# Achieving Accurate Chemical Characterization Using Laser Ablation Direct Solid Sampling

**Richard E. Russo**

Lawrence Berkeley National Laboratory

Berkeley, CA 94720

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# Characterization in the EM Program

- **Advanced characterization technology needed for wastes and contaminants:**
  - first step in the clean-up scenario
  - accelerate treatment and immobilization programs

- **Characterization listed as high priority in 6 of the 7 EM problem areas:**
  - High Level Waste
  - Spent Nuclear Fuel
  - Mixed Waste
  - Nuclear Materials
  - Remedial Actions
  - Decontamination and Decommissioning (including LA cleaning)

# Overview

**Laser ablation is an advanced analytical technology ideally suited for characterization within the DOE EM program.**

**The EMSP research project was initiated to understand and develop laser ablation sampling as an accurate and sensitive analytical technology for rapid, safe, and cost effective characterization of DOE EM wastes.**

- **EMSP - fundamental and applied science**
- **Example EM applications**
  - **Savannah River Prototypic Waste Glass**
  - **$PuO_2$ for MD program**
  - **Refractory Pressed Pellets**

# Laser Ablation for Characterization

» Any solid (liquid) sample!

» Any sample form!

» No sample digestion!

» No solvents or additional waste!

» Minimal sample quantity (μg - ng)!

» Direct multi-component analysis!

» Spatial (micro) analysis!

» Remote analysis (LIBS)!

# Research Issues

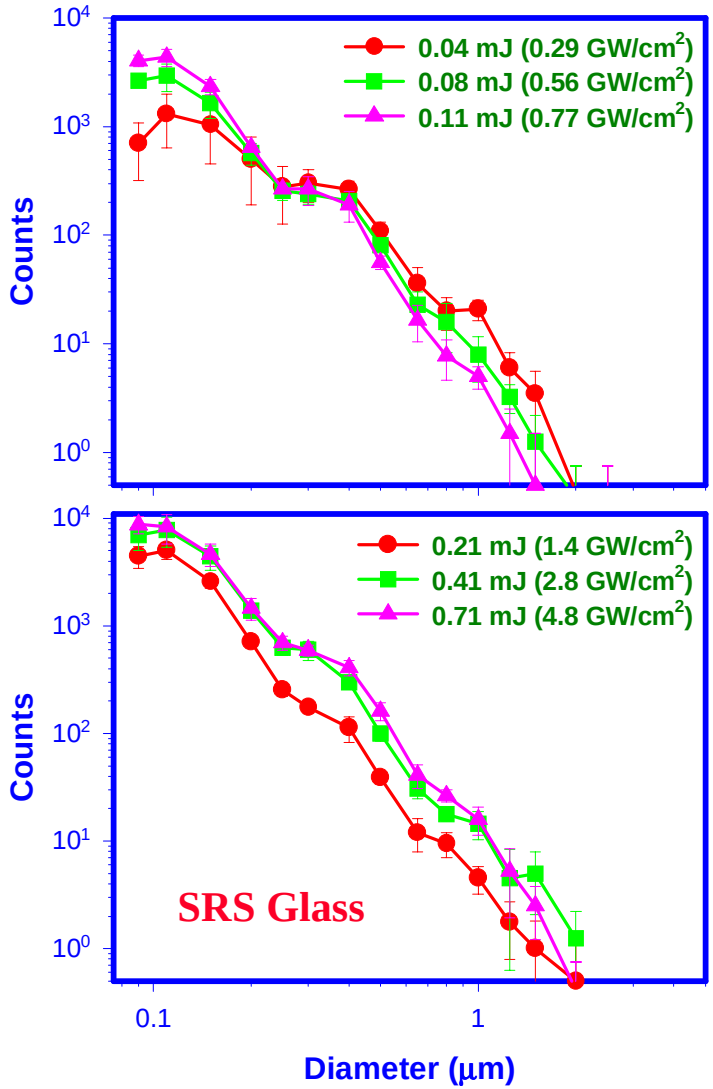
Matrix matched standards will not be available!

- Even with conventional analytical methods, need good standards!
  - Many critical issues (contamination, acid waste)!

## Laser Ablation Sampling

- **Quantitative Analysis - calibration**
- **Matrix Matching - chemistry**
- **Ablation Rate (quantity)**
- **Fractionation (stoichiometry)**
- **Particle Size Distribution - transport**
- **Chemical Matrix Effects in the ICP**
- **Chemical Matrix Effects in the MS**

# Particle Size Distribution




**Particle size distribution influences transport and therefore calibration for non matrix-matched standards.**

**Particle size distribution is governed by the laser and sample conditions.**

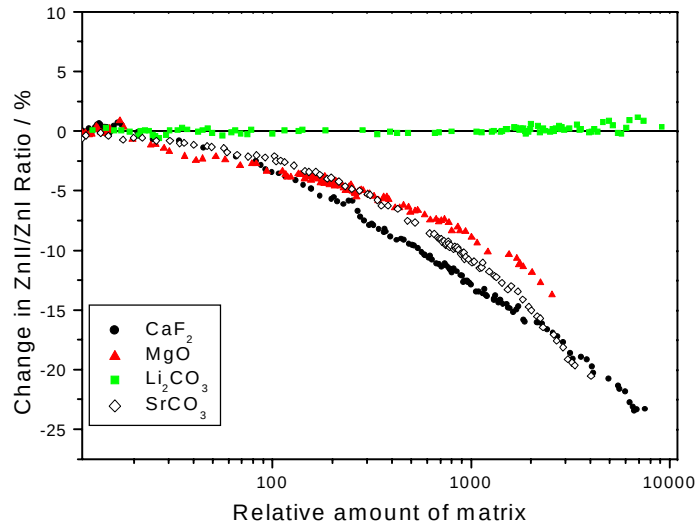
**Laser conditions established such that particle size distribution was similar for various samples (glasses and alloys).**

**The research established that changes in transport efficiency were nominal and can be neglected for calibration when using non matrix-matched standards!**

# Accurate ICP-MS Response

**Issue: 'mass loading'**

- ICP-MS signal is proportional to amount and concentration of sample.
- ICP conditions (temperature and electron number density) may be effected by chemistry of the sample.
- Ionic-to-atomic line intensity ratio changes if ICP effected by chemistry.




**Fundamental:**

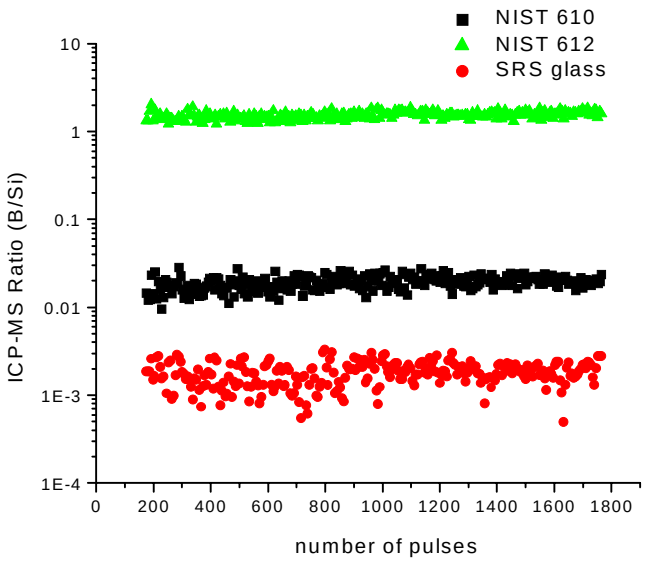
- The mass loading effect correlates to 2nd ionization potential but not 1st ionization potential.
- Energy of doubly charged ions > IP of Ar and < He. Change in plasma equilibrium.

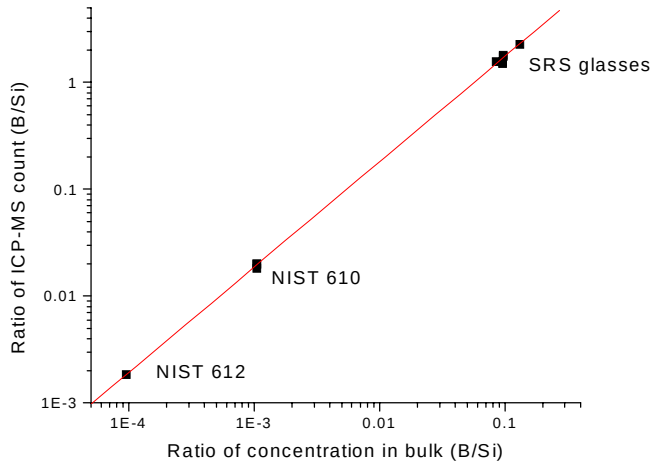
**Solution:**

- **Using Helium in the central channel of the ICP suppress the mass loading effect!**

# Characterization of SRS Glasses

- **Using 266nm laser, internal standard (Si) was needed for quantitative analysis.**
- **Fractionation was not an issue at optimum irradiance (2 GW/cm$^2$).**
- **The quantity of mass ablated was influenced by the matrix of SRS glasses compared to the NIST standards.**
- **Accurate quantitative measurements were achieved using NIST and internal standards.**



# Quantitative Analysis of SRS Prototypic Glasses Using NIST Standards @ 213nm

**Accurate quantitative analysis of SRS prototypic glasses without an internal standard by using NIST glass standards and 213nm laser wavelength for ablation!**

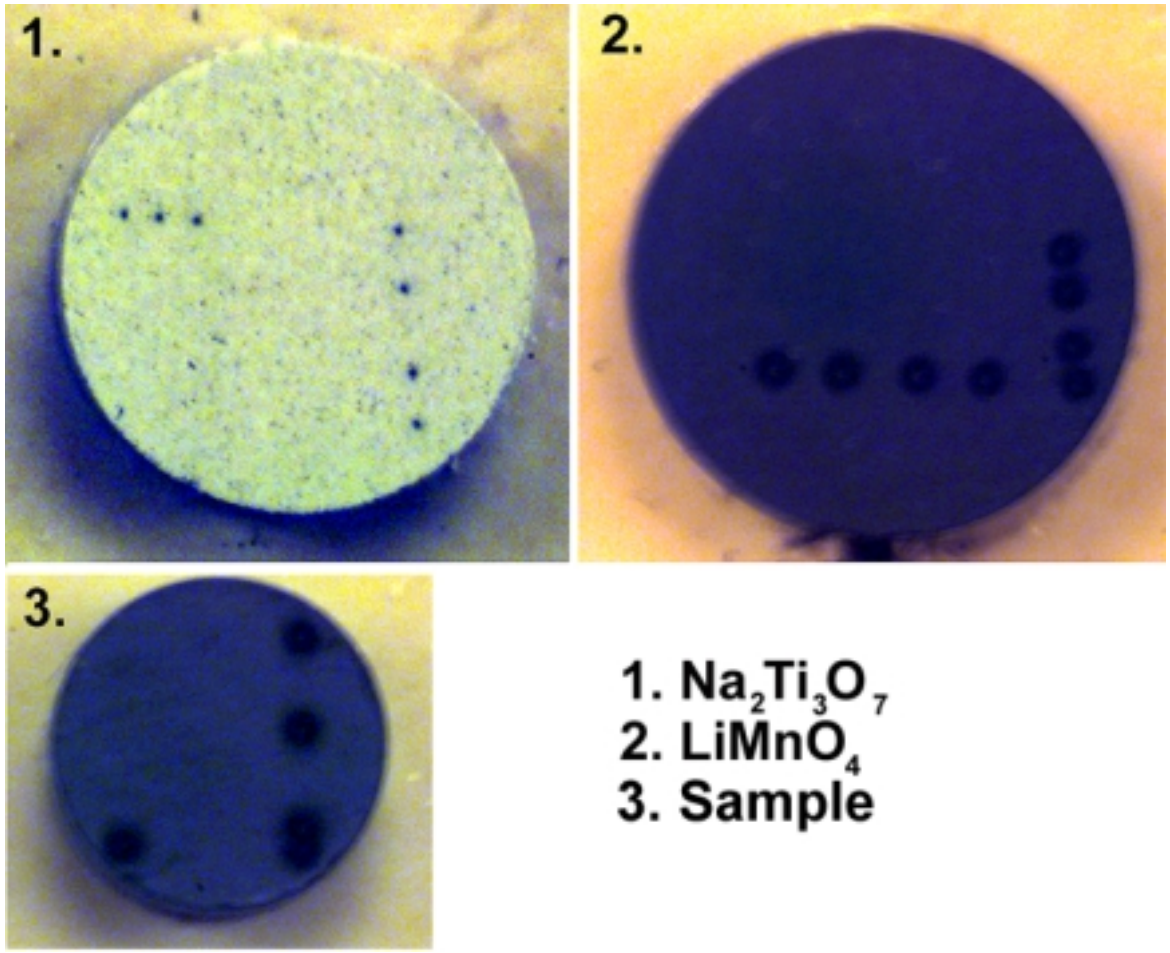
**Matrix dependence reduced at 213nm. Fractionation and matrix matching not critical for analysis.**

| Element | SRS 131FE | LA-ICP-MS | SRS 165AV | LA-ICP-MS | SRS 200AL | LA-ICP-MS |
|---|---|---|---|---|---|---|
| Li | 1.89 ± 0.01 | 1.61 ± 0.18 | 2.33 ± 0.01 | 3.60 ± 0.39 | 1.23 ± 0.02 | 1.12 ± 0.14 |
| K | | 0.056 ± 0.020 | | 0.170 ± 0.023 | 2.59 ± 0.04 | 2.48 ± 0.23 |
| Ti | 0.030 ± 0.006 | 0.033 ± 0.005 | | 0.035 ± 0.006 | 1.02 ± 0.02 | 0.89 ± 0.07 |
| Mn | 0.72 ± 0.01 | 0.91 ± 0.06 | 1.99 ± 0.02 | 2.67 ± 0.27 | 1.93 ± 0.03 | 1.87 ± 0.10 |
| Fe | 12.2 ± 0.13 | 11.9 ± 1.4 | 8.11 ± 0.07 | 8.6 ± 1.3 | 3.12 ± 0.03 | 2.43 ± 0.24 |
| Ni | 2.01 ± 0.02 | 2.1 ± 0.6 | 0.79 ± 0.01 | 1.08 ± 0.14 | 0.48 ± 0.01 | 0.46 ± 0.37 |
| Zr | 0.64 ± 0.01 | 0.660 ± 0.035 | 0.56 ± 0.01 | 0.51 ± 0.07 | 0.021 ± 0.007 | 0.010 ± 0.001 |
| Pb | | | | | | 0.035 ± 0.015 |

# Quantitative Analysis of Refractory Pressed Pellets

**Samples cannot be acid digested and analyzed by conventional methods - high TiO concentration prevents accurate dissolution**

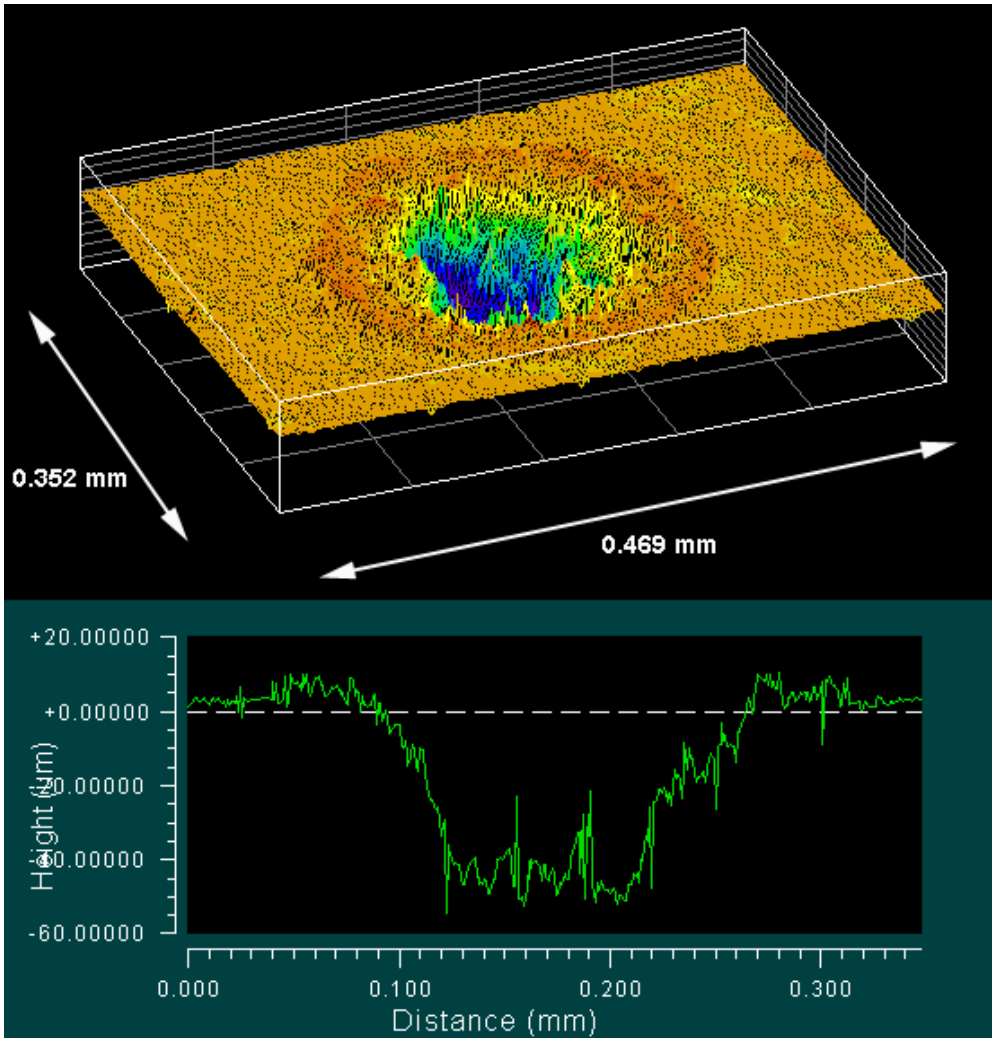
- **Single standard**
- **Non matrix matched standard**
- **Differences in ablation behavior - quantity**
- **Measurement of crater volume allows calibration when changes in mass occur between standard and sample**



# Ablated Mass Quantity

- **When the quantity of mass ablated is matrix dependent, the volume of the crater can be measured for calibration.**

- **Laser Energy 150 μJ**
- **Beam Spot Size *ca.* 200 μm**



# Quantitative Analysis of Refractory Pressed Pellets

**Non Matrix-matched standards, Single point calibration.**
**Use crater measurements for mass ablated.**
**No fractionation!**

| Sample | Li, % | | Ti, % | | Mn, % | |
|---|---|---|---|---|---|---|
| | Measured | Expected | Measured | Expected | Measured | Expected |
| Li11 | 4.2 | 3.42 | 7.6 | 5.91% | 64.4 | 54.80% |
| Li22 | 3.8 | 3.45 | 20.4 | 11.92 | 68.6 | 48.45% |
| Li33 | 2.8 | 3.48 | 34.8 | 18.03 | 51.6 | 41.99% |
| Li44 | 3.1 | 3.51 | 27.9 | 24.25% | 30.0 | 35.41% |
| Na11 | ND | 0.00 | 8.4 | 5.47% | 59.4 | 50.78% |
| Na22 | ND | 0.00 | 14.2 | 11.03% | 46.6 | 44.87% |
| Na33 | ND | 0.00 | 17.7 | 16.69% | 30.9 | 38.86% |
| Na44 | ND | 0.00 | 28.0 | 22.43% | 27.4 | 32.74% |
| 1a | ND | 0.00 | ND | 0.00% | ND | 0.0 |
| 1b | 2.3 | 3.39 | ND | 0.00% | 51.2 | 61.05% |

**Accuracy can be improved by raster scanning laser beam (homogeneous)**

# Characterization of $PuO_2$ Surrogates

- **Direct elemental characterization for the DOE materials disposition (MD) program presents unique challenges for analytical chemical analysis**
  - **Successful Pu disposition by immobilization into a glass or ceramic form requires accurate and precise knowledge of sample impurities.**
  - **Analysis of Pu samples by conventional liquid nebulization requires elaborate and time consuming sample dissolution procedures.**
  - **Dissolution is complicated due to a refractory nature of the samples and the range of elemental contaminants.**

  - **Laser ablation sampling can provide direct elemental characterization of Pu powder samples without dissolution procedures.**
  - **Need to establish laser and sample (pressed pellets) conditions for quantitative analysis**

# $CeO_2$ ($PuO_2$ Surrogate) Sample Preparation

**Binder (Teflon)**

**+**

**Internal Standard ($In_2O_3$)**

**+**

**Base Oxide ($CeO_2$)**

**+**

**Oxide Mix (Analytes)**

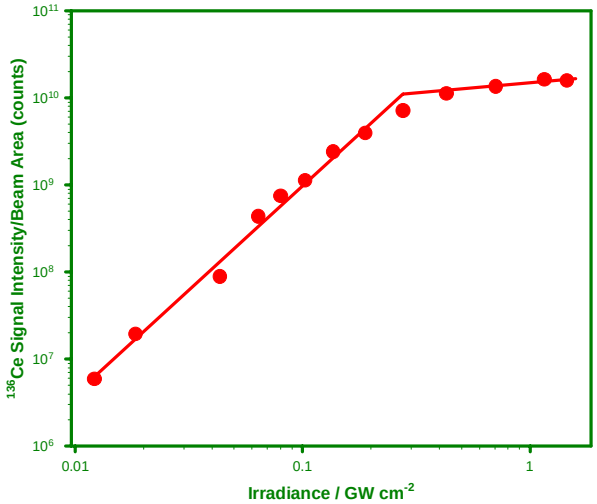
**⇓**

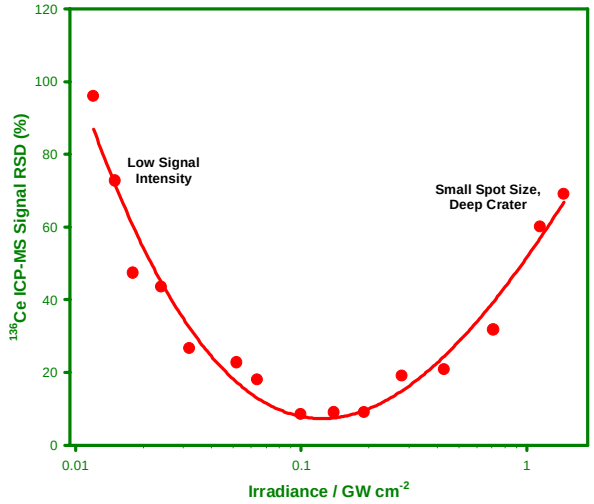
**Mixing (Mixer mill, agate vessels, 50 min)**

**⇓**

**Pressing Pellets**

# Selecting Laser Ablation Conditions: $CeO_2$ Pressed Pellets

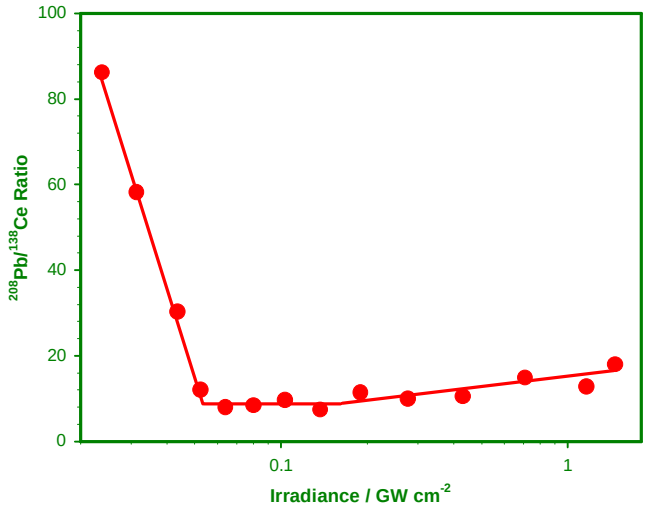



**Sensitivity**

**Signal Stability**

**Result: 0.1 - 0.2 Gw/cm$^2$ excellent irradiance for analysis!**



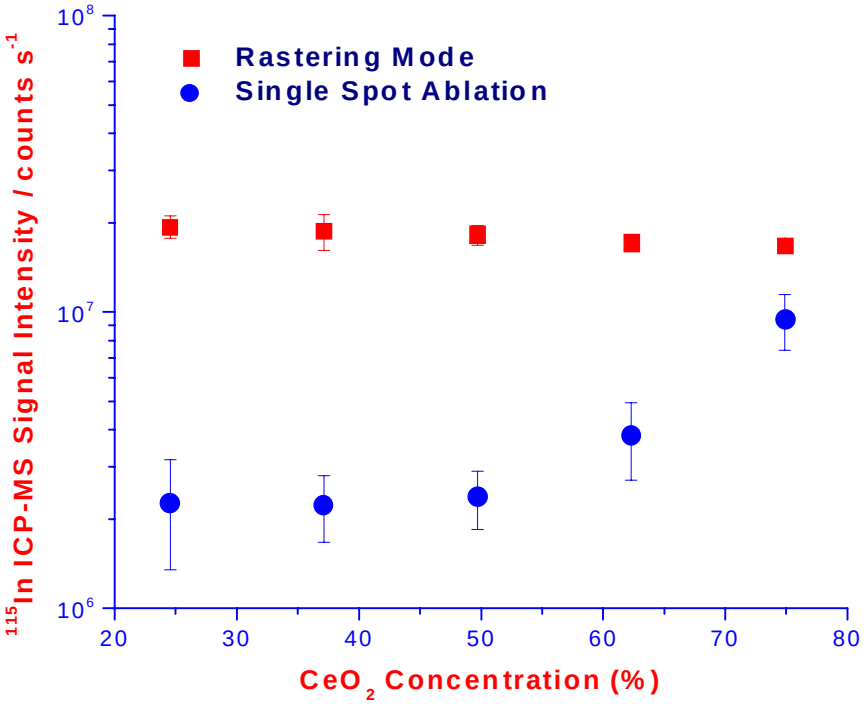

**Stoichiometry**

# Quantitative Analysis: Calibration

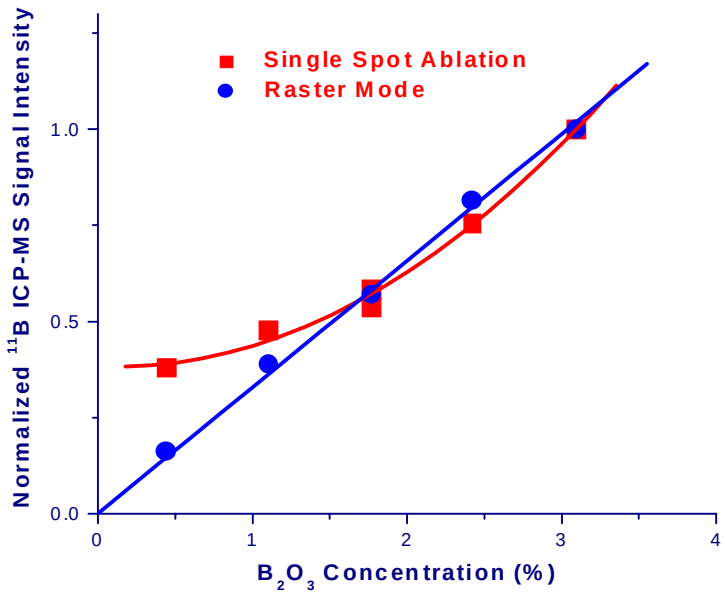
**Problem: quantity of mass ablated per pulse changes as as crater develops in the $CeO_2$ samples.**

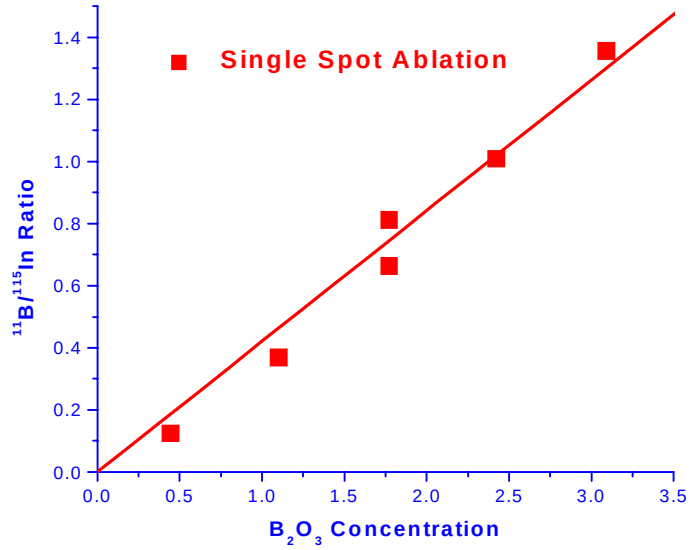
**Same indium concentration in each sample.**

- **Single spot ablation - crater effect**
- **Raster mode - eliminate effects (crater effect)**



# Quantitative Analysis




**When ablation is matrix dependent, the amount of mass ablated will depend on the aspect ratio of the crater. Calibration will be non linear and an internal standard will be required. By raster scanning the laser beam and eliminating a high aspect ratio crater, calibration can be achieved without an internal standard.**

# Quantitative Analysis of $CeO_2$ Pressed Pellets

**Laser Ablation ICP-MS Quantitative Analysis of Pressed Pellets.**
**(Nd:YAG 266 nm, 90 s pre-ablation, 10 s integration)**

| Element | Target con., g/g | Base oxide | | | |
|---|---|---|---|---|---|
| | | $CeO_2$ | $Bi_2O_3$ | $PtO_2$ | MgO |
| $B_2O_3$ | 0.0176 | 0.0160 ± 0.0041 | 0.0126 ± 0.0028 | 0.0278 ± 0.0045 | 0.0158 ± 0.0038 |
| NaCl | 0.0176 | 0.0212 ± 0.0081 | 0.0104 ± 0.0052 | 0.0376 ± 0.0098 | 0.0630 ± 0.0166 |
| MgO | 0.0176 | 0.0186 ± 0.0066 | 0.0146 ± 0.0027 | 0.0153 ± 0.0030 | |
| $Al_2O_3$ | 0.0176 | 0.0187 ± 0.0067 | 0.0141 ± 0.0033 | 0.0148 ± 0.0027 | 0.0087 ± 0.0013 |
| $SiO_2$ | 0.0176 | 0.0162 ± 0.0063 | 0.0050 ± 0.0044 | 0.0264 ± 0.0064 | 0.0504 ± 0.0180 |
| $CaF_2$ | 0.0176 | 0.0193 ± 0.0074 | 0.0133 ± 0.0019 | 0.0152 ± 0.0030 | 0.0086 ± 0.0012 |
| $Cr_2O_3$ | 0.0176 | 0.0178 ± 0.0062 | 0.0141 ± 0.0030 | 0.0140 ± 0.0026 | 0.0123 ± 0.0032 |
| $Fe_2O_3$ | 0.0176 | 0.0178 ± 0.0062 | 0.0130 ± 0.0030 | 0.0146 ± 0.0024 | 0.0176 ± 0.0031 |
| NiO | 0.0176 | 0.0181 ± 0.0064 | 0.0141 ± 0.0038 | 0.0117 ± 0.0022 | 0.0145 ± 0.0037 |
| ZnO | 0.0176 | 0.0171 ± 0.0058 | 0.0175 ± 0.0031 | 0.0201 ± 0.0033 | 0.0159 ± 0.0011 |
| $Ga_2O_3$ | 0.0176 | 0.0185 ± 0.0066 | 0.0146 ± 0.0036 | 0.0154 ± 0.0030 | 0.0102 ± 0.0019 |
| $MoO_3$ | 0.0176 | 0.0186 ± 0.0071 | 0.0148 ± 0.0035 | 0.0161 ± 0.0033 | 0.0129 ± 0.0028 |
| $SnO_2$ | 0.0176 | 0.0186 ± 0.0071 | 0.0152 ± 0.0032 | 0.0144 ± 0.0030 | 0.0136 ± 0.0023 |
| $La_2O_3$ | 0.0176 | 0.0189 ± 0.0077 | 0.0146 ± 0.0030 | 0.0170 ± 0.0032 | 0.0097 ± 0.0016 |
| $Nd_2O_3$ | 0.0176 | 0.0185 ± 0.0061 | 0.0142 ± 0.0029 | 0.0163 ± 0.0037 | 0.0120 ± 0.0008 |
| $Ta_2O_5$ | 0.0176 | 0.0185 ± 0.0067 | 0.0145 ± 0.0030 | 0.0156 ± 0.0031 | 0.0111 ± 0.0026 |
| $WO_3$ | 0.0176 | 0.0188 ± 0.0071 | 0.0144 ± 0.0031 | 0.0156 ± 0.0033 | 0.0121 ± 0.0016 |
| PbO | 0.0176 | 0.0190 ± 0.0060 | 0.0206 ± 0.0010 | 0.0183 ± 0.0040 | 0.0161 ± 0.0015 |

**Calibration with $CeO_2$ standards: non-matrix matched!**

**Raster scanning laser beam over small area of sample eliminates crater and allows accurate characterization based on non matrix-matched standards.**

# Summary

**Laser ablation is a viable sampling technology for rapid, safe, and cost effective characterization of DOE wastes.**

**EMSP research addressed issues effecting accurate and sensitive laser ablation sampling (fundamental and applied science).**

**Demonstrated characterization for SRS prototypic glasses and $PuO_2$ surrogate samples using non matrix-matched standards.**

# Future Efforts

- ICP studies to guarantee accuracy for complex samples
  - matrix and mass loading effects (chemistry)
- MS studies to improve sensitivity
  - throughput efficiency and space charge for dry conditions
- Wavelength and Pulse Duration
  - reduce matrix dependence with shorter pulse and wavelength
- Transport studies to further improve sensitivity
  - new chamber design for efficient transport
- Technology Transfer to EM Users

# EMSP Publications and Interactions

- 13 Journal Publications (1 Encyclopedia Chapter)
- 4 Refereed Proceedings
- 12 Presentations (9 Invited)
- 2 PhD Students, 1 Post Doc
- Visiting Scientists:
  - Univ of Caracus, Venezuela
  - Univ of Hong Kong, Hong Kong
  - Guangzhou Institute of Geochemistry, China
- Collaborations/Interactions:
  - Universities
    - » UC Berkeley, U. of Illinois, WSU, HKU
  - National Labs
    - » PNNL, ANL (West), LANL, LLNL, SRS

# Scientific Reporting

**JOURNAL PUBLICATIONS (13):**

Comparison of Different Wavelengths for Laser Ablation ICP-MS, R.E. Russo, X.L. Mao, and O.V. Borisov, *submitted to J. Analy. Atomic. Spectrosc., March 2000.*

Understanding Gas Flow and Ion-Optics Optimization for Laser Ablation ICP-MS, O.V. Borisov, X.L. Mao, G.C.Y. Chan, M. Liezers, and R.E. Russo, *submitted to Analytical Chemistry, February 2000.*

Pb/U Fractionation During Nd:YAG 213 nm and 266 nm Laser Ablation Sampling With ICP/MS, H.C. Liu, O.V. Borisov, X.L. Mao, S. Shuttleworth, and R.E. Russo, *submitted to Applied Spectroscopy, February 2000.*

Investigation of Matrix Effects on Dry Inductively Coupled Plasma Conditions using Laser Ablation Sampling, G.C.-Y. Chan, W.-T. Chan, X.L. Mao, and R.E. Russo, Spectrochimica Acta B, **55B**, 221-235 (2000).

Time-Resolved Plasma Diagnostics and Mass Removal during Single-Pulse Laser Ablation, R.E. Russo, X.L. Mao, H.C. Liu, J.H. Yoo, and S.S. Mao, *Applied Physics A, **69**, S887-894 (2000).*

Effects of Particle Size Distribution on Inductively Coupled Plasma Mass Spectrometry Signal Intensity During Laser Ablation of Glass Samples, S.H. Jeong, O.V. Borisov, J.H. Yoo, X.L. Mao, and R.E. Russo, *Analytical Chemistry, **71**, 5123-5130 (1999).*

Early Phase Laser Induced Plasma Diagnostics and Mass Removal During Single Pulse Laser Ablation of Silicon, H.C. Liu, X.L. Mao, J.H. Yoo, and R.E. Russo, *Spectrochimica Acta B, **54**, 1607-1624 (1999).*

Inductively Coupled Plasma Mass Spectrometric Study of Non-Linear Calibration Behavior During Laser Ablation of Binary Cu-Zn Alloys, O.V. Borisov, X.L. Mao, A. Fernandez, M. Caetano, and R.E. Russo, *SPECTROCHIMICA ACTA PART B-ATOMIC SPECTROSCOPY, **V54(N9):** 1351-1365 (1999).*

Laser Ablation Sampling, R.E. Russo, X.L. Mao, and O.V. Borisov, *Trends in Analytical Chemistry, **17**, 461-469 (1998).* **(Invited Paper)**

Influence of gas environment on picosecond laser ablation sampling efficiency and ICP conditions., A.P.K. Leung, W.T. Chan, X.L. Mao, and R.E. Russo, *Analytical Chemistry, **V70(N22),** 4709-4716 (1998).*

Optical Emission Spectroscopy Studies of the Influence of Laser Ablated Mass on Dry Inductively Coupled Plasma Conditions, A.C. Ciocan, X.L. Mao, O.V. Borisov, and R.E. Russo, *Spectrochimica Acta, **53B**, 463-470 (1998).*

Time Resolved Parametric Studies of Laser Ablation Using ICP-AES, O.V. Borisov, X.L. Mao, A.C. Ciocan, and R.E. Russo, *Applied Surface Science **129**, 315-320 (1998).*

Effects of Gas Environment on Pico-Second Laser Ablation, W.T. Chan, A.P.K. Leung, X.L. Mao, and R.E. Russo, *Applied Surface Science **127-129**, 269-273 (1998).*

**Encyclopedia Chapter:**

Laser Ablation in Atomic Spectrometry, Richard E. Russo, Xianglei Mao, Oleg V. Borisov, and Haichen Liu, *invited chapter in "Encyclopedia of Analytical Chemistry: Instrumentation and Applications, John Wiley & Sons, July 2000.*

# Scientific Reporting

**Refereed Proceedings (4)**

Direct Characterization of Solid Waste Forms Using Laser Ablation ICPMS, O.V. Borisov, X.L. Mao, and R.E. Russo, *Waste Management Science and Technology in the Ceramic and Nuclear Industries, American Ceramic Society, April 1999.*

Effects of Gas Atmosphere on Pico-Second Laser Ablation Sampling for ICP-AES, W.T. Chan, A.P.K. Leung, X.L. Mao, and R.E. Russo, *Fourth International Conference on Laser Ablation (COLA 97), July 1997, Asilomar CA.*

Time Resolved Parametric Studies of Laser Ablation of Brass Using ICP-AES, X.L. Mao, A.C. Ciocan, O.V. Borisov, and R.E. Russo, *COLA, July 1997, Asilomar CA.*

Optical Emission Spectroscopy Studies of Ablated Material on Dry Inductively Coupled Plasma Conditions, A.C. Ciocan, X.L. Mao, O.V. Borisov, and R.E. Russo, *COLA, July 1997, Asilomar CA.*

**Presentations (12)**

A Comparison of Different Wavelengths for Laser Ablation ICPMS, R.E. Russo, X.L. Mao, O.V. Borisov and S. Shuttleworth, *Winter Plasma Conference on Spectrochemistry, January 2000, Ft. Lauderdale, FL* **(Invited)**

Laser Ablation ICPMS with Synthetic Pressed Pellers, O.V Borisov, C. Bannochie, and R.E. Russo, *Winter Plasma Conference on Spectrochemistry, January 2000, Ft. Lauderdale, FL*

Matrix Effects in Laser Ablation ICPMS, O.V. Borisov, X.L. Mao, and R.E. Russo, *26th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), October 1999, Vancouver, CA.* **(Invited)**

Improving Direct Characterization of Glass Waste Forms Using Laser Ablation with ICP-MS, R.E. Russo, O.V. Borisov, and X.L. Mao, *"International Symposium on Waste Management Science and Technology in the Ceramic and Nuclear Industries." American Ceramic Society Annual meeting April 1999, Indianapolis IN.* **(Invited)**

Fundamental and Applied Aspects of Laser Ablation for Chemical Analysis, *Frontiers in Chemistry Lecture Series, Wayne State University, April 1999* **(Invited)**

Laser Ablation Sampling using ICP AES and MS, R.E. Russo, *Macquarie University Physics and Geochemical Departments, December 1998, Sydney Australia* **(Invited)**

Fundamental and Experimental Factors Influencing Laser Ablation for Chemical Analysis, R.E. Russo, *5th Australian Conference on ICP-MS, November 1998, Perth Australia* **(Invited)**

Laser Ablation and Chemical Analysis, R.E. Russo, *VIEPS Workshop on Laser Ablation ICP-MS, November 1998, Melbourne, Australia* **(Keynote Lecture)**

Particle Generation and Transport During Laser Ablation Sampling for Chemical Analysis, R.E. Russo, S.H. Jeong, X.L. Mao, O.V. Borisov, and J. Yoo, *25th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), October 1998, Austin, TX* **(Invited).**

Some Chemistry and Physics of Laser Ablation, R.E. Russo, X.L. Mao, O.V. Borisov, and S.S. Mao, *25th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), October 1998, Austin, TX*

Laser-Ablation Sampling with ICP/AES and ICP/MS: Fundamental Issues to Improve Analytical Applications, R.E. Russo, *Society of Applied Spectroscopy California Section Meeting, September 1998, Fremont, CA*

Laser Ablated Mass Influence on the Properties of the ICP, R.E. Russo, X.L. Mao, A.C. Ciocan, and B.V. Borisov, *Twenty-Fourth Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, (FACSS) October 1997, Providence, RI* **(Invited).**