Measurement and Control of Glass Feedstocks

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2004 OIT Glass Project Review

June 22, 2004

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Batch Measurements at PPG

PPG Product Manager Kevin Streicher Operating ERCo LIBS Batch Sensor

Chester Fiber Glass Plant

Test Sample (blind)	Boron Concentration Difference
A	0.00 %
A	0.03 %
B	0.24 %
B	0.30 %

Agenda

- Project Summary
- Project Approach
- Participants
- Brief Summary of Accomplishments
- Problem Statement
- Concept Description
- Experimental Data
- Discussion and Conclusion

Project Summary

- Goal: Develop a plant instrument for rapidly measuring oxides in batch materials
- Challenge: Bringing LIBS technology from the lab to the plant with the accompanying issues of accuracy, robustness, ease of use, and low maintenance
- Benefits: 20 percent reduction in product defects, saving the glass industry $220 to 440 million. Energy savings of 260 to 520 billion Btu per year
- FY05 Activities: Long term testing of instrument at PPG fiber glass plant while continuing to upgrade the instrument's capabilities

Barrier-Pathway Approach

- Barriers
  - Using LIBS to measure many elements rapidly and simultaneously with widely varying concentrations (fractions of % to tens of %)
  - Ruggedizing LIBS for plant environment
    - Ease of use, low maintenance
- Pathway
  - State-of-the-art LIBS hardware components
  - Innovative software algorithms
  - Complete automation
- Critical Metrics
  - 5% relative error or 0.05% absolute error in concentration measurements

C-LESS™ LIBS Software

- ERCo has Proprietary Software Using First Principles that Translates LIBS Spectra into Concentration Measurements
- Calibration Not Required
- Method is Automatic – no user assistance necessary
- Method Applies to both Molten and Solid Data
- Method is Independent of Experimental Parameters that Can Fluctuate such as Laser Power

Participants in Glass Project

- DOE Industrial Technologies Program – Industries of the Future: Glass
- Energy Research Company
- PPG Industries (Fiber Glass)
- Fenton Art Glass
- Oak Ridge National Laboratory

U.S. Department of Energy
Energy Efficiency and Renewable Energy

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PPG

FENTON
Handcrafted American Glass Artistry

OAK RIDGE NATIONAL LABORATORY

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Accomplishments

- Built Full Scale Sensor
  - Automated & Robust LIBS Hardware
  - Developed “1-click” LIBS Software
- Installation and Testing at PPG
  - Extensive ulexite testing
  - Limestone residue testing
  - Installation for long term test scheduled
  - Upgrades for glass buttons, clay, colemanite, and silica

Accomplishments

- Applied Advanced Calibration-less (C-LESS™) LIBS Analysis to Batch Materials
- Demonstrated LIBS Utility for Cullet Sorting
- Measured Molten Glass Composition
- Related Funded Work in:
  - Coal
  - Aluminum
  - Steel
  - Alloy sorting

Problem Statement

- The Glass Industry Technology Roadmap emphasizes this need for accurate process and feedstock sensors (p. 12):

  "The lack of effective in-process sensors and control systems is the most serious barrier to better production efficiency."

Problem Statement

- Lack of Effective Way to Ensure Accurate Batch Oxide Concentrations
  - An indeterminate mixture of prior deliveries to a silo exits the silo
- Oxide Fluctuations Lead to
  - Wasted Feedstock
  - Quality Problems
  - Increased Energy Use and Emissions
  - Wasted Product

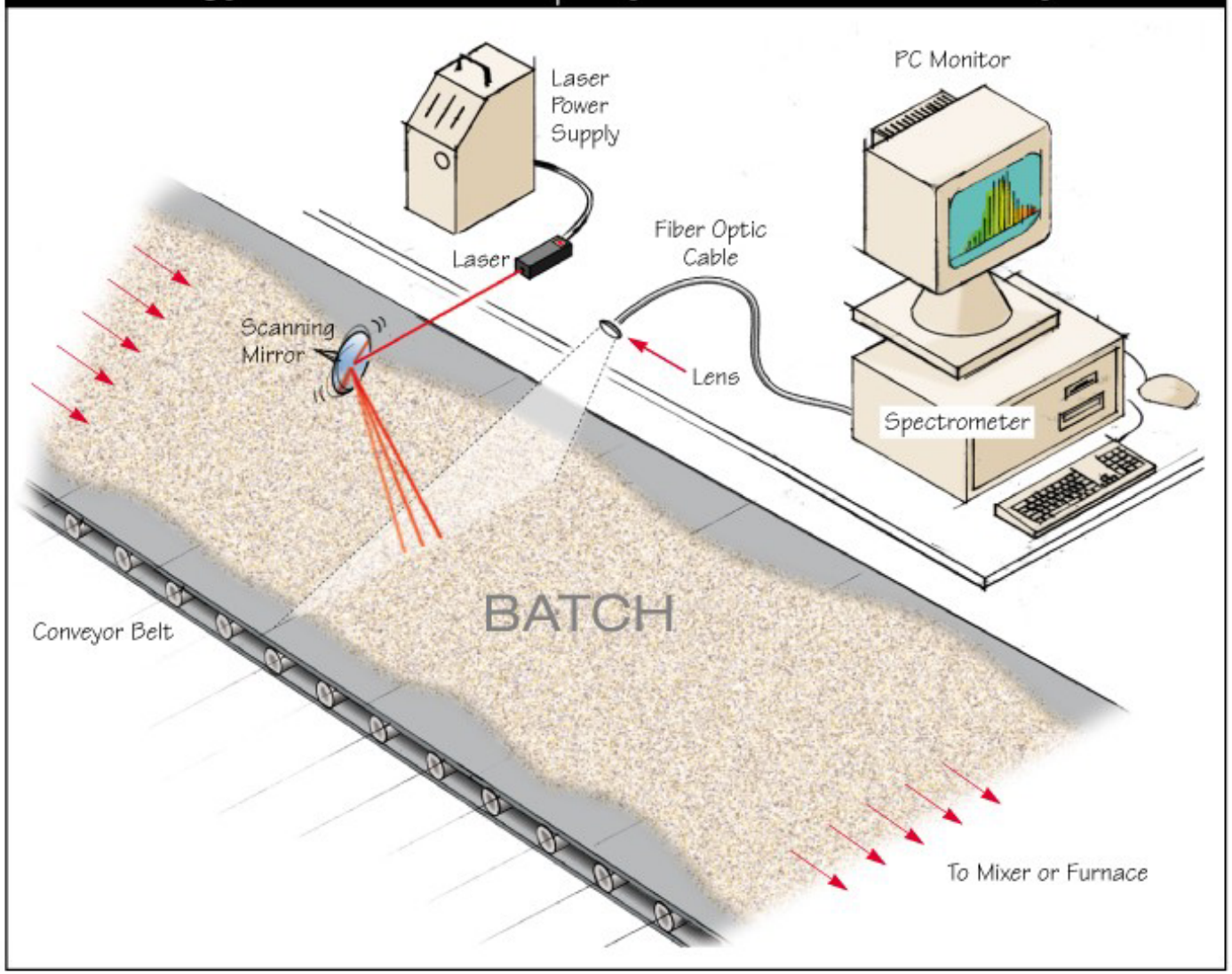
Benefits for PPG

- Knowledge of batch oxides is expected to significantly improve plant efficiency leading to:
  - Energy savings
  - Material savings
  - Overall financial savings
- Result: Payback on the instrument less than 1 year

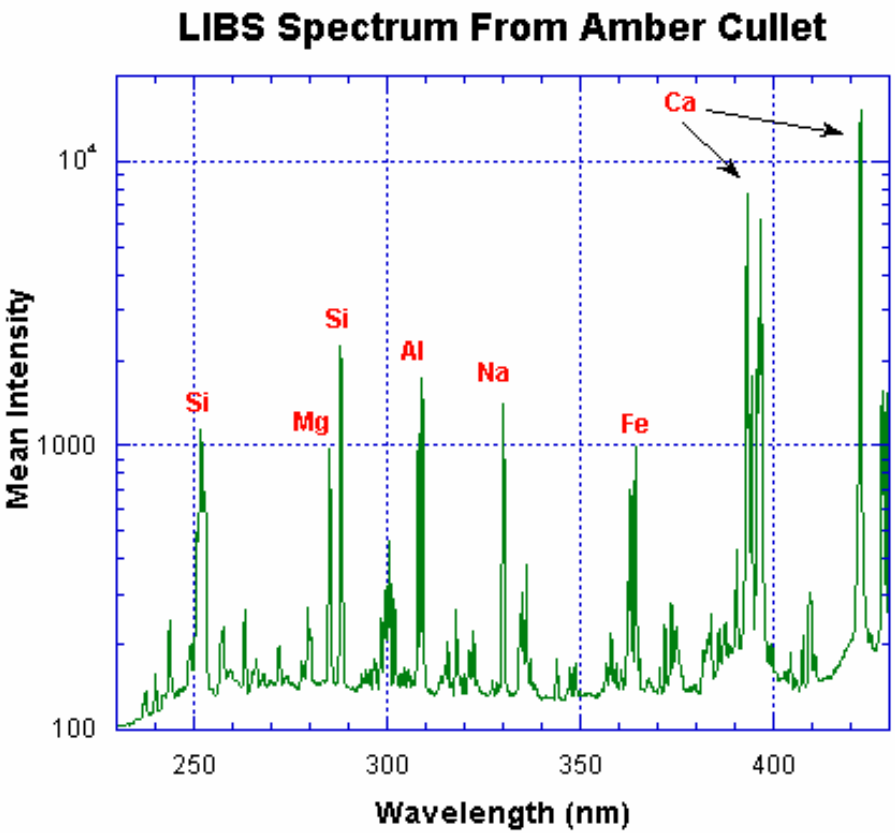
Goal

- Develop a plant instrument for rapidly measuring oxides in batch materials

Energy Research Company's LIBS Batch Analyzer



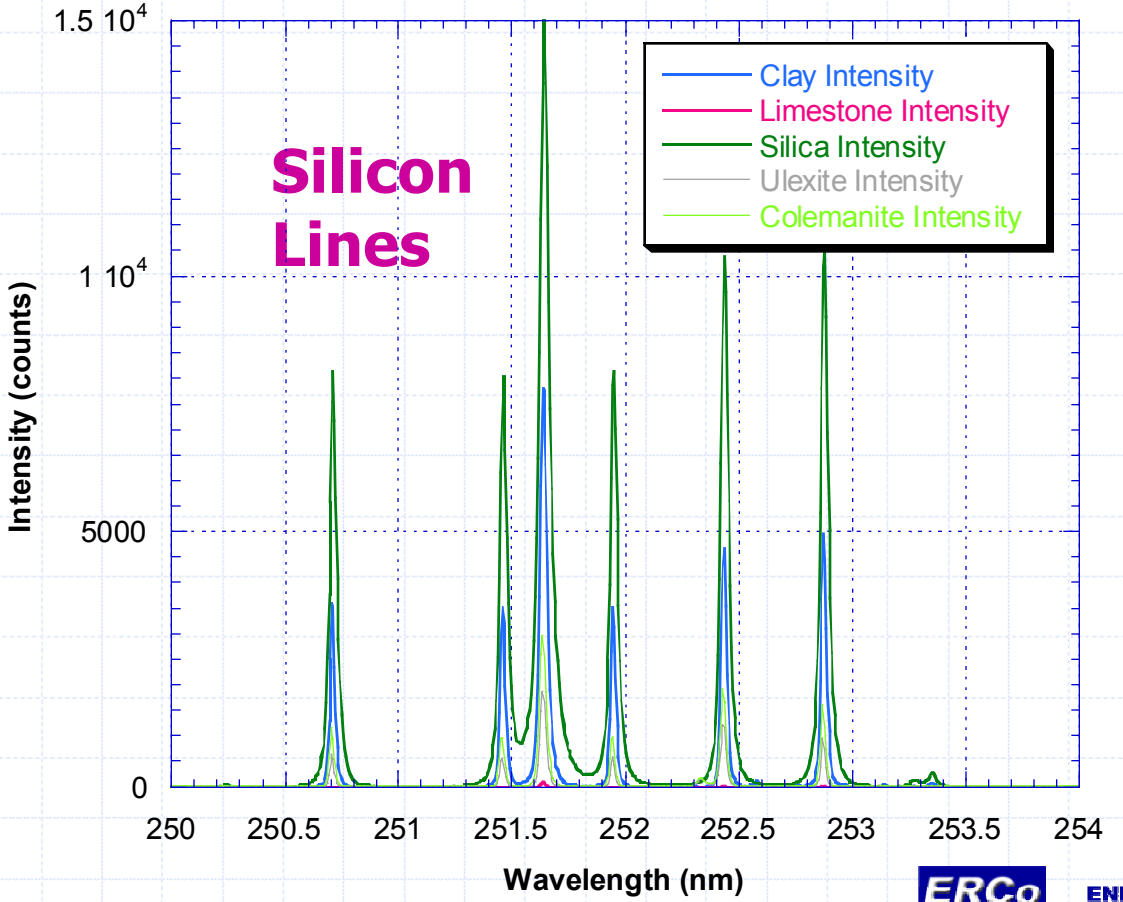
LIBS Technology



Spectrometer gathers the plasma light and spreads it, like a prism, into a spectrum where the contribution of each element can be seen

Batch Constituents

- LIBS Spectra Collected from Each Sample



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Batch Constituents

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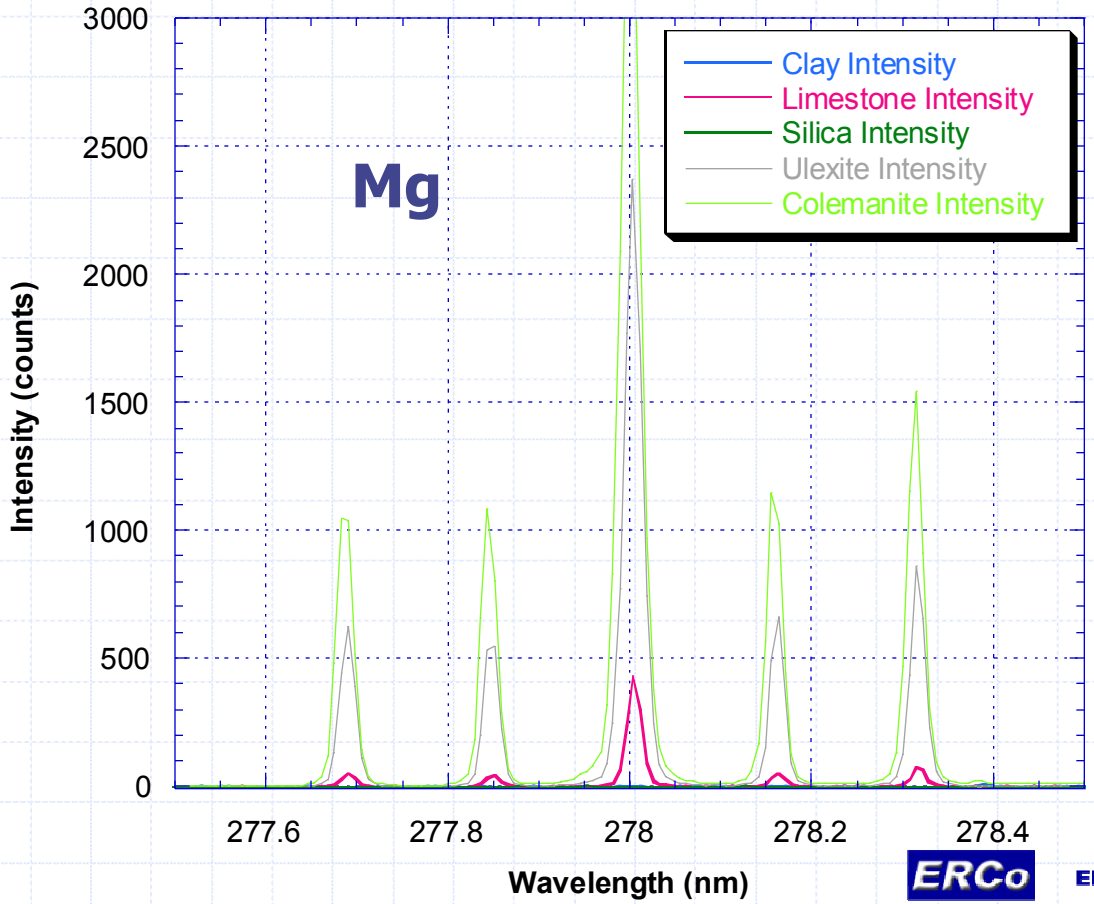

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LIBS Advantages

- Fast
  - A few minutes to perform a complete elemental analysis
- Accurate
  - Fractions of a percent to ppm
- Applicable to a wide range of materials
  - Glass, Batch
  - Metals, other solids, liquids, gases
- Proven
  - Extensive literature on use of the process in lab environments
  - **ERCo's** LIBS installation in aluminum plant production line

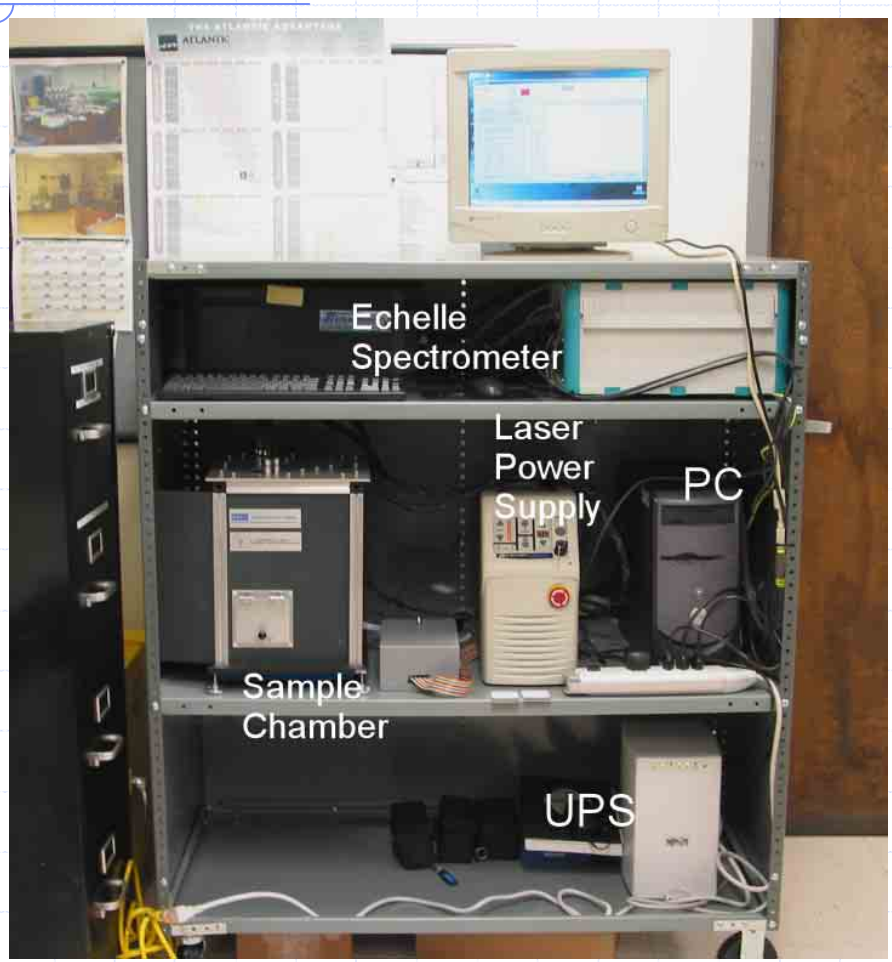
Experimental Results

- Apparatus and method
- Concentration measurements from PPG on-site test

Apparatus

- PPG requested an off-line analyzer
  - Ability to measure more than one material more important than continuous operation
    - Batch minerals such as ulexite, clay, limestone, silica
    - Limestone residue from scrubber system
    - Glass "buttons" taken from furnace
  - Batch materials likely not varying within any one 24 hour period
  - Potential for analysis of glass "buttons" in same instrument

ERCo LIBS Batch Analyzer at PPG's Chester Plant



- Laser
  - Big Sky Laser ULTRA-CFR, 1064nm
  - Up to 20 Hz , 50 mJ
  - Industrial Design
  - Low Maintenance
- Spectrometer
  - LLA ESA 3000
  - 200-850nm Echelle
  - $\lambda/\delta\lambda$=40,000 (7 pm @ 300nm)

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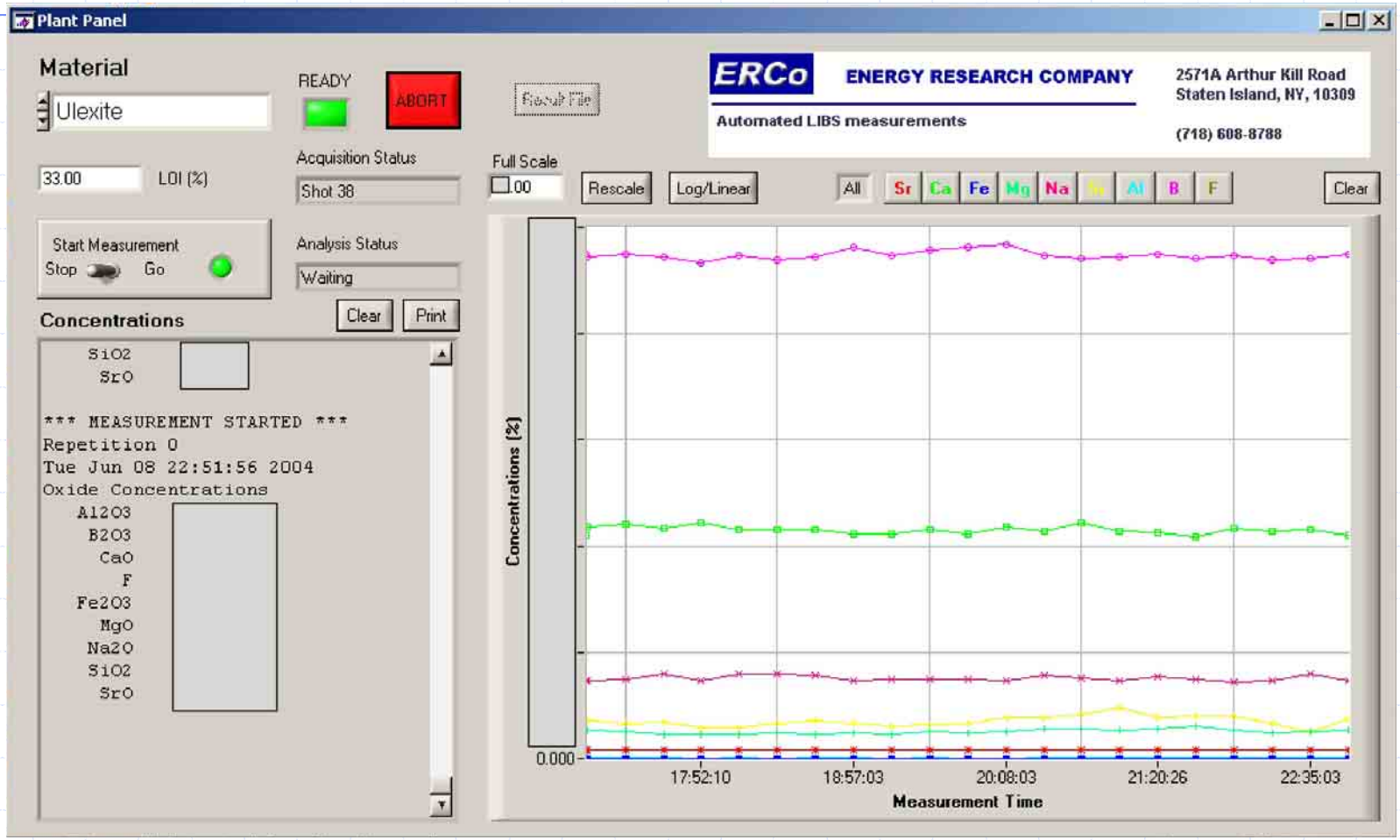
ERCo LIBS Batch Analyzer

- Sample Chamber
  - Contains laser head, motorized stages, and detection optics
  - Samples consist of a few grams on custom holder and placed inside the chamber door
- Completely Computer Controlled
- Laser light is contained – Eye Safe
- Low Maintenance

ERCo LIBS Batch Analyzer



Materials

- Materials choice determined by PPG
  - Single batch ingredient analysis more useful than mixed batch analysis
  - Ulexite is the top priority material
  - Limestone used in scrubber system is next most important

» Sensor will analyze all of PPG's materials of interest

PPG Testing Program

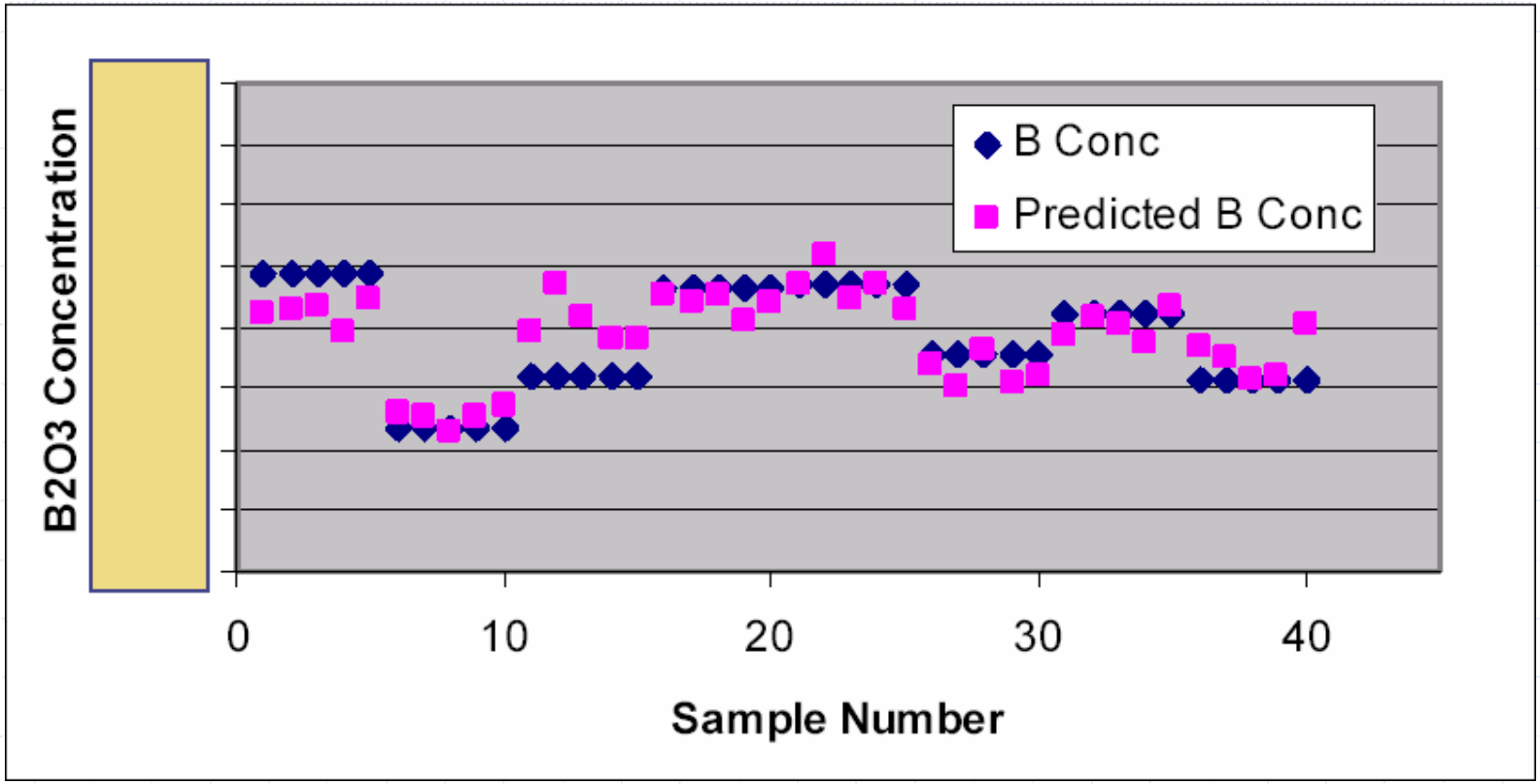
- Ulexite samples provided by PPG together with compositional analyses prior to testing
  - 3 different mine locations
  - Samples from same mine location illustrative of variability in shipments
  - Each delivery to PPG sampled only once by mining company

PPG Testing Program

- Ulexite samples provided to ERCo during testing without compositional analyses for “blind” testing for boron content

PPG Chester Test Results

Boron



Average difference: 0.54% ± 0.43%

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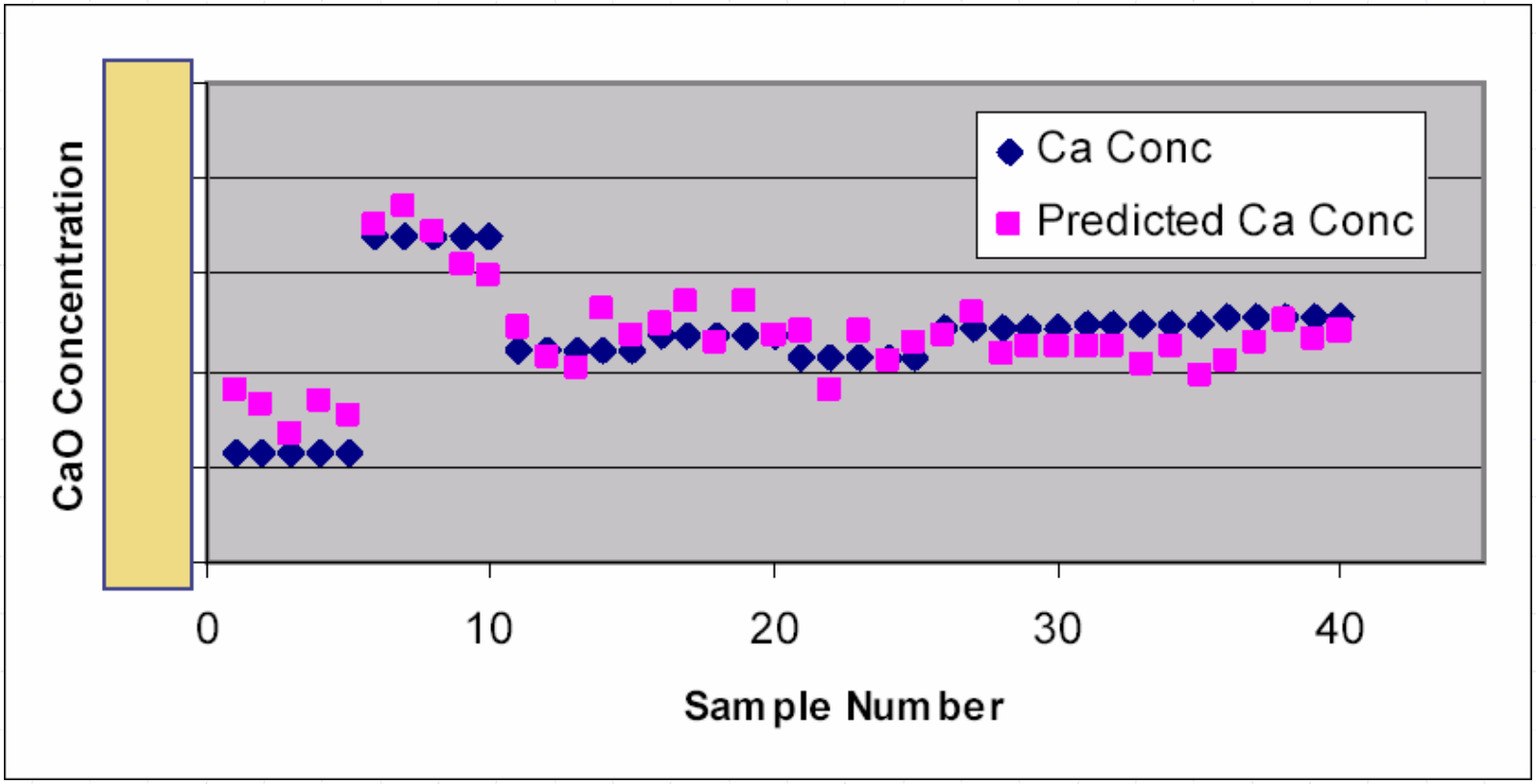
Calcium



Average difference: 1.51% ± 0.94%

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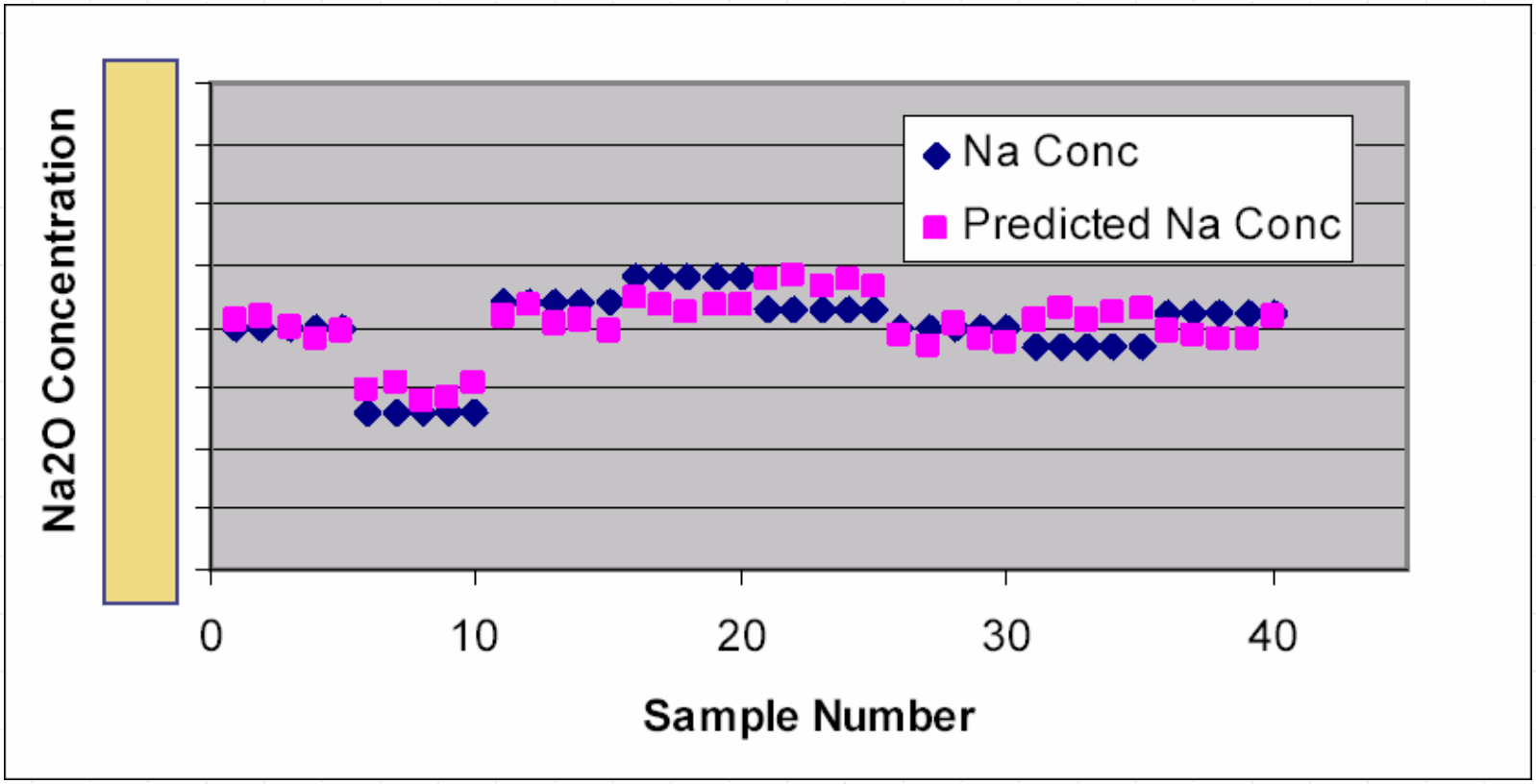
Sodium



Average difference: 2.75% ± 1.34%

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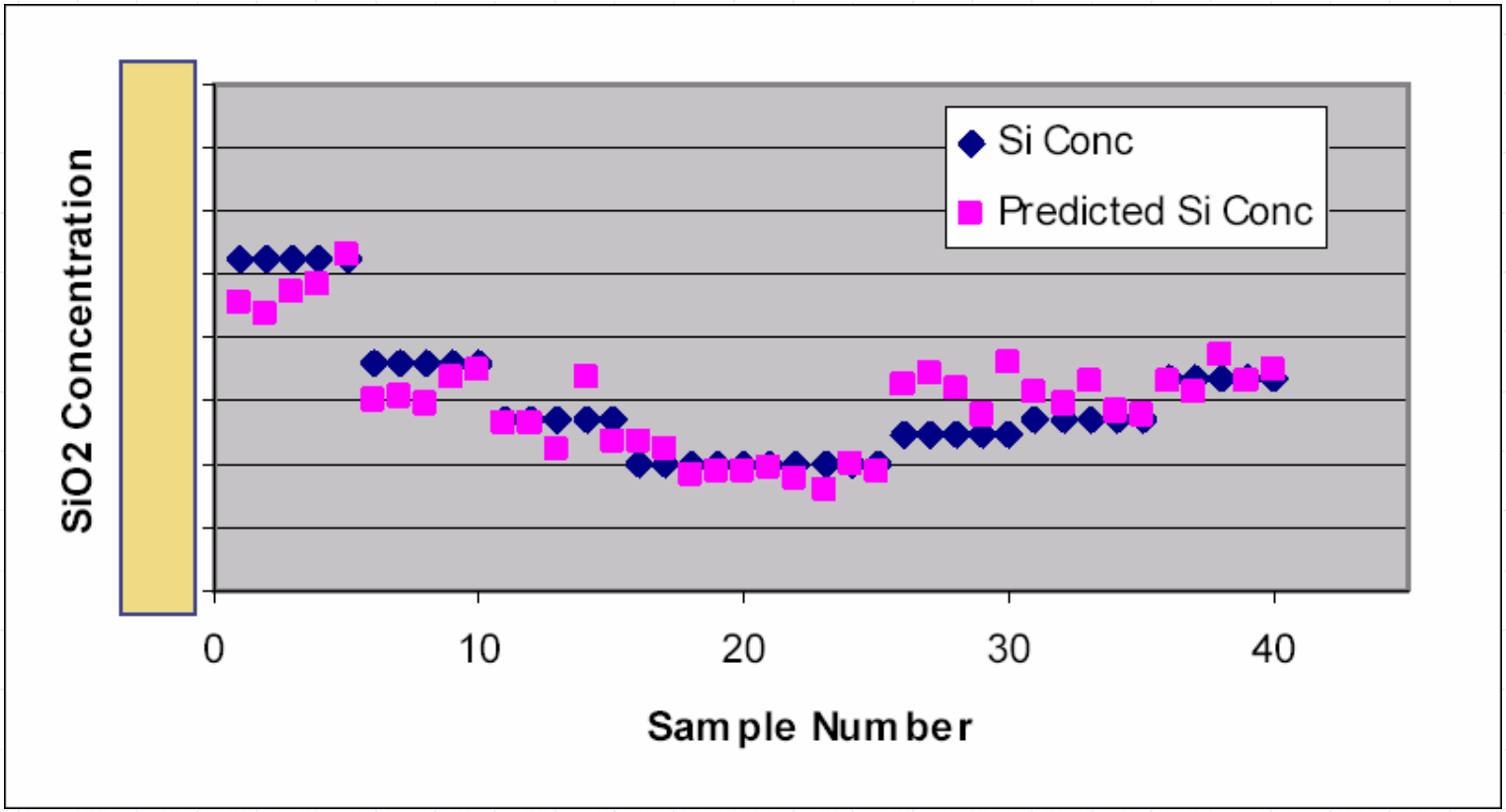
Silicon



Average difference: 4.98% ± 4.02%

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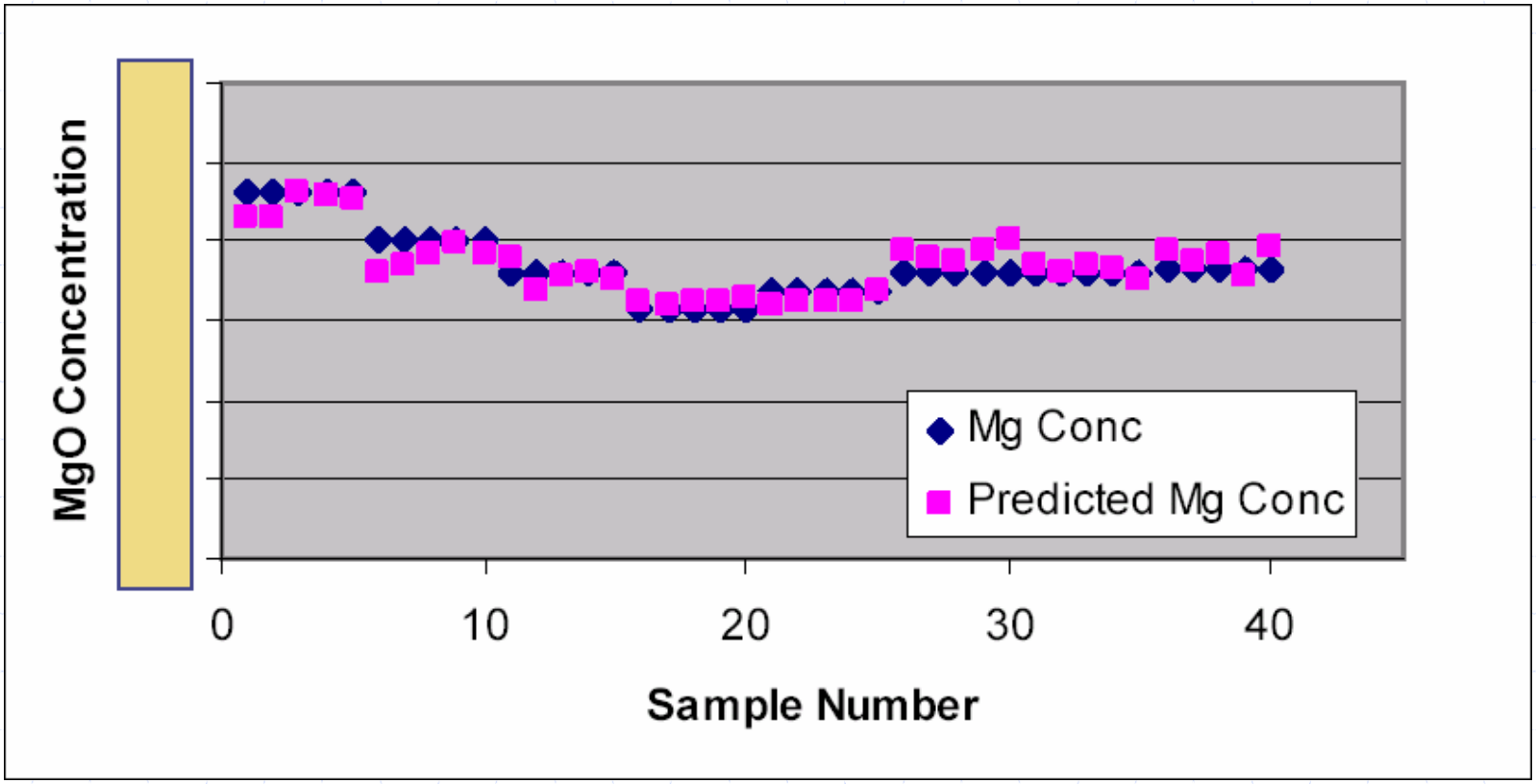
Magnesium



Average difference: 4.06% ± 2.72%

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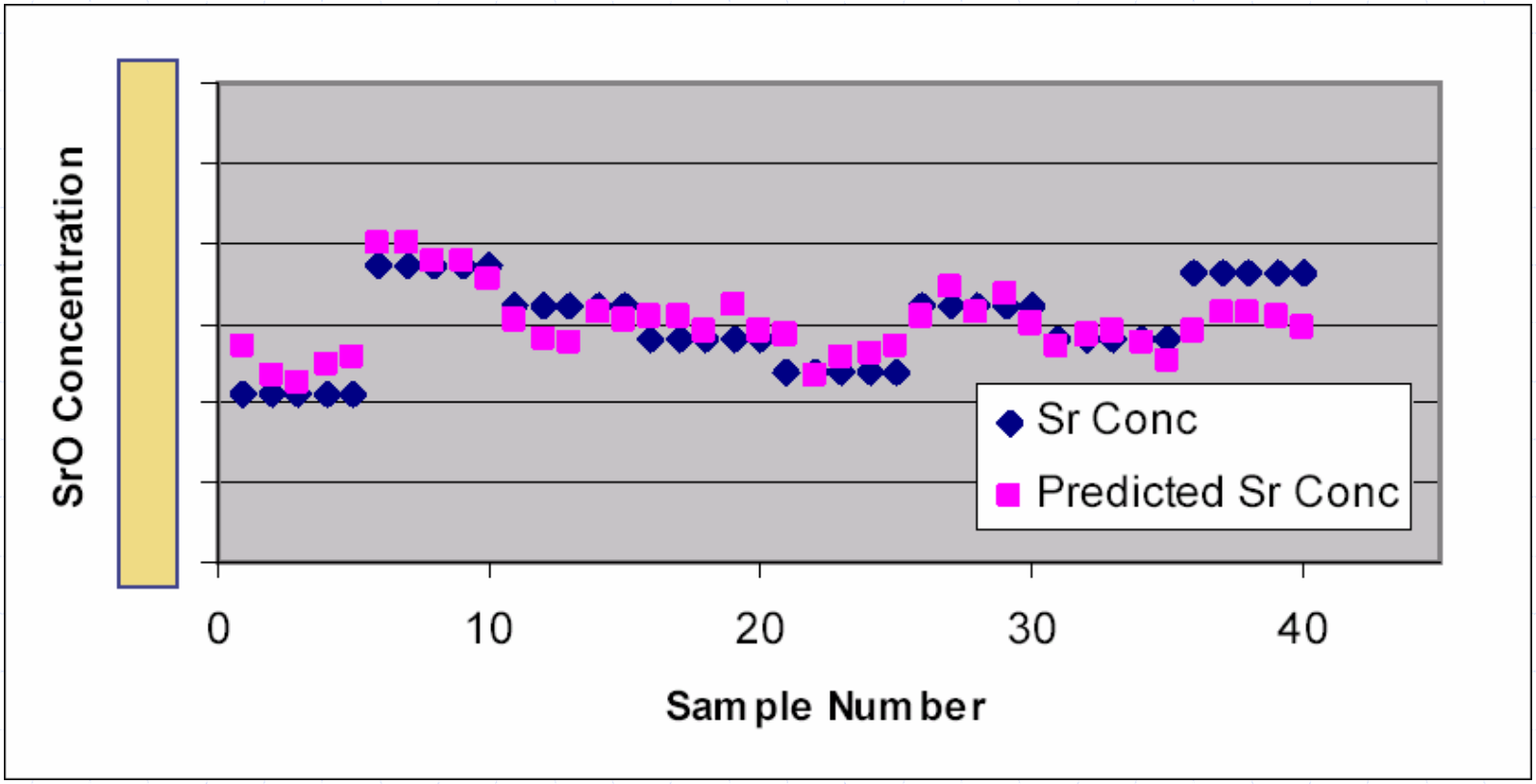
Strontium



Average difference: 0.026% ± 0.018%

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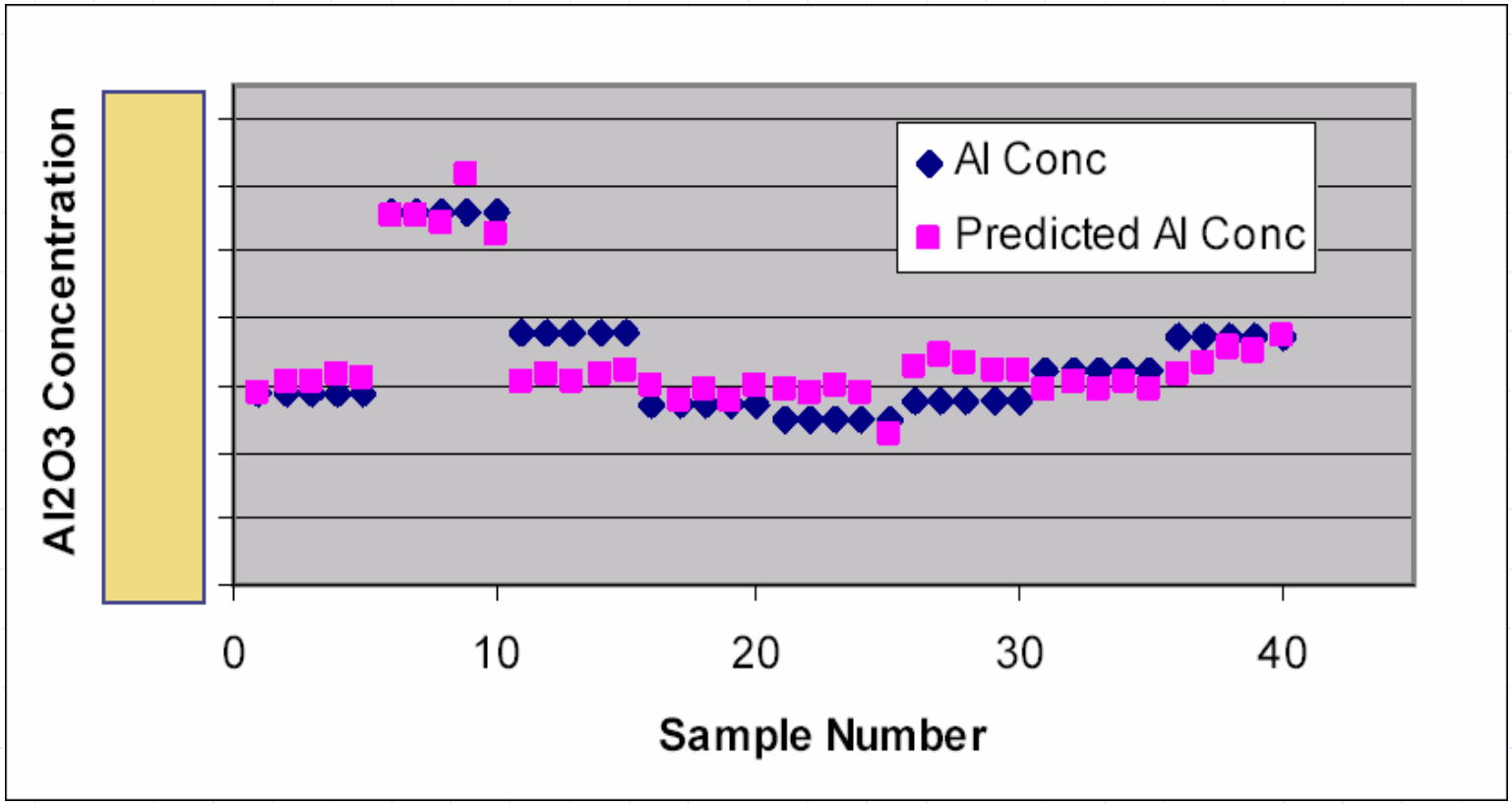
Aluminum



Average difference: 0.007% ± 0.004%

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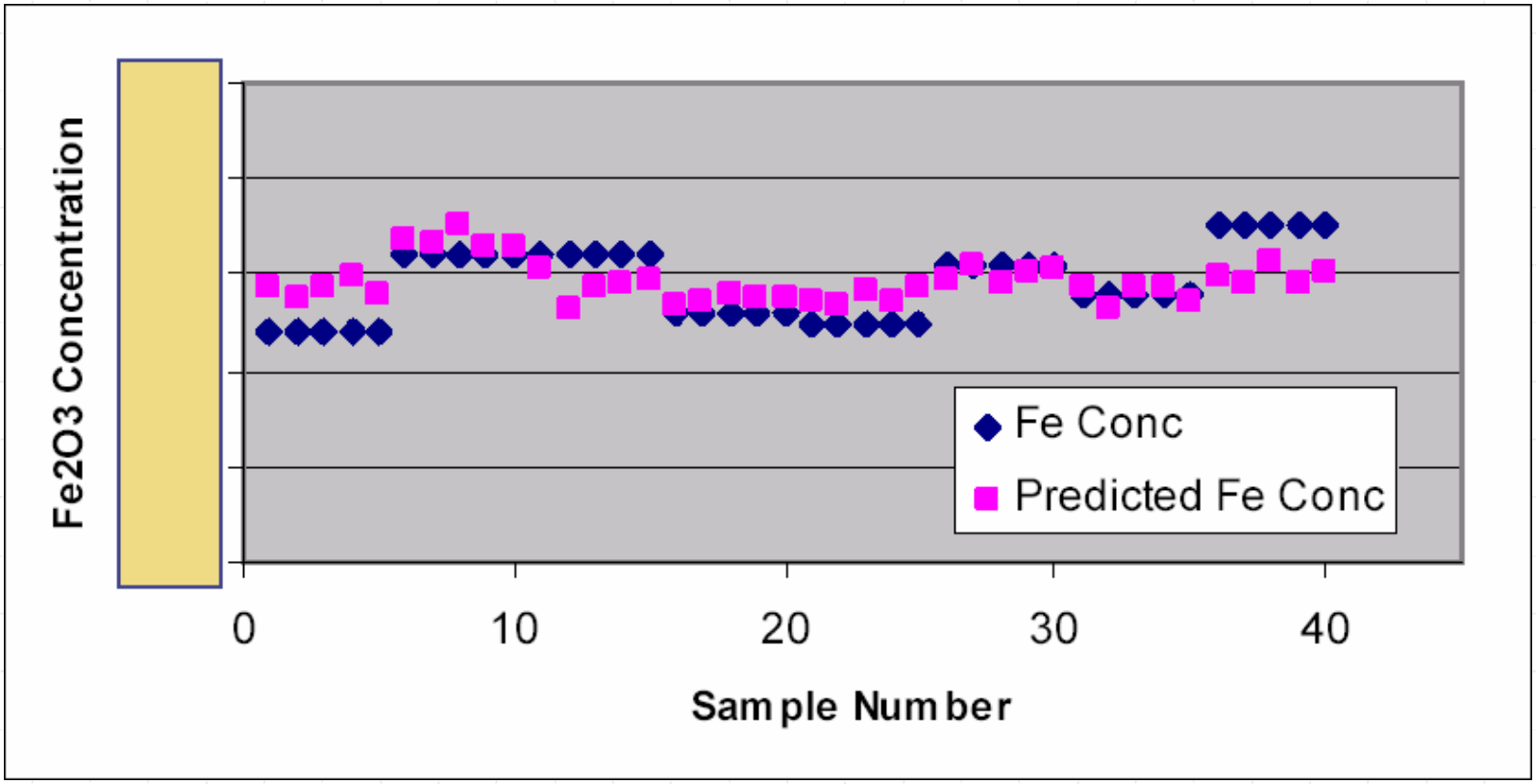
Iron



Average difference: 0.003% ± 0.002%

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"Blind" Ulexite Samples

- Samples A & B analyzed twice
- 0.3% change or variability in boron measurement not significant

Test Sample (blind)	Boron Concentration Difference
A	0.00 %
A	0.03 %
B	0.24 %
B	0.30 %

PPG Test Summary

- Equipment successfully transported and installed
- Sensor operation is reliable
  - 20 days equivalent testing performed
- PPG personnel satisfied with accuracy, repeatability, ease of use
- "Blind" tests successful

PPG Test Follow On Program

- Return to plant in July with improved sensor for long term testing by PPG employees
- Add capability for limestone residue analysis
- Add capability for glass “button” analysis
- Add capability for other batch materials

Clay Results (% difference)

El.	A	B	C	D	E	Avg.
Si	0.21	2.64	2.64	2.16	2.37	**2.00**
Al	0.10	1.38	0.65	1.42	1.93	**1.10**
Ti	0.13	0.04	0.04	0.37	0.23	**0.16**
Fe	0.08	0.01	0.09	0.09	0.06	**0.07**
Na	0.03	0.03	0.03	0.03	0.03	**0.03**

Major Minor

Silica Results (% difference)

El.	A	B	C	D	E	Avg.
Si	0.10	0.20	0.23	0.18	0.18	**0.18**
Al	0.05	0.02	0.04	0.01	0.01	**0.03**
Ti	0.01	0.01	0.01	0.00	0.00	**0.03**
Fe	0.01	0.02	0.02	0.00	0.00	**0.01**

Major Minor

Limestone Results (% difference)

El.	A	B	C	D	E	Avg
C	1.28	0.62	1.54	1.59	0.09	**1.02**
Ca	0.26	0.09	0.57	0.41	0.18	**0.30**
Mg	0.00	0.00	0.01	0.01	0.00	**0.00**
Al	0.01	0.01	0.00	0.01	0.01	**0.01**
Si	0.08	0.07	0.10	0.10	0.13	**0.10**
Fe	0.00	0.00	0.01	0.04	0.02	**0.01**

Major Minor

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Future Interest

- Measure Concentrations of Molten Glass in Tank in Real-Time, In-Situ
- LIBS probe patent granted
- NYSERDA seed money received in 2nd quarter ’04 towards a furnace suitable for extensive molten glass LIBS work

Molten Glass Data

Element	Result	% Outside Range
Si	Good	0.81
Na	Good	
Ca	Good	
Mg	Out	5.2
Ba	Out	2.8
Fe	Good	
Sr	Good	
Mn	Good	

Actual Concentrations Proprietary

Glass Analyzed Before And After Melting

Industrial Installation

- Molten Aluminum LIBS Probe Installation at Commonwealth Aluminum Newport Rolling Mill

LIBS Sensor for Molten Aluminum

Commercial Installation

- Industrial Cabinet

- Sealed, Air Conditioned, EMI Shielded

Molten Aluminum Concentrations

Aluminum Alloy 3105

	Al	Cu	Fe	Mg	Mn	Si	Cr
LIBS Average	97.87	0.17	0.65	0.47	0.52	0.28	0.04
Commonwealth Average	97.56	0.18	0.65	0.49	0.56	0.30	0.05
% Difference	0.32	5.6	0.0	4.1	7.1	6.7	20.0
LIBS RSD	0.09	5.0	4.87	11.61	4.54	6.29	5.52
Commonwealth RSD	0.03	3.51	3.65	1.53	3.57	2.25	2.17

Discussion and Conclusions

- ERCo's LIBS Batch Analyzer proven in role as rapid glass batch analysis
- Follow on testing and upgrades to continue in FY05
- Oxide concentrations in PPG batch and other materials measured using ERCo's C-LESS™ method
- Molten glass preliminary concentration measurements successful

Schedule

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	**Laboratory Development**			
1.1	Facility Modification	9/30/01	9/30/01	
1.2	Testing	3/31/02	2/28/02	
1.3	Initial Software Development	3/31/02	3/31/02	
1.4	Performance Evaluation	3/31/02	3/31/02	
2	**Sensor Fabrication**			
2.1	Facility Construction	9/30/02	8/31/02	
2.2	LIBS Testing	8/31/03	5/31/04	
2.3	Modifications to PPG Facility	12/31/03	3/31/04	Not necessary
2.4	Procure System	6/30/04	5/31/04	
3	**Sensor Testing**			
3.1	Testing at PPG	2/28/05		Commenced in 6/04
3.2	System Integration	12/31/04		

Commercialization Plans

- Intellectual Property Consisting of Issued Patent and Trade Secrets
- Commercialization Study Completed
- Licensee Discussions Underway
  - ERCo Fabricates, Services, and Installs
  - Licensee Sells
  - Approach Fits in with ERCo's Business Model for All of its LIBS Products