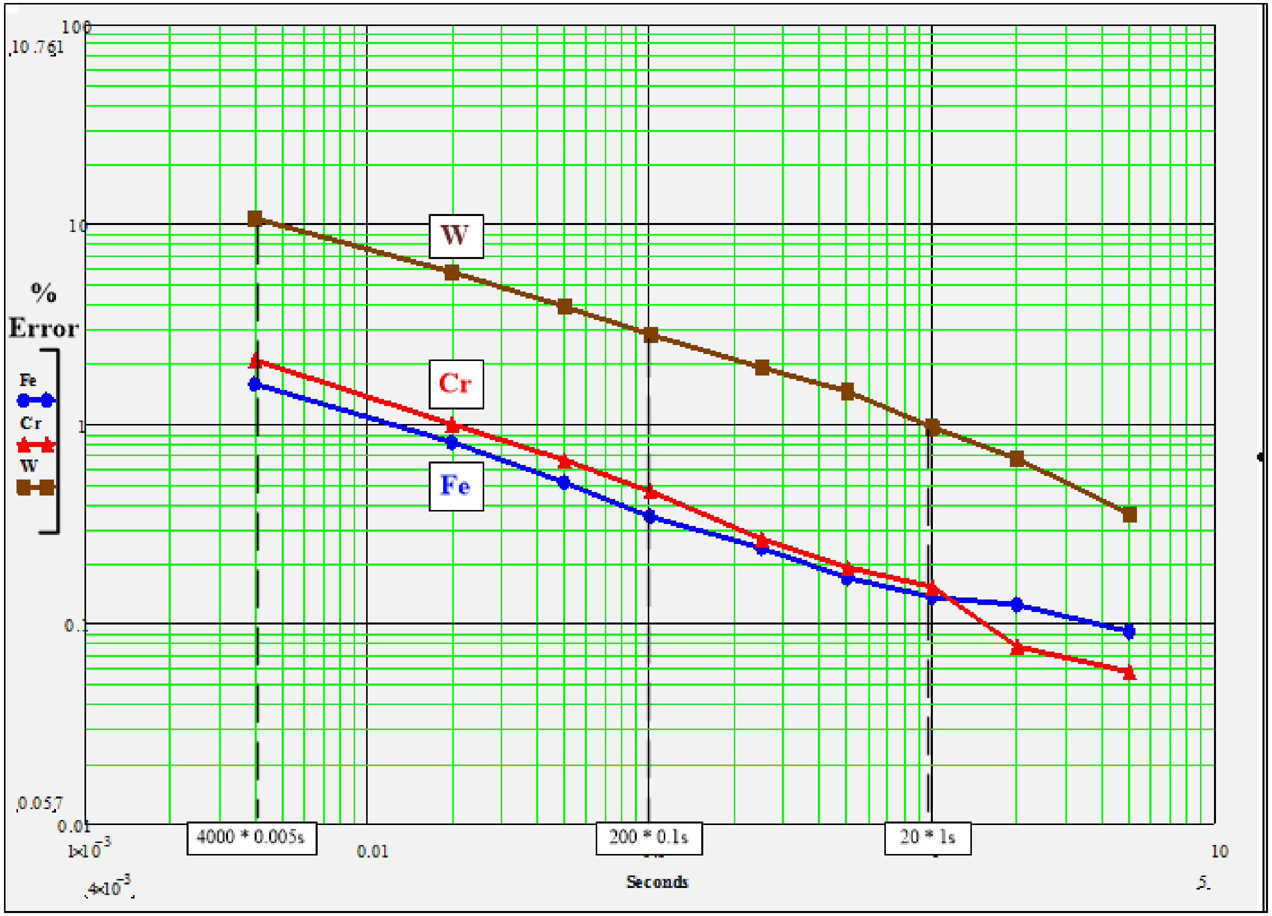
Carbon Signal Reconstructed from Filtered FFT




Carbon
Stainless Steel Passivation Layers
Relative Intensity
Time (ms)
Unfiltered
Filtered @ 160Hz
r^2 = 0.9991 (160Hz filter)
r^2 @ 200Hz
is 0.9993
0
5
10
15
20
25
30
35
40
0
20
40
60
80
100

RMS Error vs. Integration Time





GDS Temporal Behavior Summary

- the glow discharge is a stable and spatially homogeneous source.
- precise measurements in GD bulk analysis can be obtain using integration times of as little as one second
- essentially all CDP measurements can be obtained with data rates of less than 400Hz
- slightly lower frequencies of 320Hz have been successfully used to monitor the fastest features we have observed in GD-CDP with essentially no sacrifice in fidelity
- combining 1Hz and 320Hz integration times in bulk analysis provides a dynamic range $>10^6$

Collection Optics
and
Light Throughput

Glow Discharge Signal Intensities

- The Grimm glow discharge is not a “bright” emission source.
- Absolute emission line intensities in the GD have been estimated:

  10^9 to 10^{17} photons cm^{-2} sr^{-1} nm^{-1} s^{-1}

  (With similar values found in both DC and RF plasmas)
- ICP intensities are estimated to be significantly higher
- The calculated photon flux's from ICP signal to background ratios of the Mg II 280.27 nm:

  10^{11} to 10^{18} photons cm^{-2} sr^{-1} nm^{-1} s^{-1} *
- Required PMT voltages on a similar instrument platform with the two different sources indicates that the ICP is approximately 20 times brighter.
- **Thus the GD is between 10 and 100 times less intense when compared to the ICP.**

* George Chan and Gary Hieftje (personal communication)

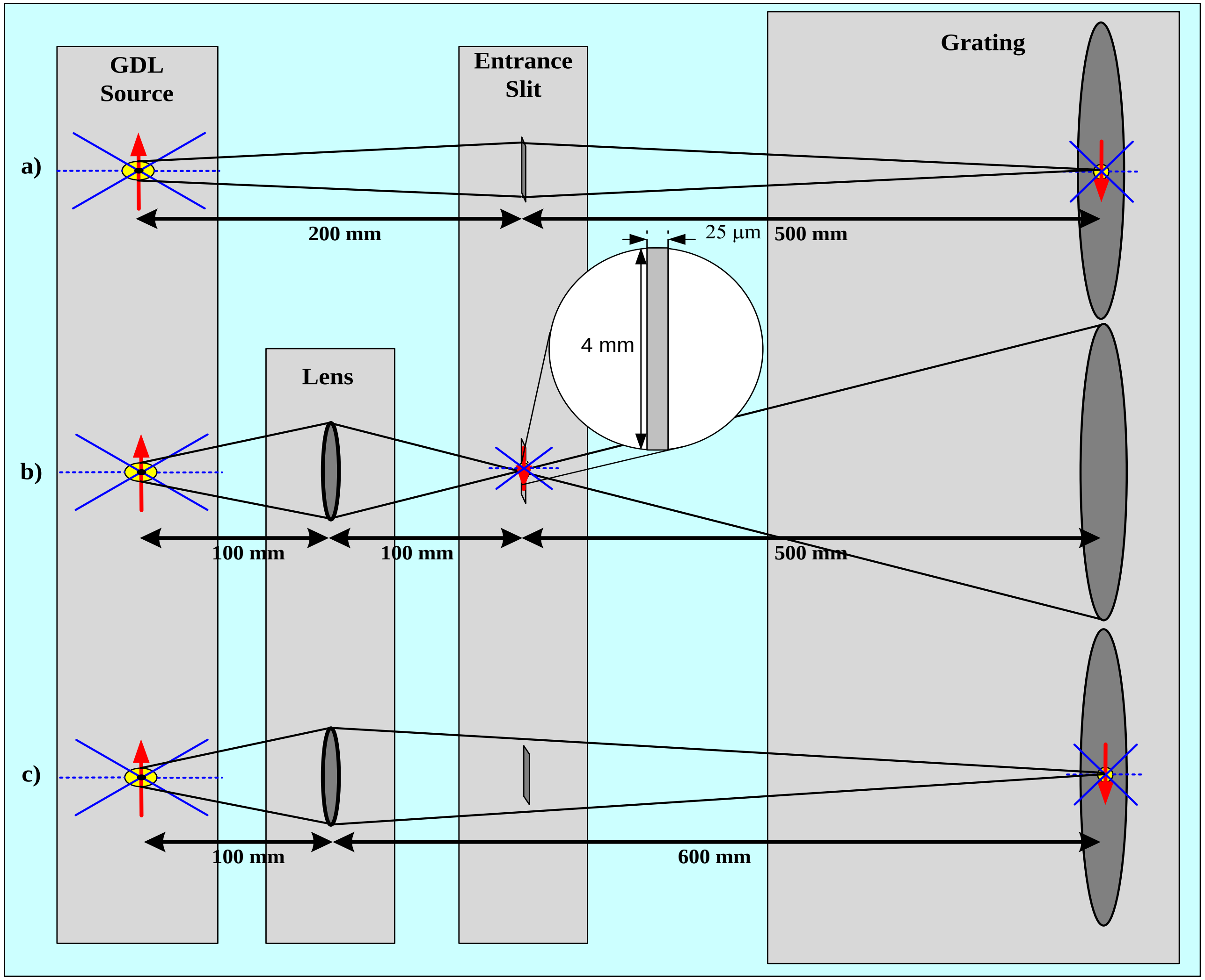
Glow Discharge Signal Intensities

The Bottom Line

Glow discharge photons are a precious commodity.

And should be treated as such by collecting and utilized them with the highest efficiency possible.

Various Optical Collection Schemes



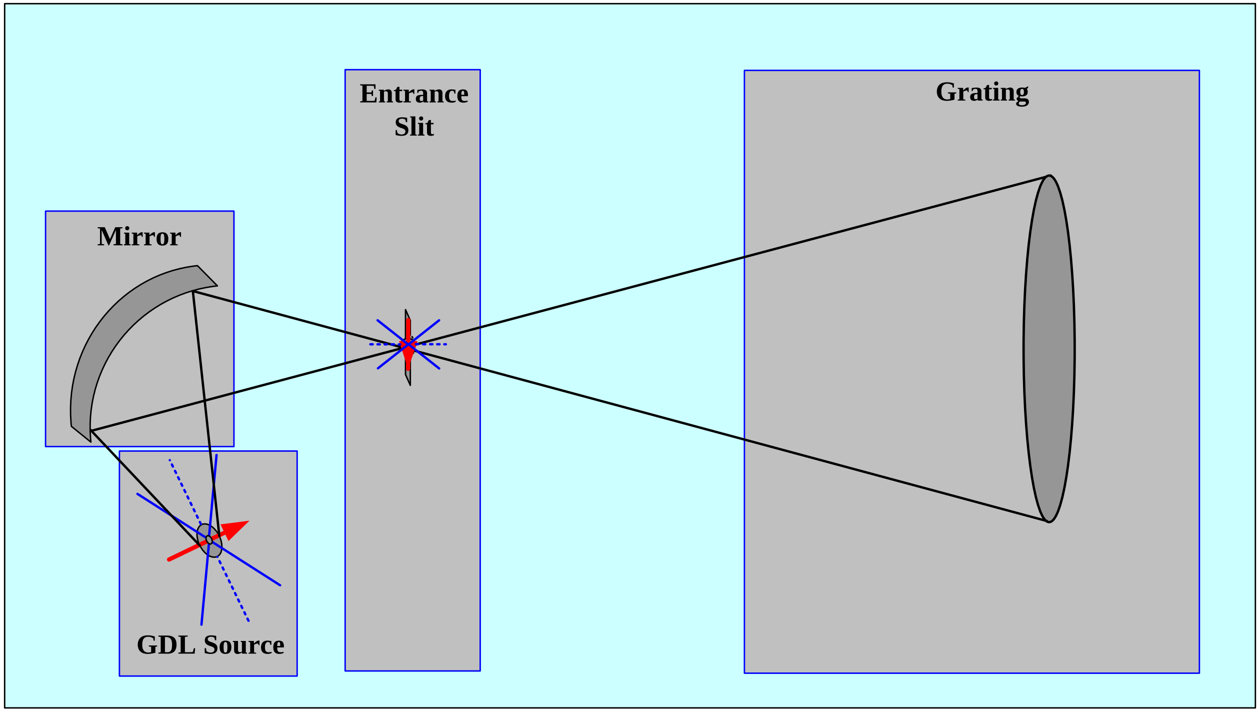
31 μm^2

4800 μm^2

(150 times that without lens)

130 μm^2

The Mirror Advantage



	Throughput (μm^2) @ Wavelength		
Focused @ 200nm on:	150nm	200nm	800nm
Mirror @ Slit	4800	4800	4800
Lens Grating	230	130	98
Slit/Grating Ratio	21	37	49

Entrance Optics Summary

- An entrance optical design that focuses light at the slit is, in almost all cases, more efficient at gathering light than one that focuses at the grating.
- The use of mirrors to focus light at the entrance slit avoids chromatic aberration and improves the light gathering capabilities by more than an order of magnitude at all wavelengths.

GDS900

•**mirror-based collection optics** focused at the entrance slit to optimize light collection at all wavelengths

•**complete spectral coverage** (160-460nm) complete spectra of both Analytes and interferences

•**combined 320Hz and 1Hz acquisition** in bulk analysis provides dynamic range >10^6

•**spectra acquisition at 320Hz** provides support for the full range of near surface CDP analysis (optional CDP - when available)

GDS900 Specifications

Optics 0.75 m focal length, Littrow-mounted, simultaneous purged spectrometer
Detector Charge-coupled array with 16,000 active pixels (0.014 mm W x 0.9 mm H pixel size)
Spectral Range Complete spectral coverage (160 nm to 460 nm)
Resolution 50 pm (0.050 nm)

Source 4 mm diameter DC glow discharge (2 mm optional)

Gas Requirements
Source/Spectrometer: Argon, 99.998% purity, 40 psi (2.8 bar) ±10%
Pneumatics: 60 psi (4.1 bar) ±10%
Purge: Nitrogen, 99.99% pure; 20 psi (1.4 bar) ±10%
Purge System 0.25 lpm N (UHP) without optional recirculating system

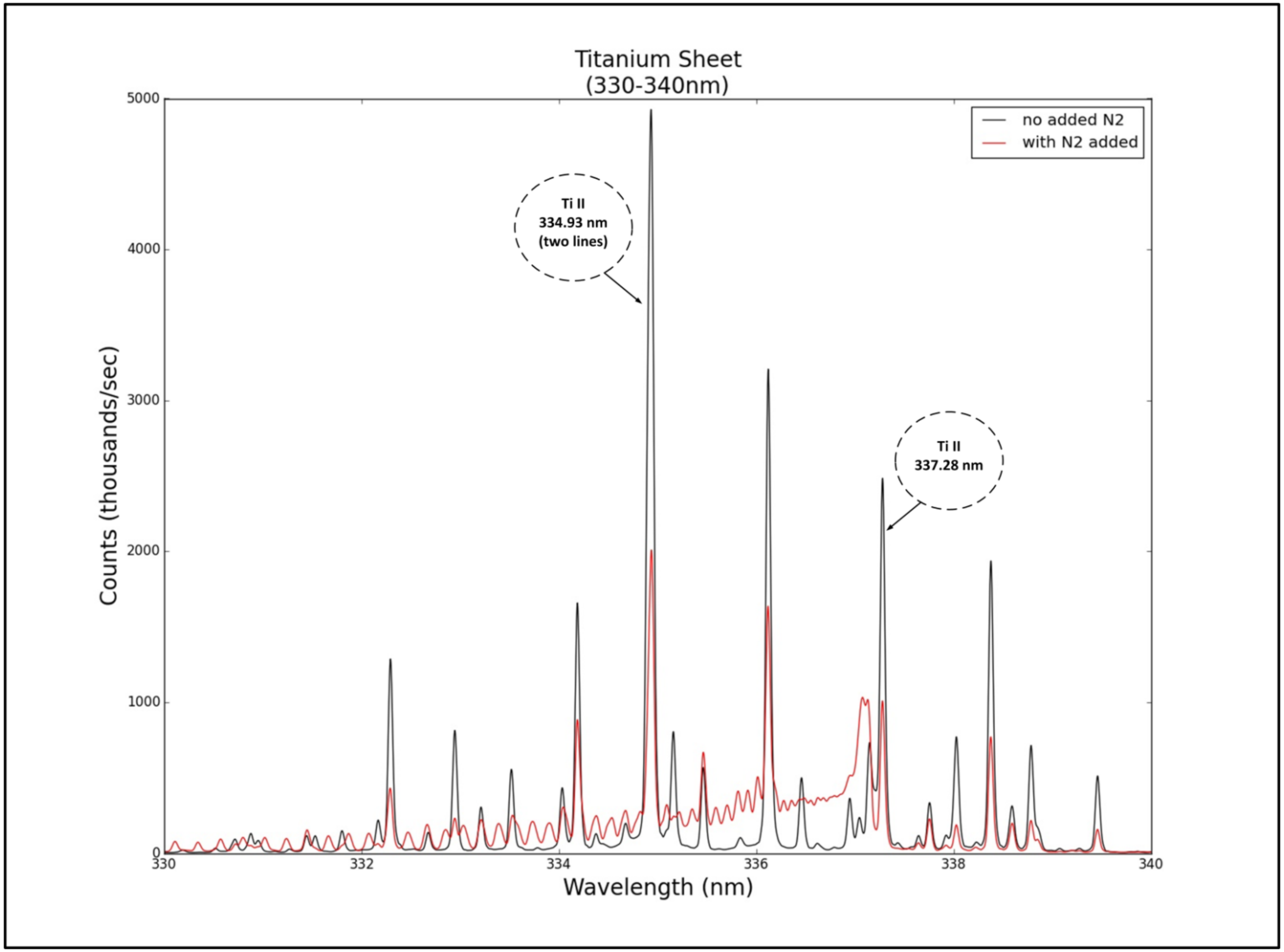
Environmental Conditions
Operating Temperature: 15 C to 35 C (59 F to 95 F)
Humidity: 20 to 80% (non-condensing)

Electrical Power Requirements 230 V~ (+10%, -15% at max load), 50/60 Hz, single phase, 15 A (breaker)

Dimensions 51 in. H 21 in. W 85 in. D (129.5 cm H 53.3 cm W 215.9 cm D); instrument only
Weight (approx.) 700 lb. (317.5 kg)

Full Spectral Data Analysis

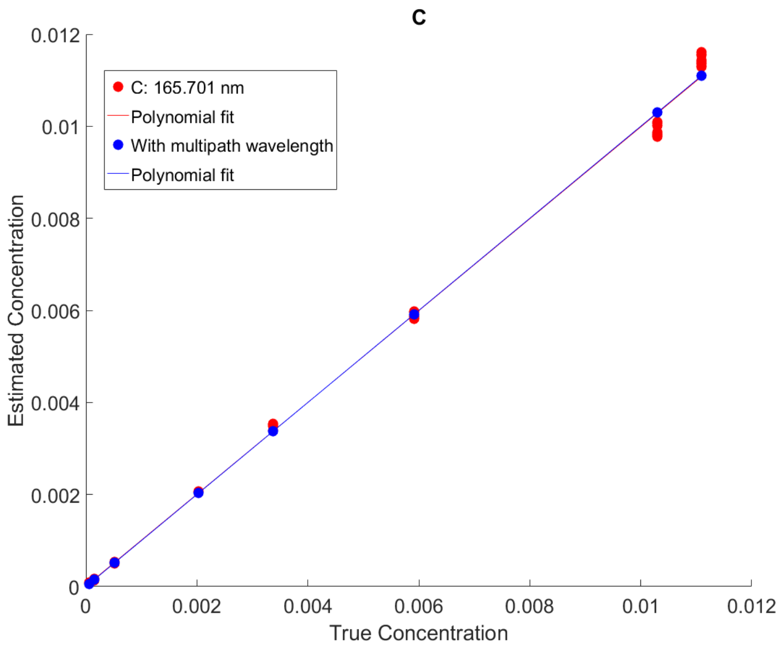
Chosen Titanium Lines

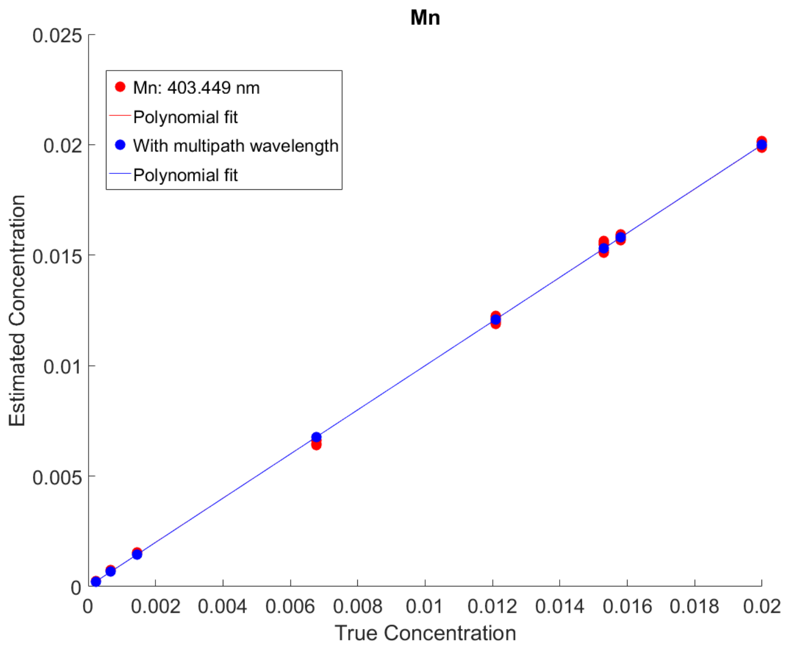


Delivering the Right Results

Concentration Using Multiple Wavelength

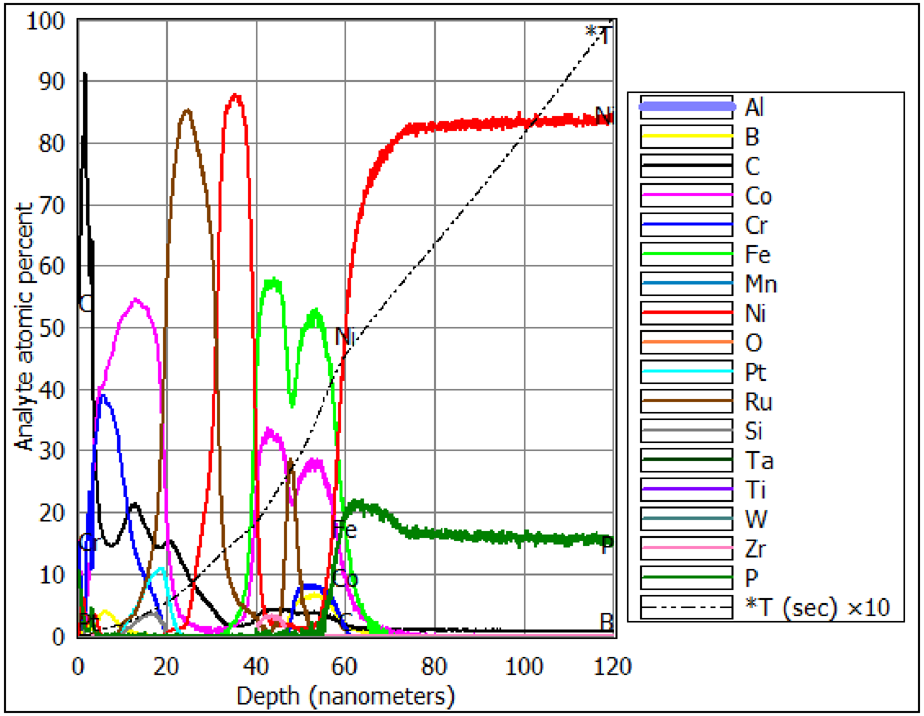
- Estimated concentrations VS true concentration
  - Dots: estimated concentration using the least fitting algorithm
  - Lines: polynomial fit between estimated concentrations and the true concentration



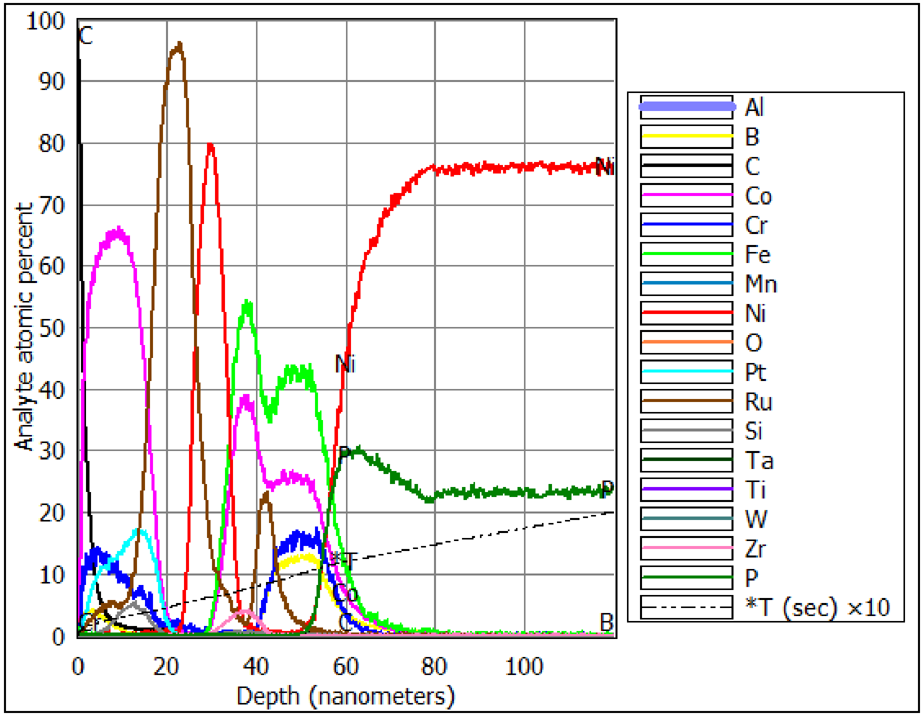


CDP Comparison Data
HD Vendor C

CCD

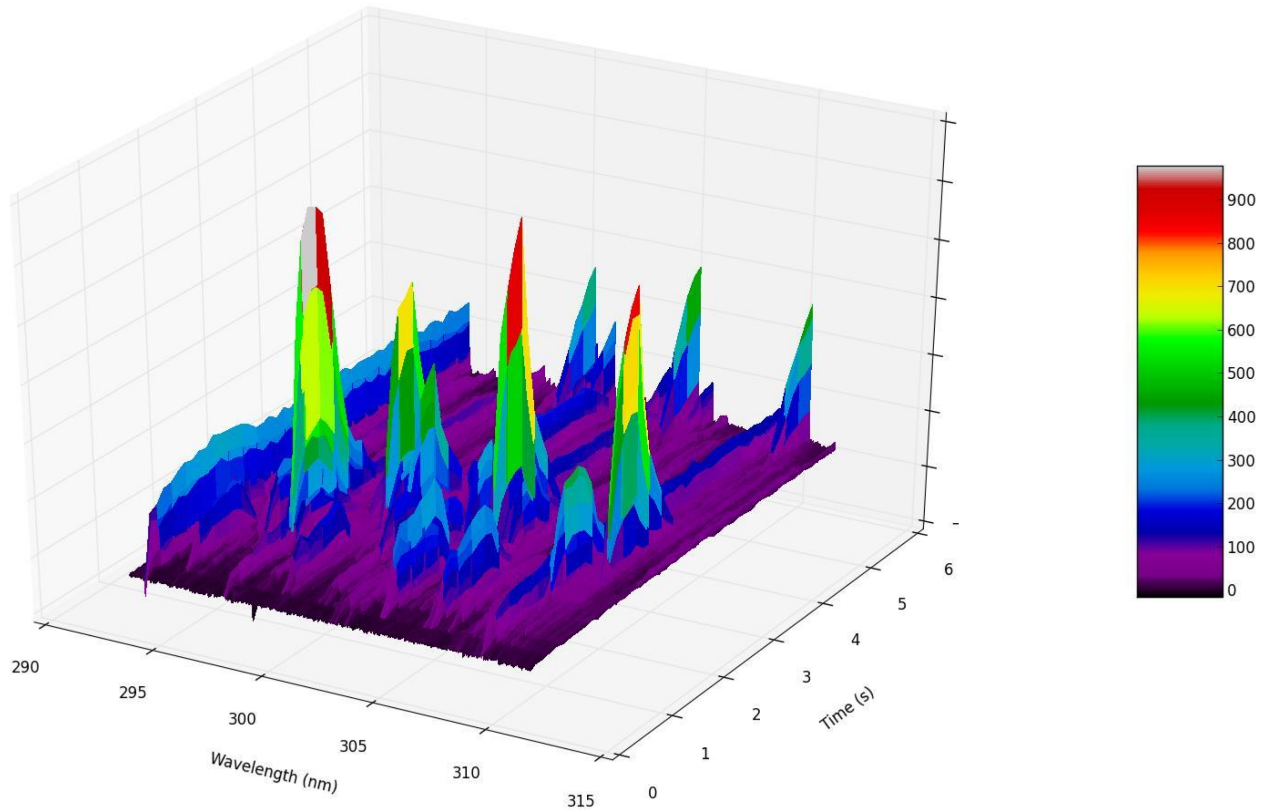


PMT



Hard Drive Spectra

(6s x 320Hz = 1920 spectra {15nm slice})



Summary and Conclusions

GD Frequency Content and Signal Processing

- integrations as short as 1-2s can provide high precision Bulk analysis
- The band width of almost all depth profile signals is less than 200Hz

GD emission signals and their collection

- Glow discharge is a relatively weak emission source and efficient collection of these signals is paramount
- The use of mirror-based optics focused at the entrance slit provide more than 20 times the measurable signal as the typical approach of lenses focused at the grating

Utilizing the information in the full GD spectra

- Array-based spectrometers can provide far more information about "problems" in our spectroscopy
- This information may be used to help choose the best analytical line for a given task or provide the necessary information to deal with molecular background interferences
- This only scratches the surface of how this plethora of spectral information may be utilized

The GDS900 Design

- This instrument was designed with all of these fundamentals in mind
- Light collection, data rates and the use of the information in the entire spectra make this instrument one of the first to be truly optimized for glow discharge analysis
- The GDS900 is the base model and development platform for an all new line of GD instruments

Acknowledgements

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Thank You For Your Attention!!!