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DOE Hydrogen Program

Montana Palladium Research Initiative

Detection of Trace Platinum Group Element Particulates with Laser Spectroscopy

S. C. Snyder and W. G. Wickun

Montana State University - Billings

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Project ID # FC49

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Overview

Timeline

- Project start date 8/31/06
- Project end date 12/31/08
- Percent complete 75%

Budget

- Total project funding
  - –DOE share $339114
  - –Contractor share $113546
- Funding received in FY06 $0
- Funding for FY07 $452660

Barriers

- Barriers
  - Reformer capital cost
  - Reformer Manufacturing
- Technical Targets
  - 3.4.15 Fuel Cell Membrane Testing, Analysis, and Characterization

Partners

- PLUG Power, Montana-Dakota Utilities
- Project management: David McGinnis

Objectives

- Develop laser-induced breakdown spectroscopy (LIBS) to detect and quantify the presence of platinum-group elements (PGE) nanoparticles in very dilute aqueous suspensions.

- Apply LIBS to determine the presence and mass concentration of PGEs in water reformed in the stack of proton exchange membrane fuel cells (PEMFC). The presence of nanoparticles of PGEs in this water is an indication of PEMFC degradation. This work supports the PEMFC field trials conducted at MSU-Billings to test and characterize the durability of PEMFC membranes.

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Milestones

Month/Year	Milestone or Go/No-Go Decision
Dec 07	**Milestone 1:** Complete the particle generator and setup the LIBS experimental arrangement
Apr 08	**Milestone 2:** Implement conditional analysis in LIBS data acquisition and establish the calibration relationship between PGE particle size and the intensity and frequency of occurrence of LIBS signals.
May 08	**Milestone 3:** Initiate analysis of PEMFC water for presence and concentration of PGE nanoparticles. This work will continue for the duration of the project.

Approach

- LIBS is a straightforward technique that has been shown to be a very sensitive analytical tool to detect and quantify metallic nanoparticles in extremely dilute aqueous suspensions
- LIBS is capable of *in situ* measurements and can be field-deployable
- LIBS provides on-site support of PEMFC field degradation studies

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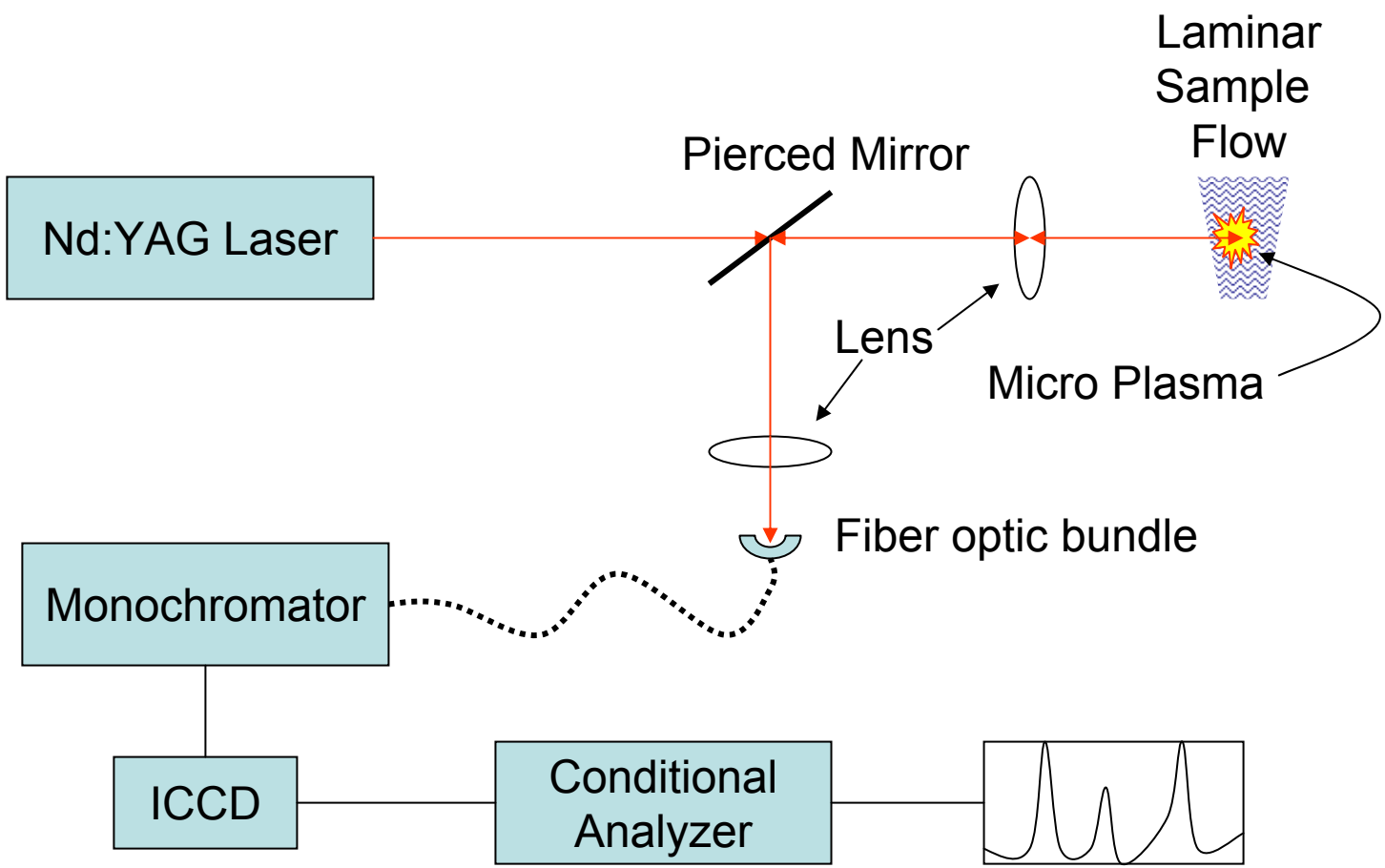
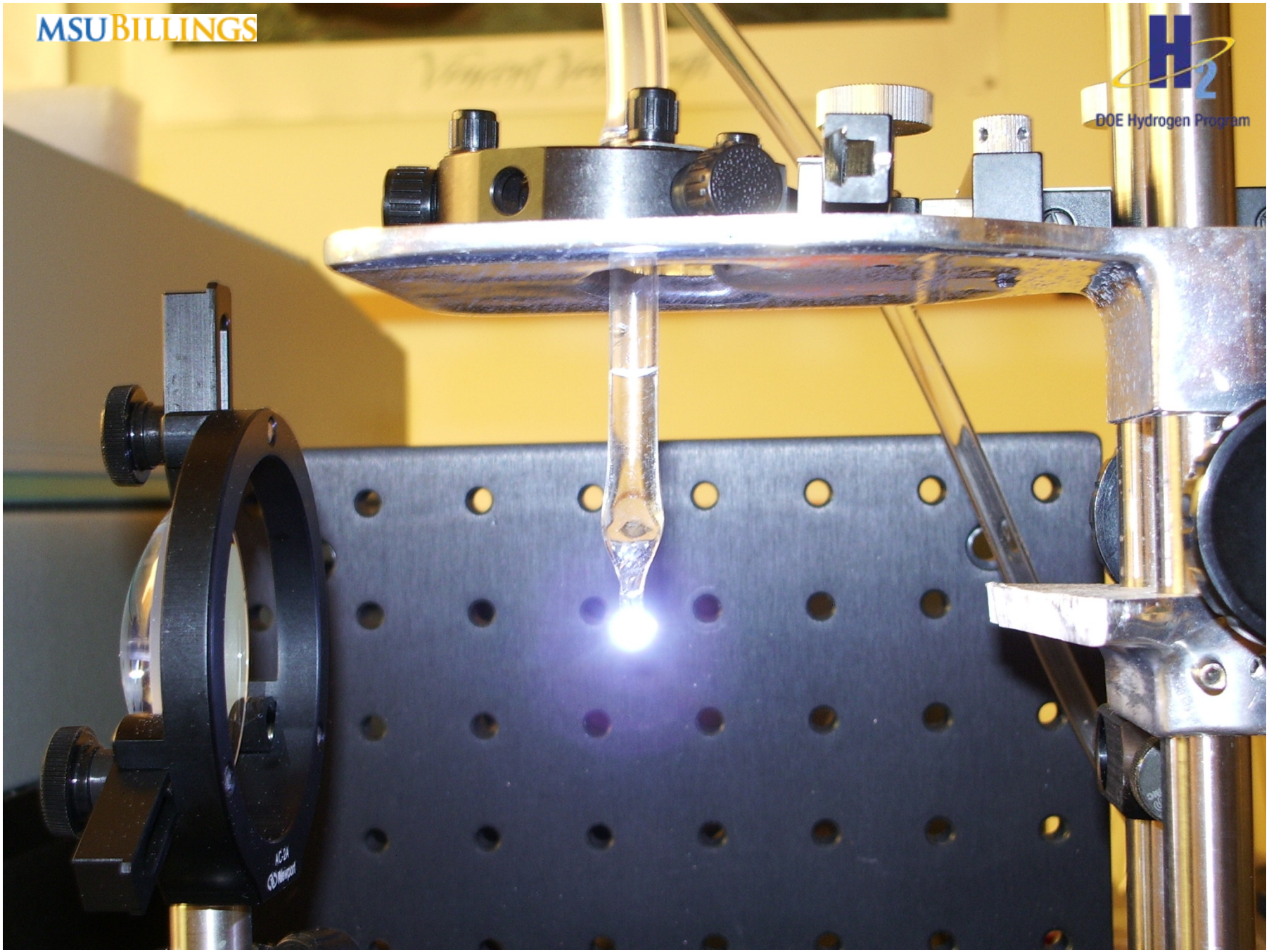
Laser-**I**nduced **B**reakdown **S**pectroscopy

- Laser beam is focused onto a substrate or into a liquid or gas
- Intense radiation at the focal point creates a micro-plasma
- Microplasma vaporizes small amount of material and excites characteristic atomic spectral lines
- Analysis of emission spectrum determines species type and concentration

Experimental Set Up of LIBS



This set up achieves Milestone 1.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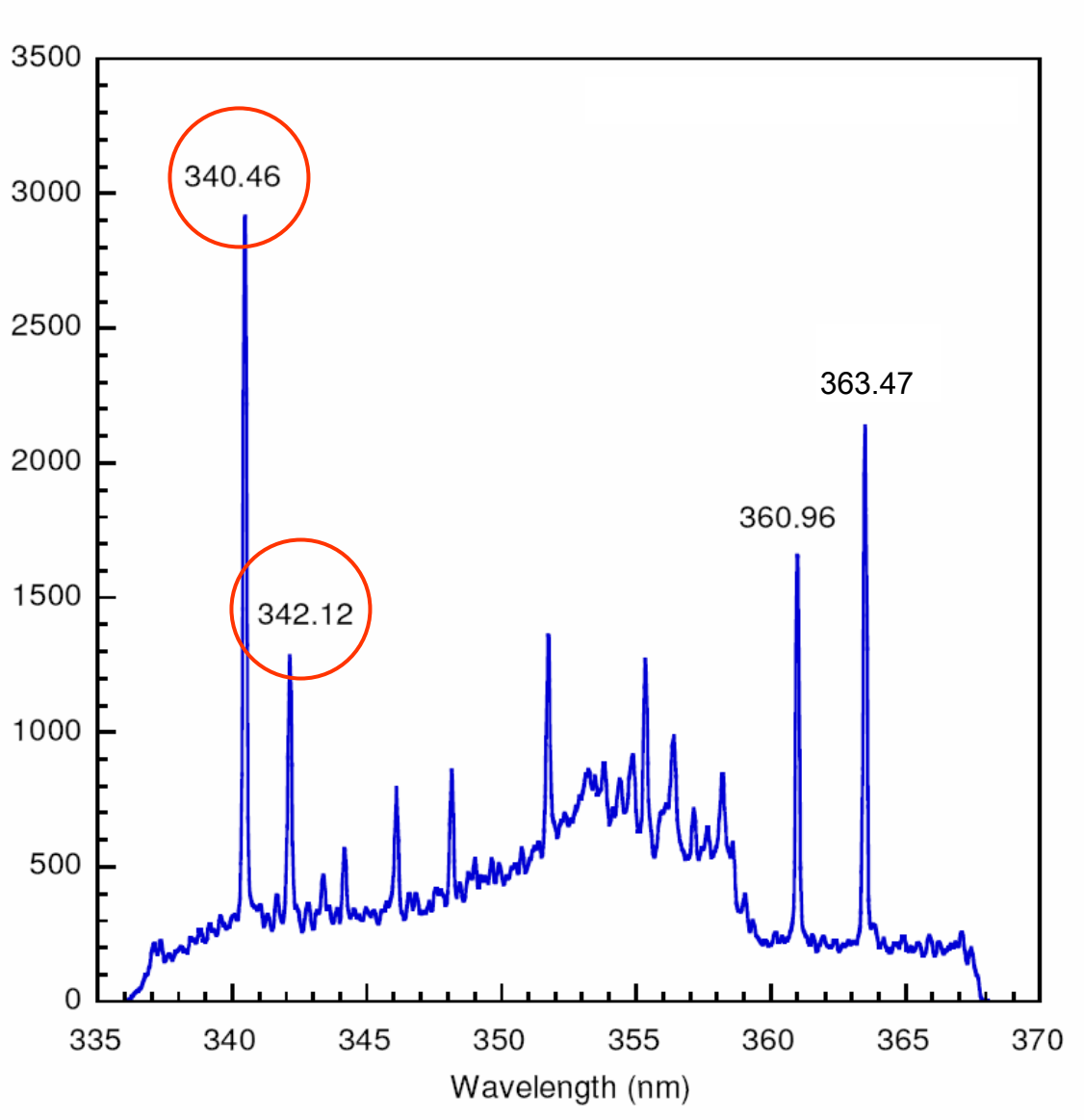
Partial Emission Spectrum of Palladium I



Courtesy of D.W. Hahn

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Conditional Data Analysis

- Intensity of spectral peak is compared to the average intensity of the background
- Spectrum is considered a "hit" if ratio of intensities exceeds a predetermined threshold value, typically 20 – 30% above background
- Performed in real time at 5 Hz laser rep rate

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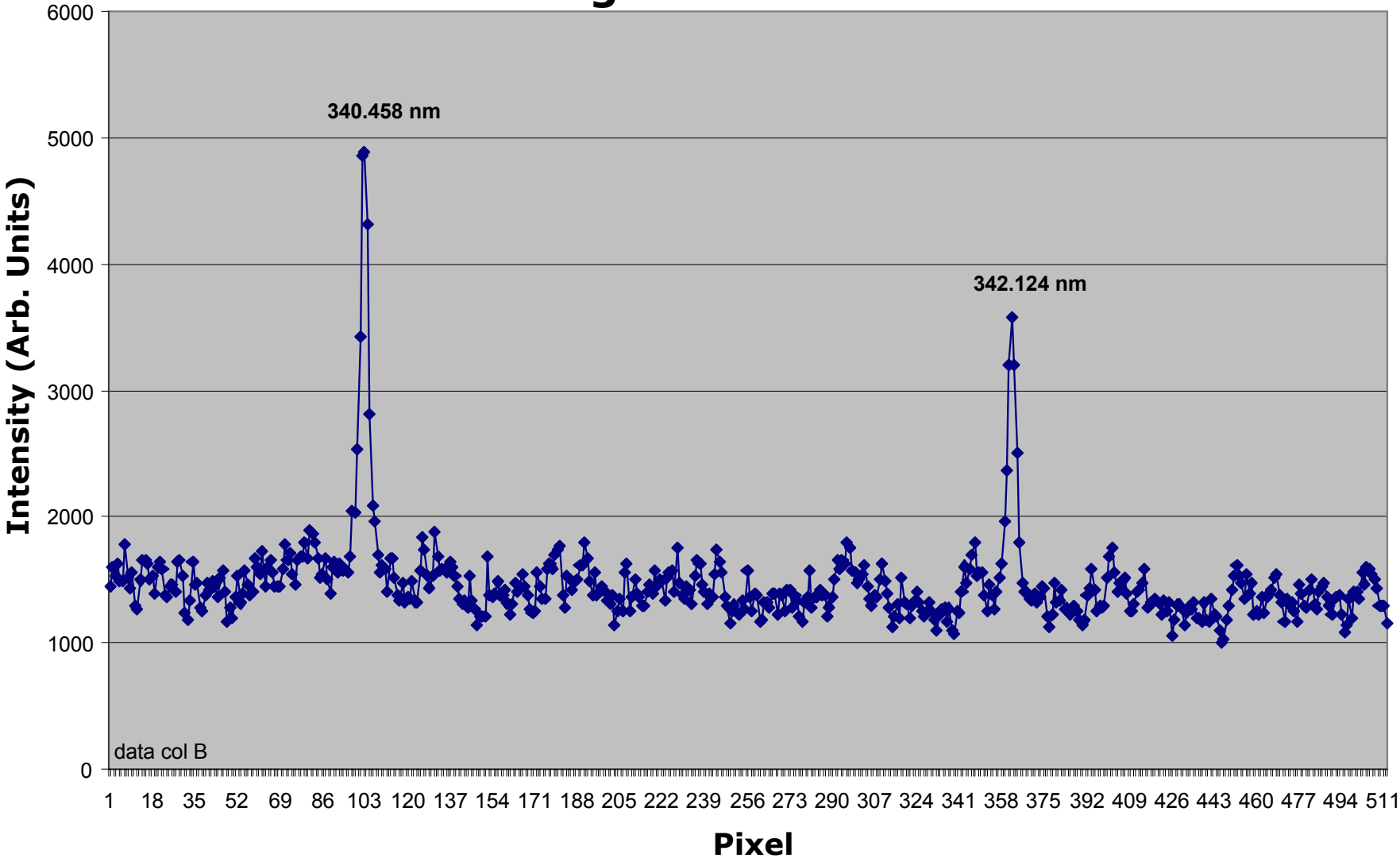
LIBS Spectrum of a Single Pd Particle



This data achieves Milestone 2 and addresses Technical Target 3.4.15.

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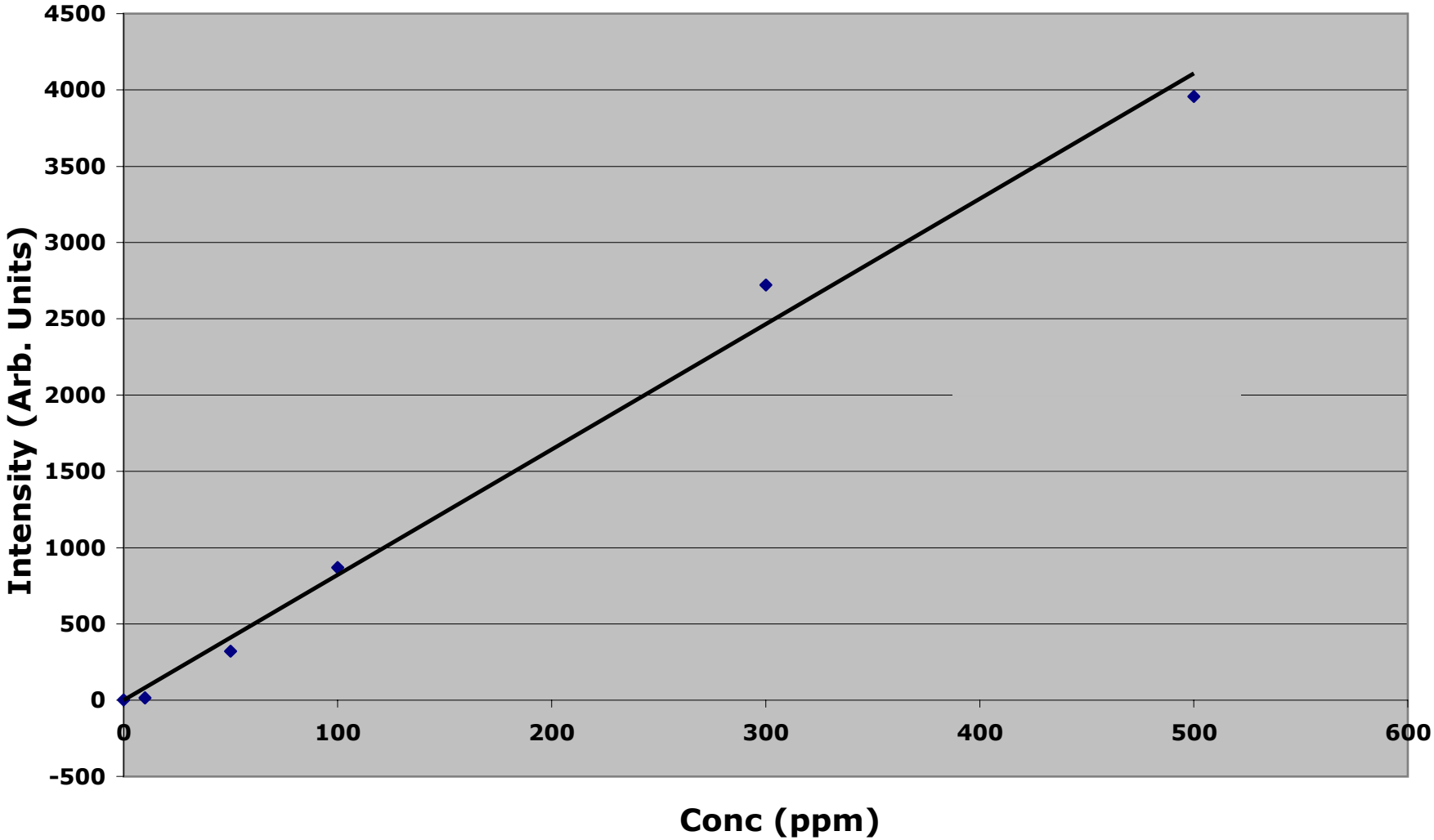
Pd Calibration Curve



This data achieves Milestone 2 and addresses Technical Target 3.4.15.

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Fuel Cell Unit

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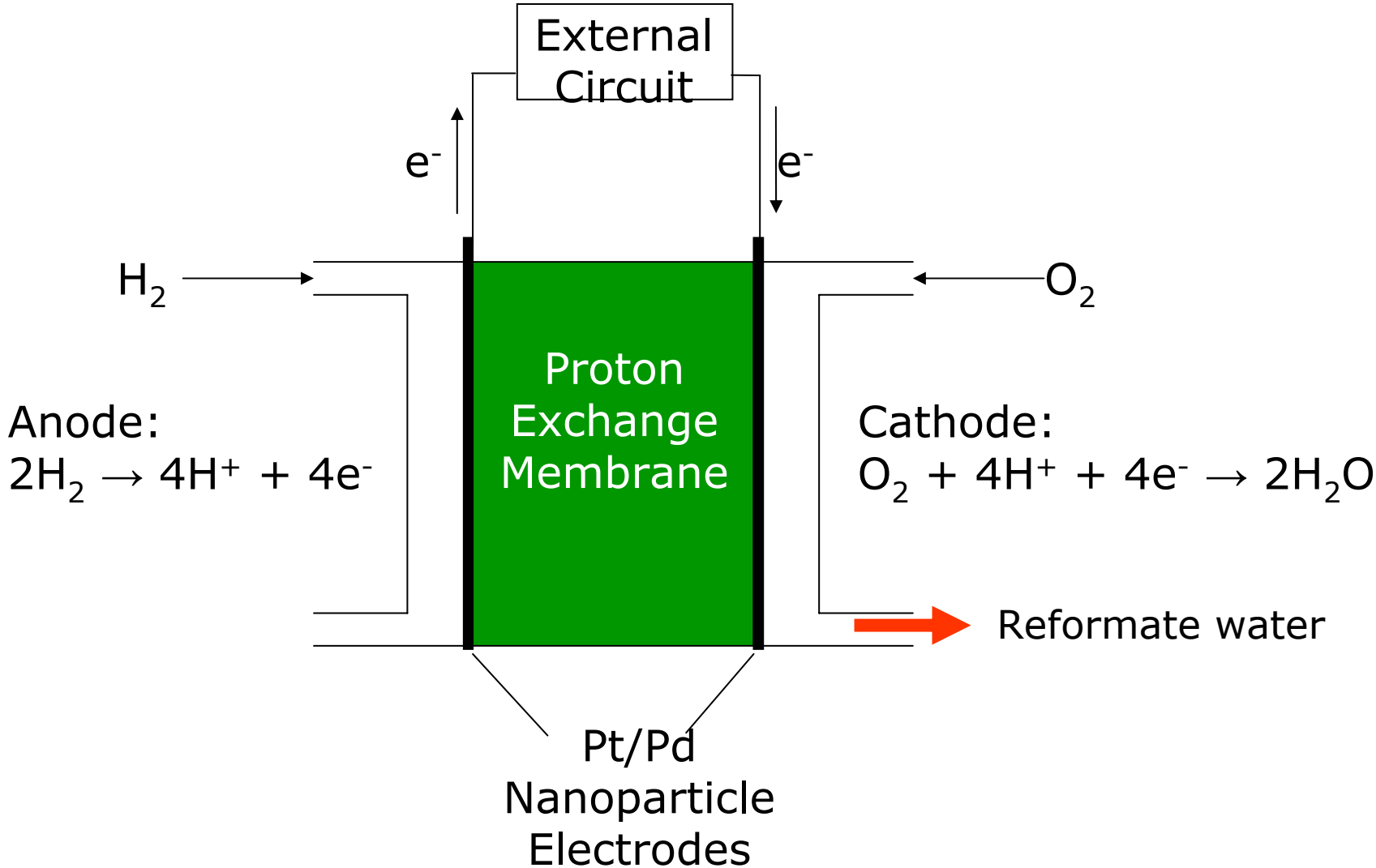
Montana Palladium Research Initiative at MSU-Billings

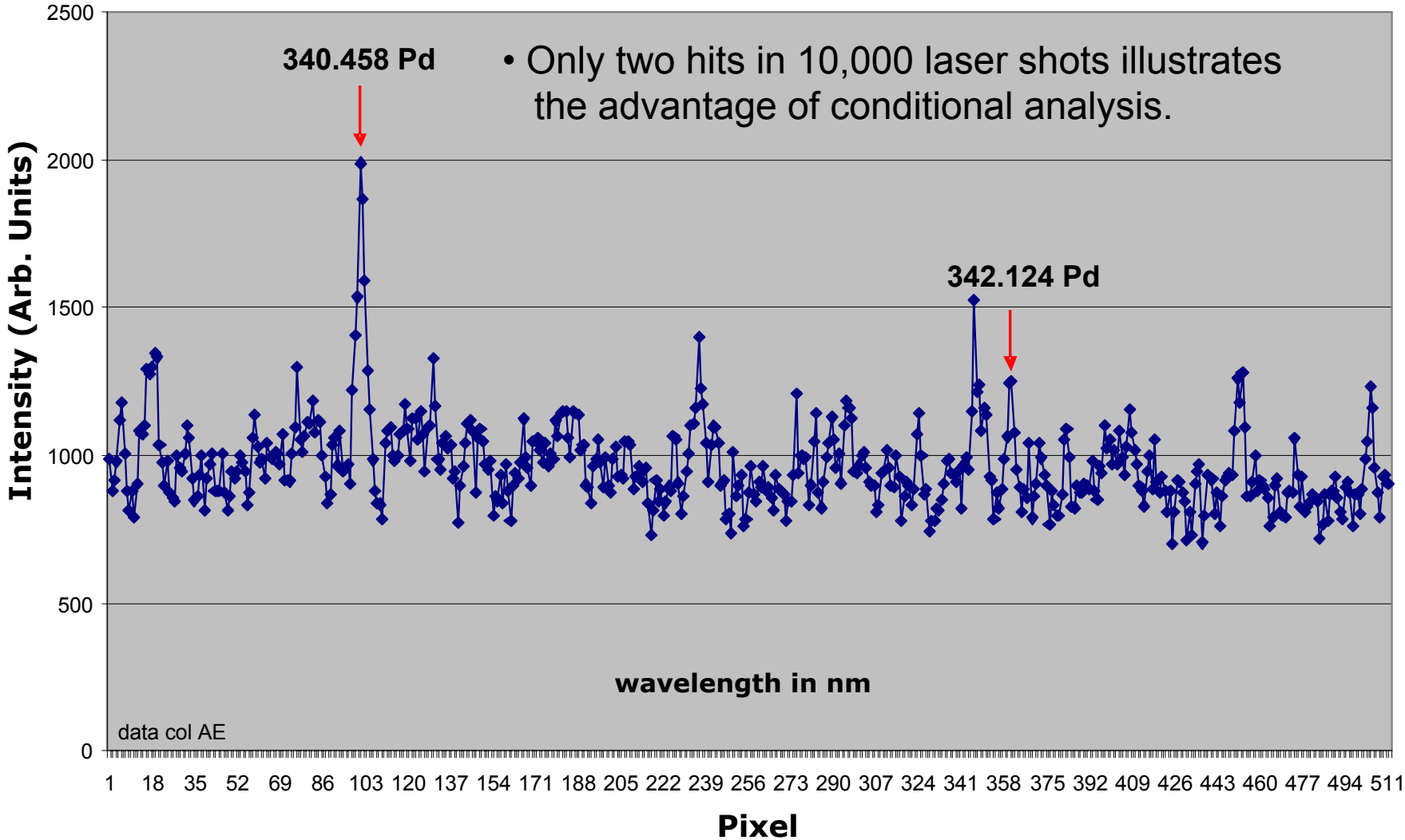
The latest generation 5 kW hydrogen fuel cells from Plug Power

A Hydrogen Fuel Cell



LIBS Single-Shot Spectrum @ 341.5 nm of a Single Pd Nanoparticle from Fuel Cell

- This spectrum corresponds to a mass-concentration ~ 10 ppb



This data achieves Milestone 3 and addresses Technical Target 3.4.15.

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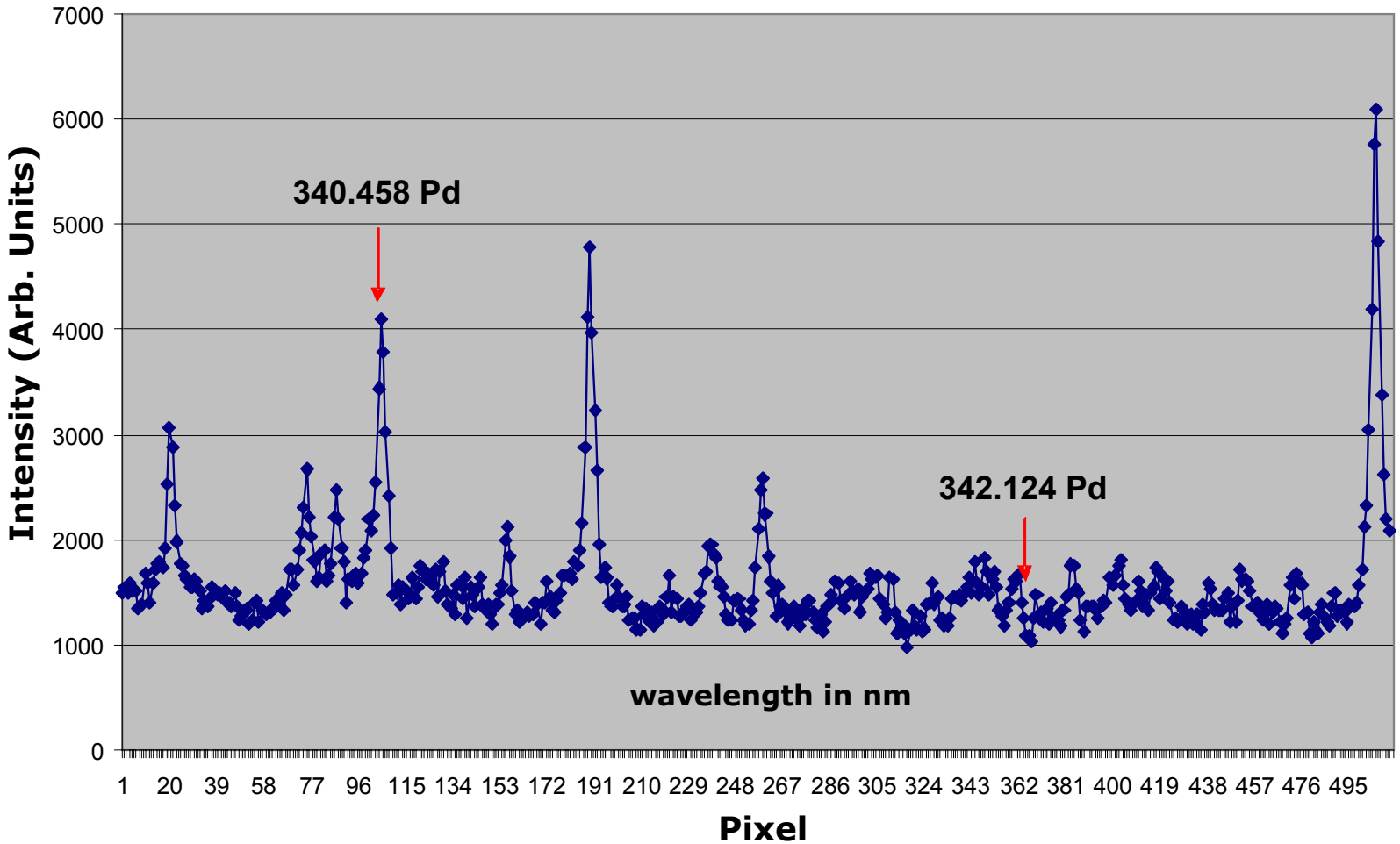
Single-Shot LIBS Spectrum of Particle in Fuel Cell Water

- Using conditional analysis, only two hits in 10,000 laser shots occurred



This data achieves Milestone 3 and addresses Technical Target 3.4.15.

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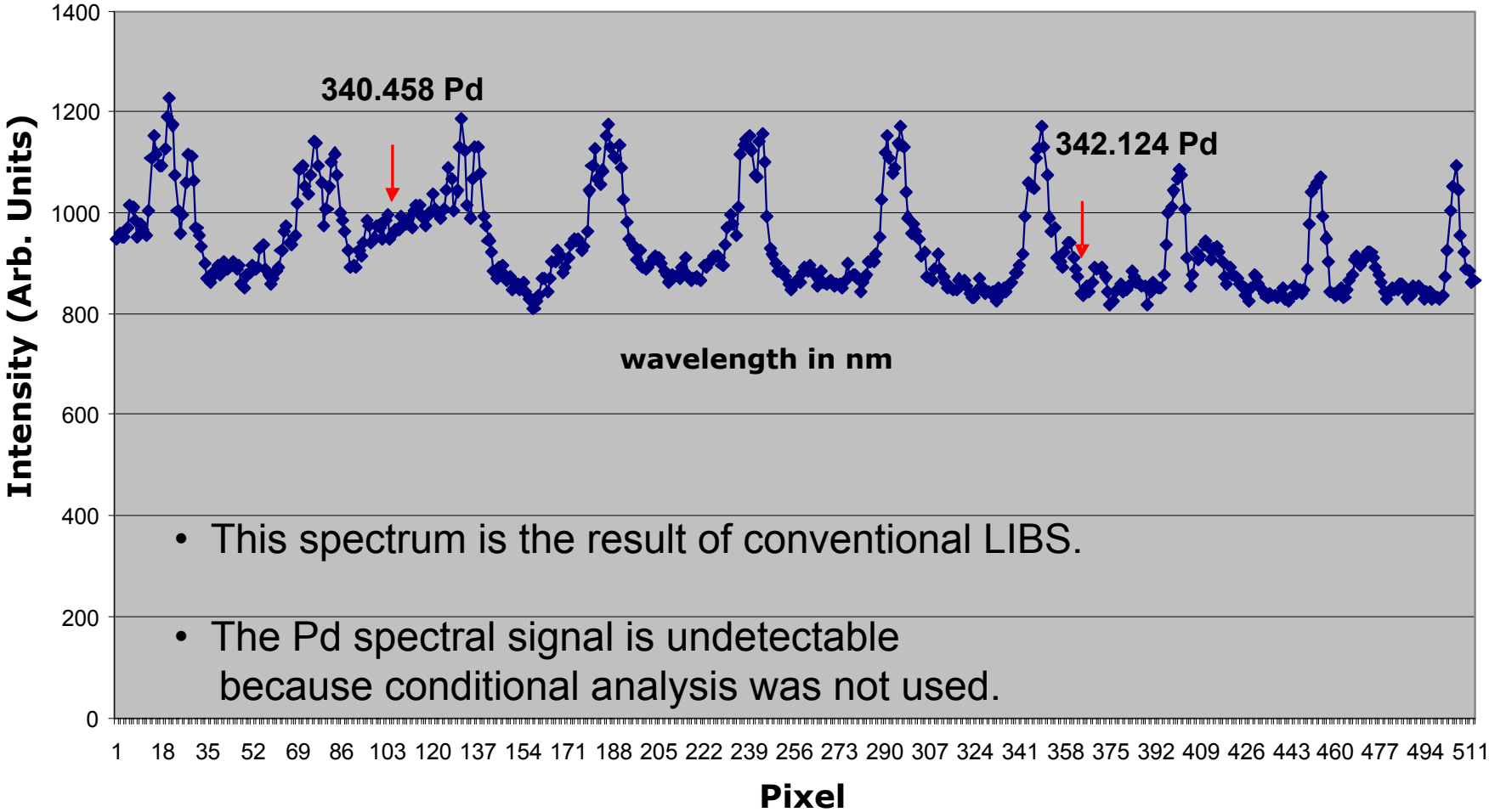
LIBS Spectrum @ 341.5 nm of Water From Fuel Cell (Ensemble Average of 10,000 Shots)



- This spectrum is the result of conventional LIBS.
- The Pd spectral signal is undetectable because conditional analysis was not used.

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Future Work

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FY 08

- Calibrate the LIBS system for platinum
- Continue analyzing fuel cell water for the the presence of platinum and palladium for the duration of the field trials

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Summary

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Relevance: **Project is critical to degradation studies of PEMFC membranes during extended operation**

Approach: **Employ LIBS to detect and quantify nanoparticles of Pd and Pt in very dilute aqueous suspensions**

Technical Accomplishments and Progress: **Extremely sensitive technique capable of detecting single nanoparticles in very dilute aqueous suspensions was developed using LIBS with conditional analysis**

Proposed Future Research: **Incorporate Laser-Induced Fluorescence to increase sensitivity of technique to smaller particles**

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