Real-Time Determination of Compositional Profiles in Structured Materials Using Laser Ablation and LA-ICPMS

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Plasma Application Group, April 29, 2013

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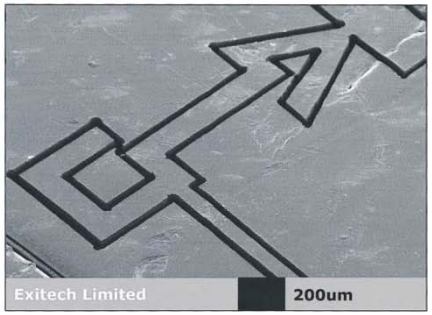
Laser ablation in applications

- Micro machining
- 3D texturing and sintering
- Chemical analysis



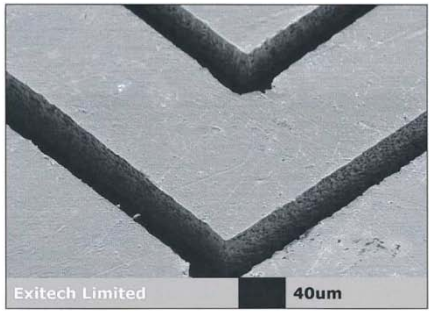
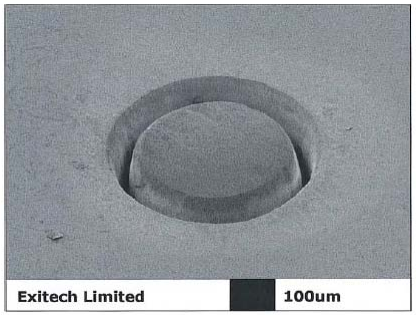
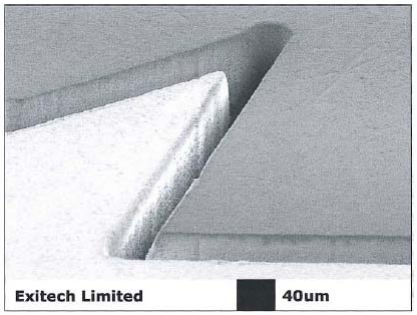


Fig. 5. Samples of FEP micromachined using a femtosecond laser.

Glass samples micromachined using a femtosecond laser.





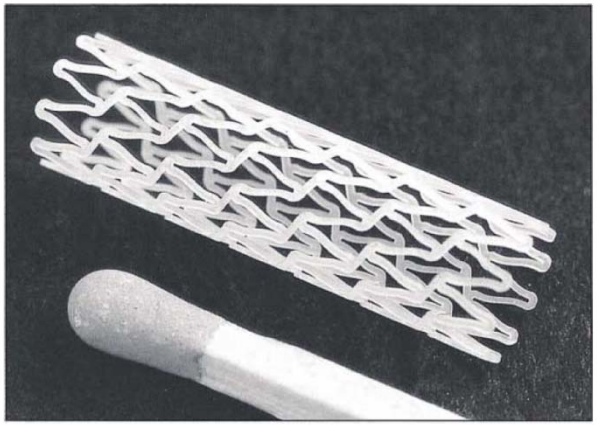
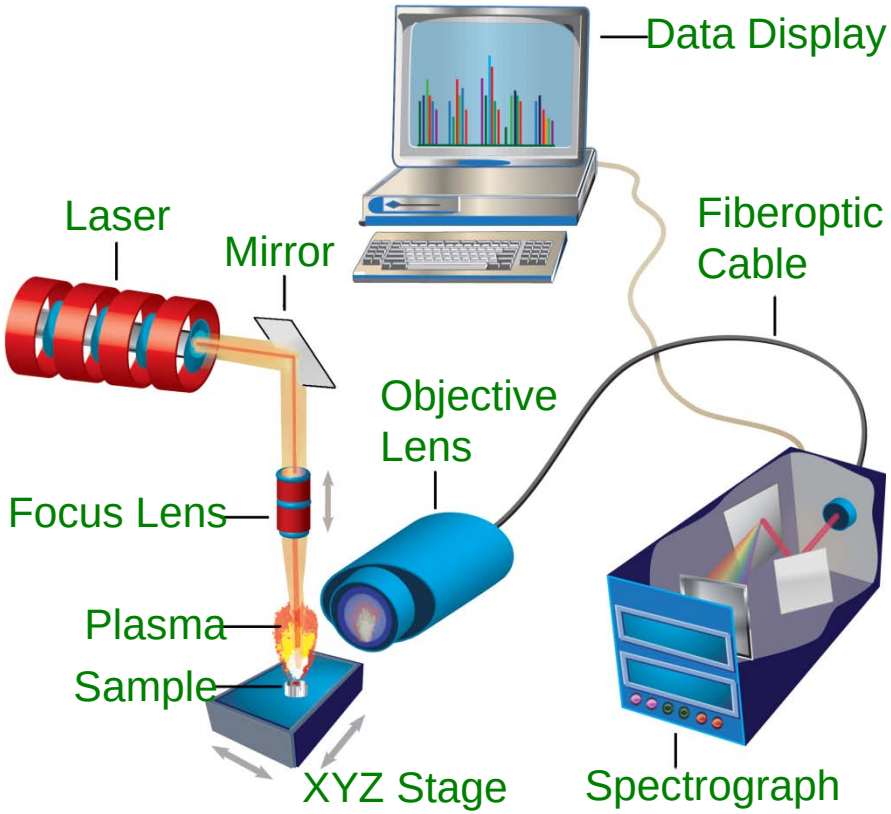


Fig. 12. A medical stent micromachined from a biodegradable polymer using a femtosecond laser (Courtesy of LZH/Cortronik).

RIKEN Review No. 50 (January, 2003): Focused on Laser Precision Microfabrication (LPM 2002)

Laser ablation chemical analysis

LIBS principle of operation:



λ, nm
266
532
1064

Laser-induced breakdown spectroscopy (LIBS)

- Simple, rapid, real-time
- Any kind of sample
- No sample preparation
- High spatial resolution ~10 μm
- Mapping, depth-profiling

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Commercial LIBS and LA-ICPMS

RT100

ns-LIBS, 20 Hz

J100-UV

femto-LA–ICPMS, 100 kHz

- Isotopic & elemental analysis
- Simple, rapid, real-time
- Any kind of sample
- No sample preparation
- High spatial resolution
- Minimum fractionation
- Mapping, depth-profiling

λ, nm	λ, nm
266	343
532	1030
1064	(150 μJ)

Patented

www.appliedspectra.com

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Tandem LA–LIBS: OES & ICPMS

LA–LIBS, Nd:YAG, 5 ns, 20 Hz

www.appliedspectra.com

λ, nm	
213	4.5 mJ
266	25 mJ
532	55 mJ
1064	100 mJ

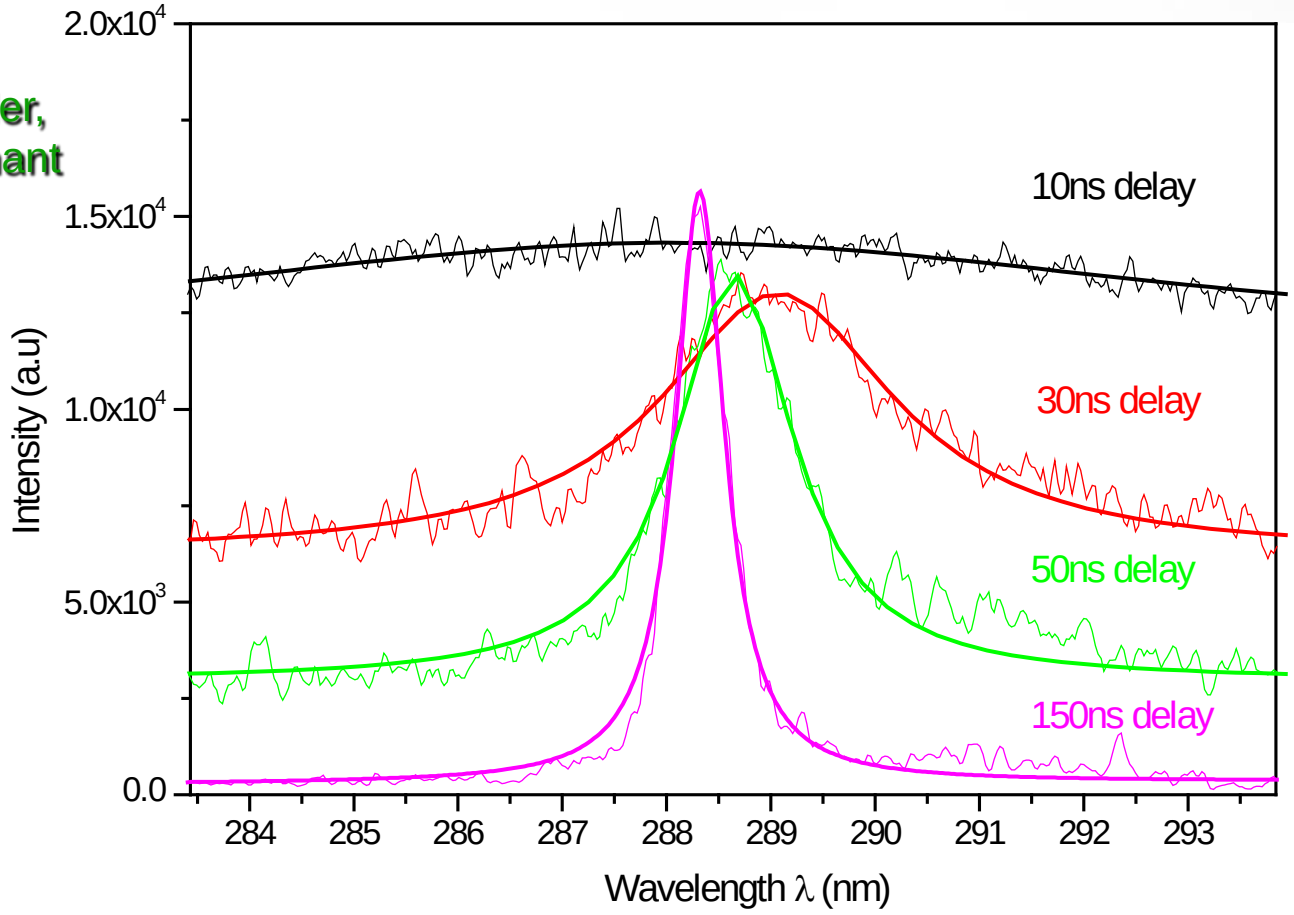
Patent Pending

- Emission and MS simultaneously
- Normalization of isotopic ICPMS
- All elements including H, C, N, O
- Modular, easily upgradable
- Up to Two LIBS spectrographs
- Easy upgrade to fs-LA–ICPMS

- Isotopic & elemental analysis
- Simple, rapid, real-time
- Any kind of sample
- No sample preparation
- High spatial resolution
- Rapid mapping, depth-profiling

Line broadening and shift

- Broadening: Stark, Doppler, collisional, resonant
- Continuum radiation:
- Free electron-ion recombination
- Bremsstrahlung



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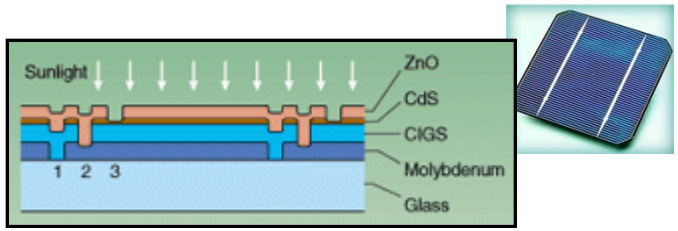
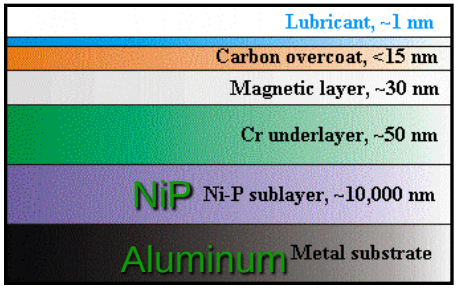
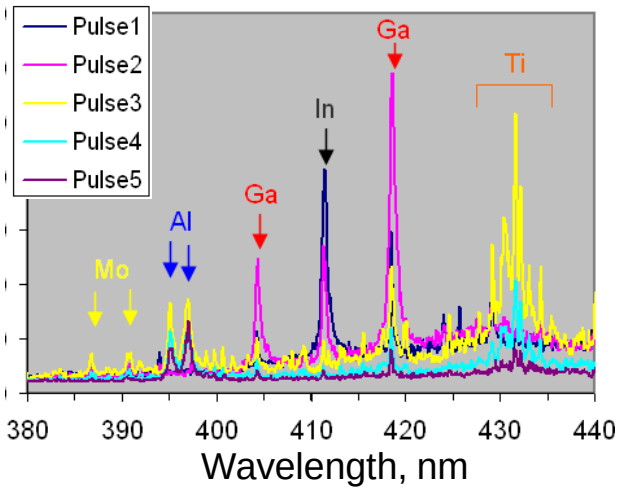
Depth profiling analysis

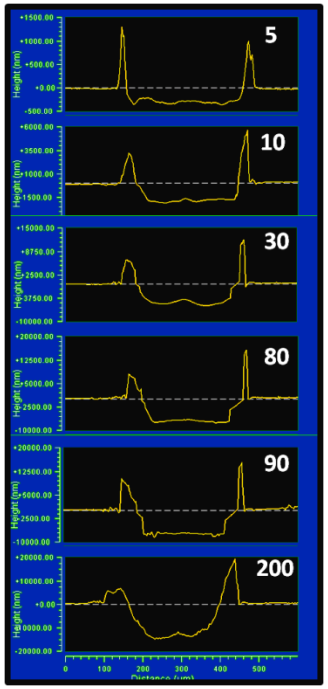
Solar cell structure



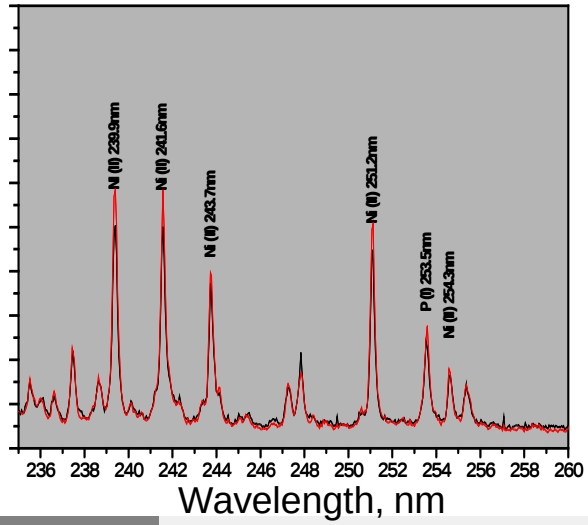
e-Storage substrate







Uniformity of 150 nm NiP layer



- Depth resolution ~20 nm

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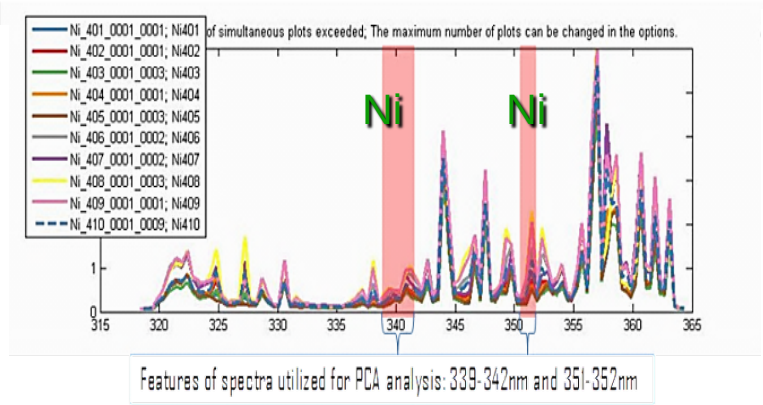
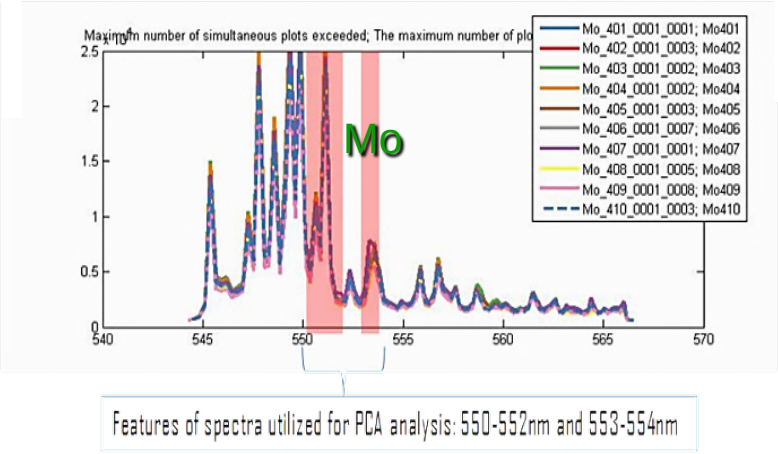
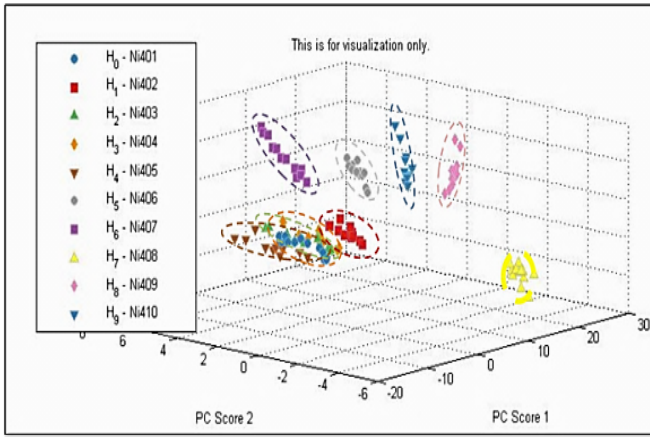
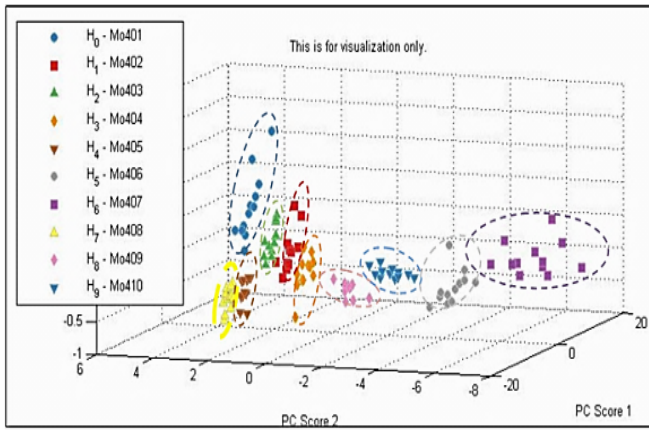
Discrimination of materials

Raw materials: 10 steel samples classified using PCA and PLS-DA





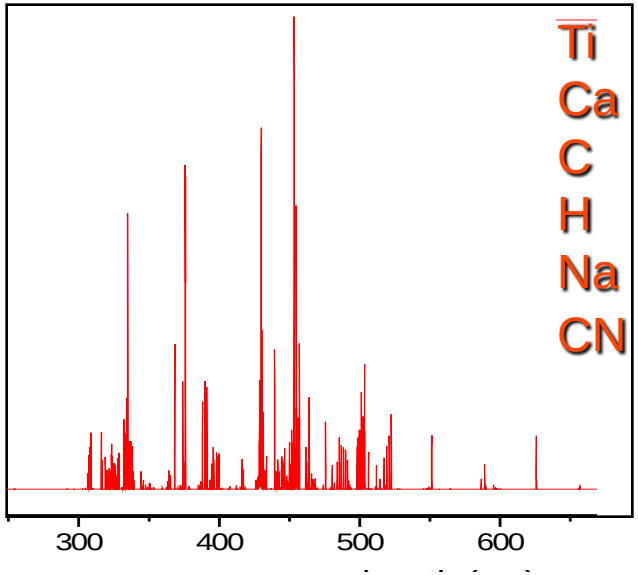




- λ = 1064 nm
- ppm sensitivity
- fast discrimination

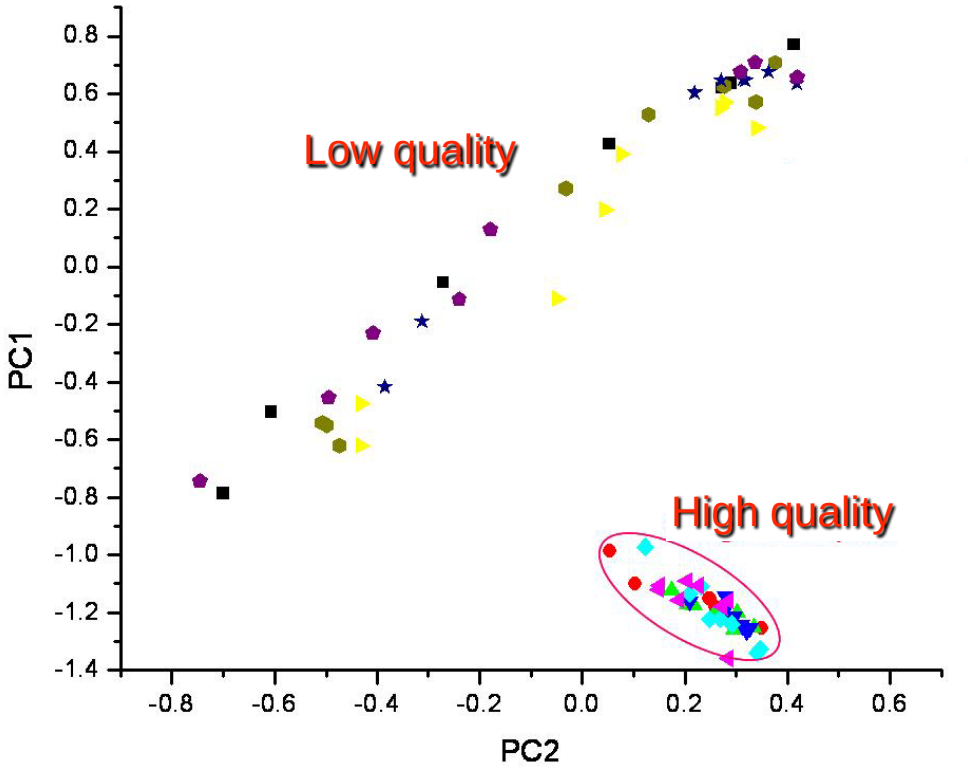
- Not possible by XRF
- Too slow by ICP

Quality of fiberglass panels



Laser 25 mJ
Spot size 300 μm
Lateral steps 500 μm

- PCA discrimination of high vs low quality of fiberglass coatings
- High-quality samples consistently demonstrate similar spectra



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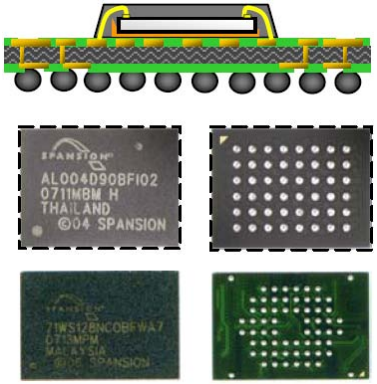
Discrimination of solders

High-lead vs. low-lead

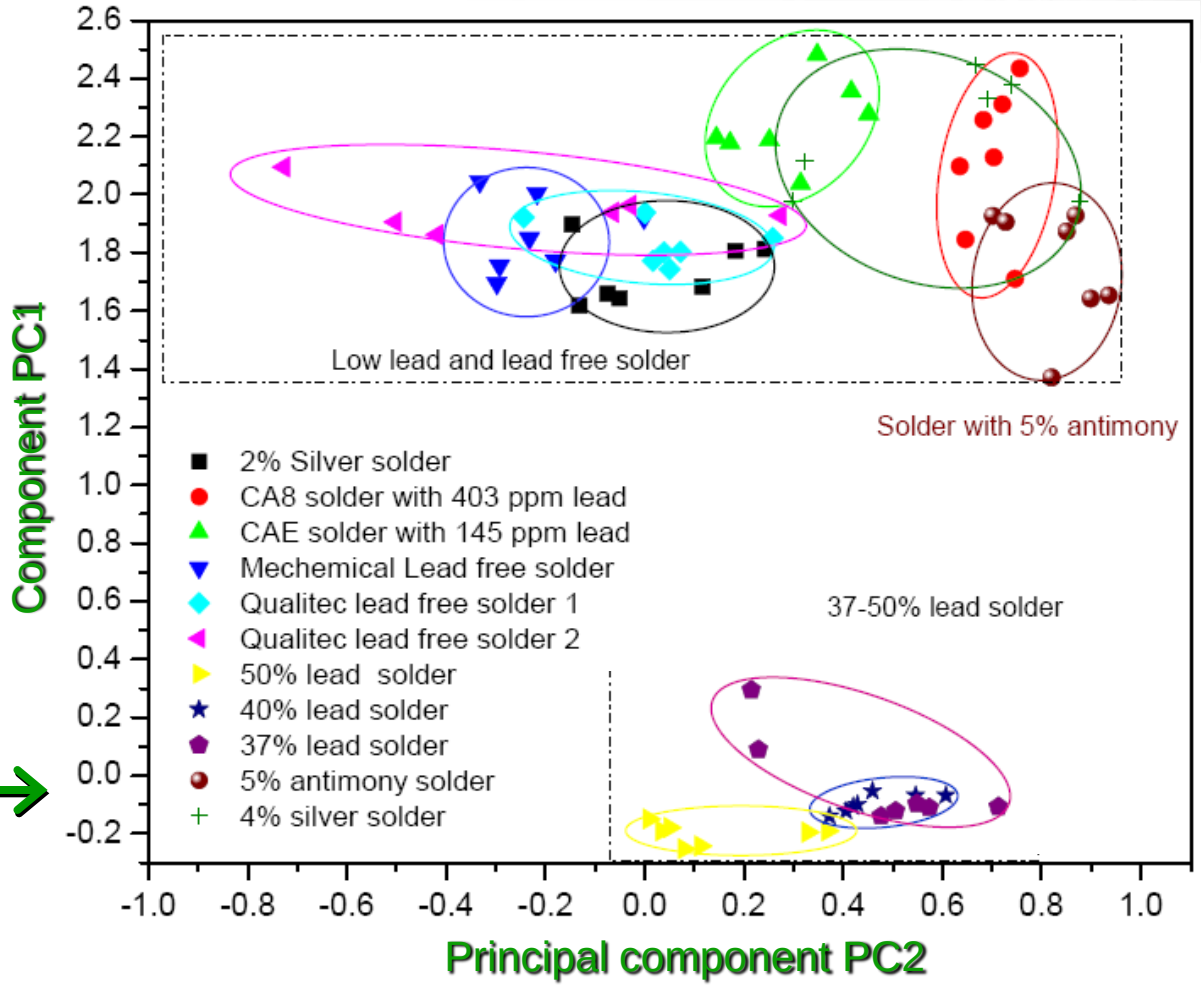


Thin plated solder leads and solder balls in chips

12 different solders tested

(RoHS limit <0.1% Pb)

- Library spectra stored



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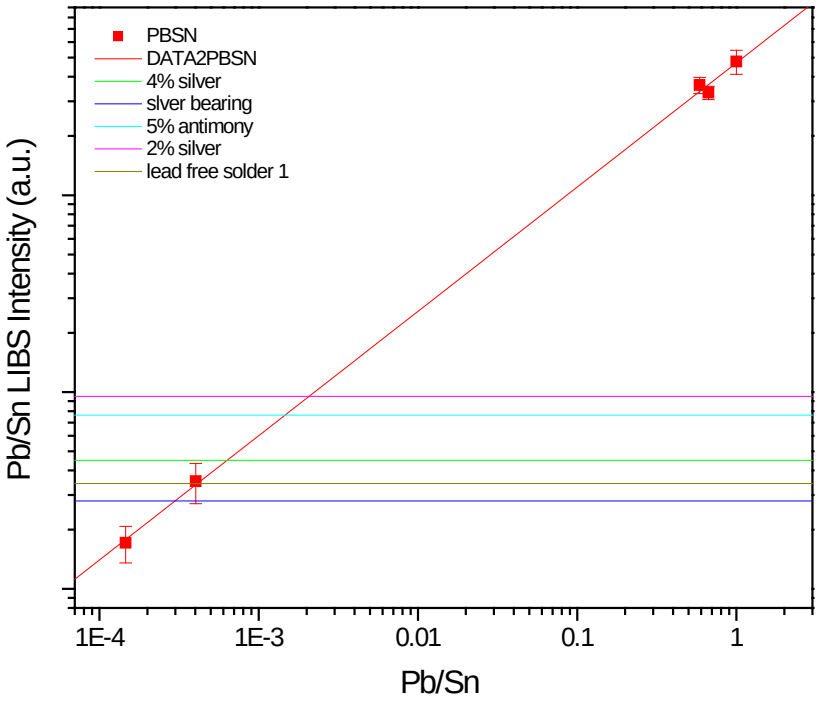
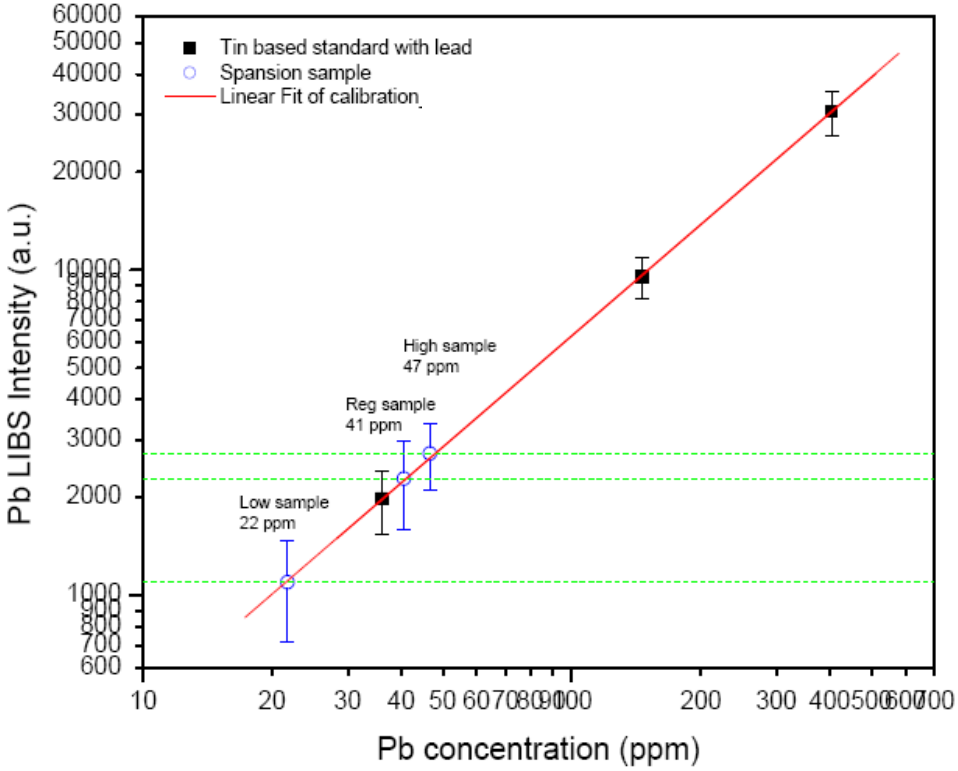
LIBS calibration for Pb



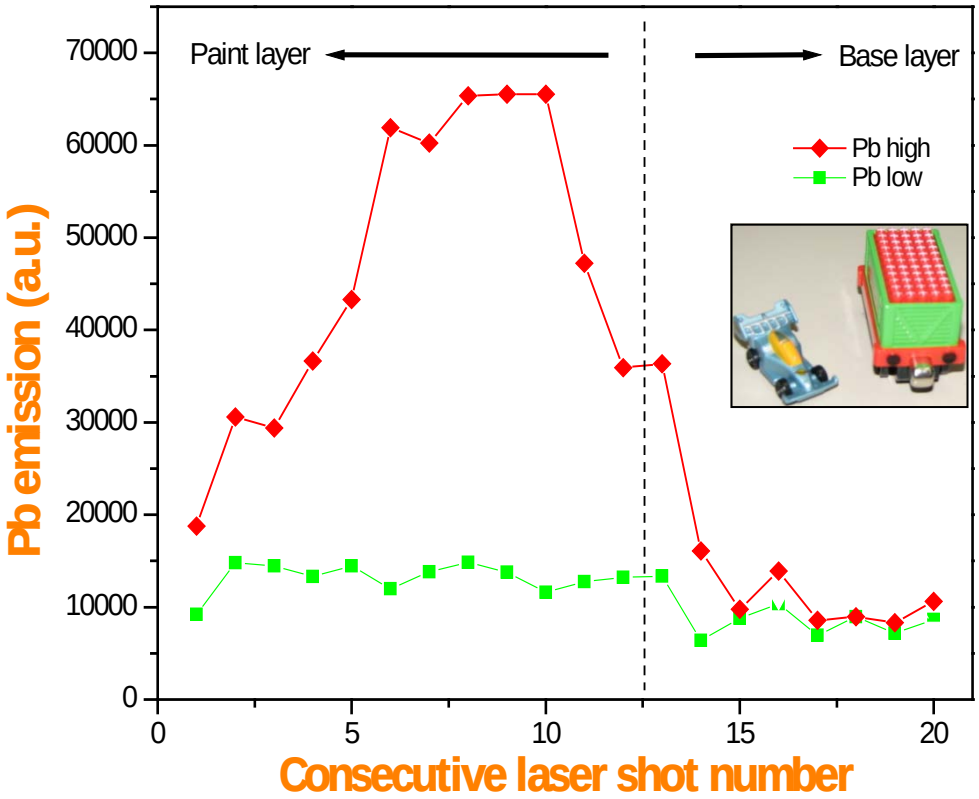


Quantitative analysis of electrical solders and solder platings

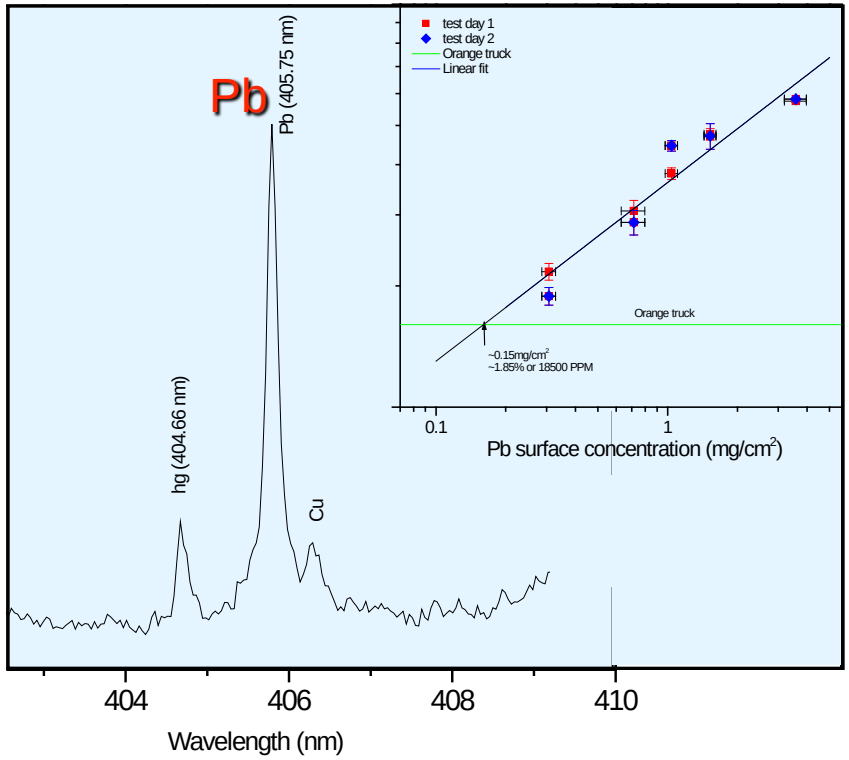
<10 sec per sample **Pb detection limit <10ppm**

Lead in paint and toys

Depth resolution ~0.5 μm



Standard sample / calibration for Pb

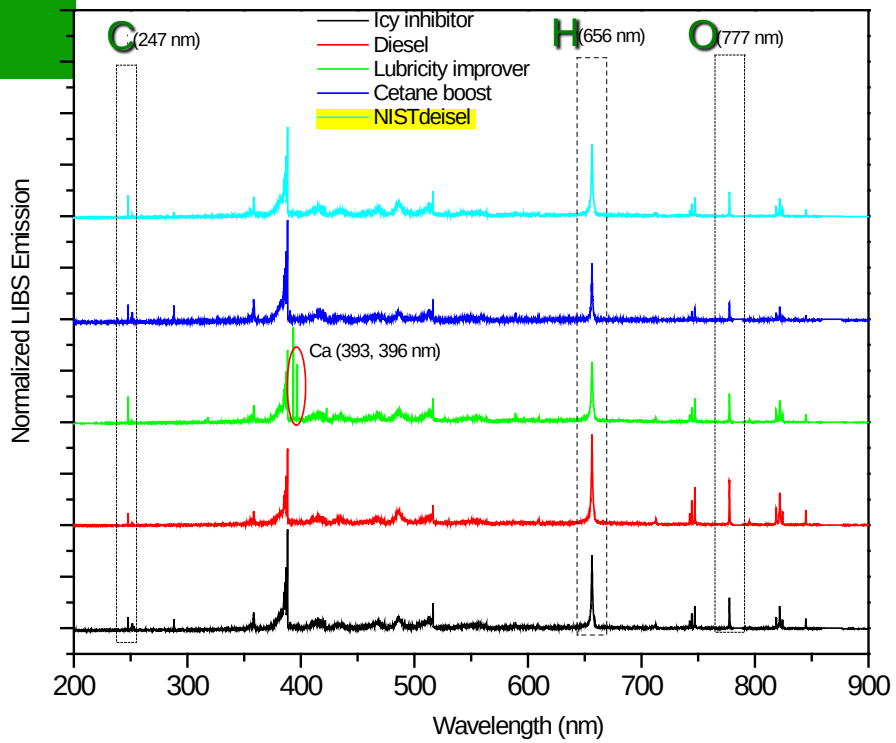


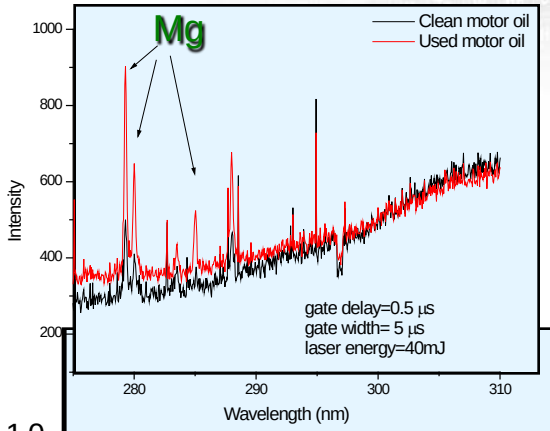
Detection limits: 15 ppm Pb (0.1 μg/cm²)

CPSC rule: 300 ppm

90 ppm in paint

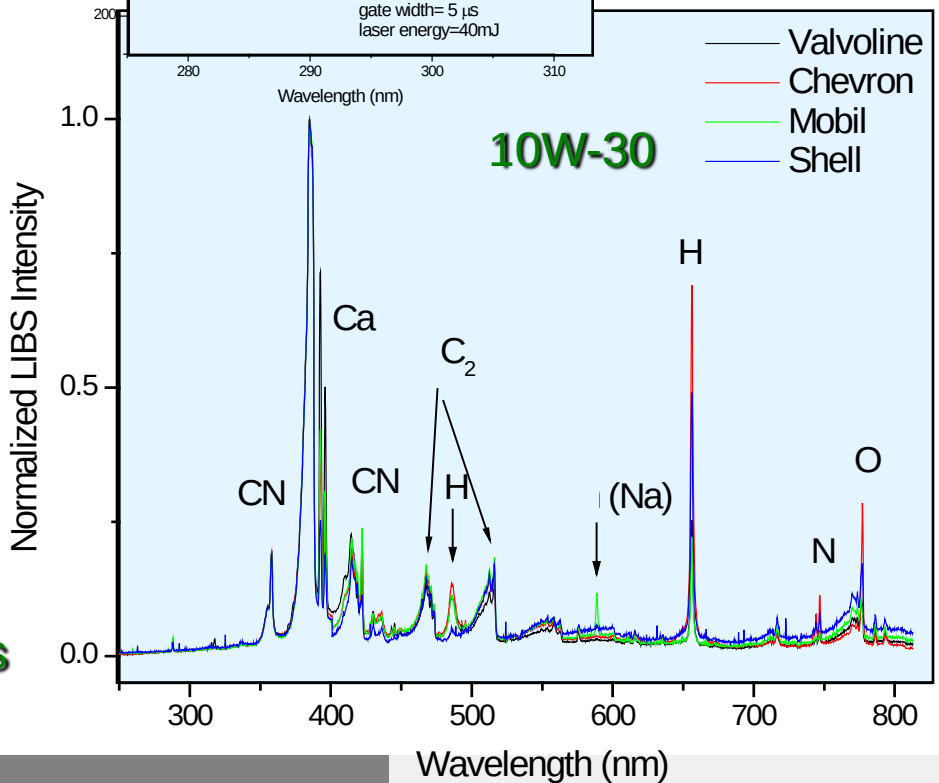
Motor oil, diesel and additives





Four oil brands

Clean vs used



Contaminant detection level: ~40 ppm (may include particulates)

PLS analysis discriminates fuels and oils

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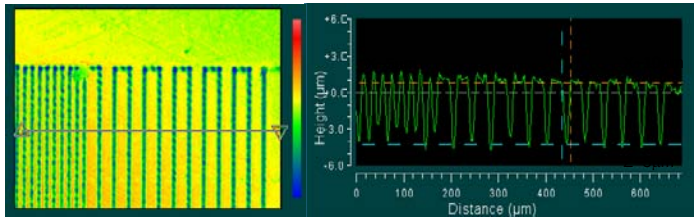
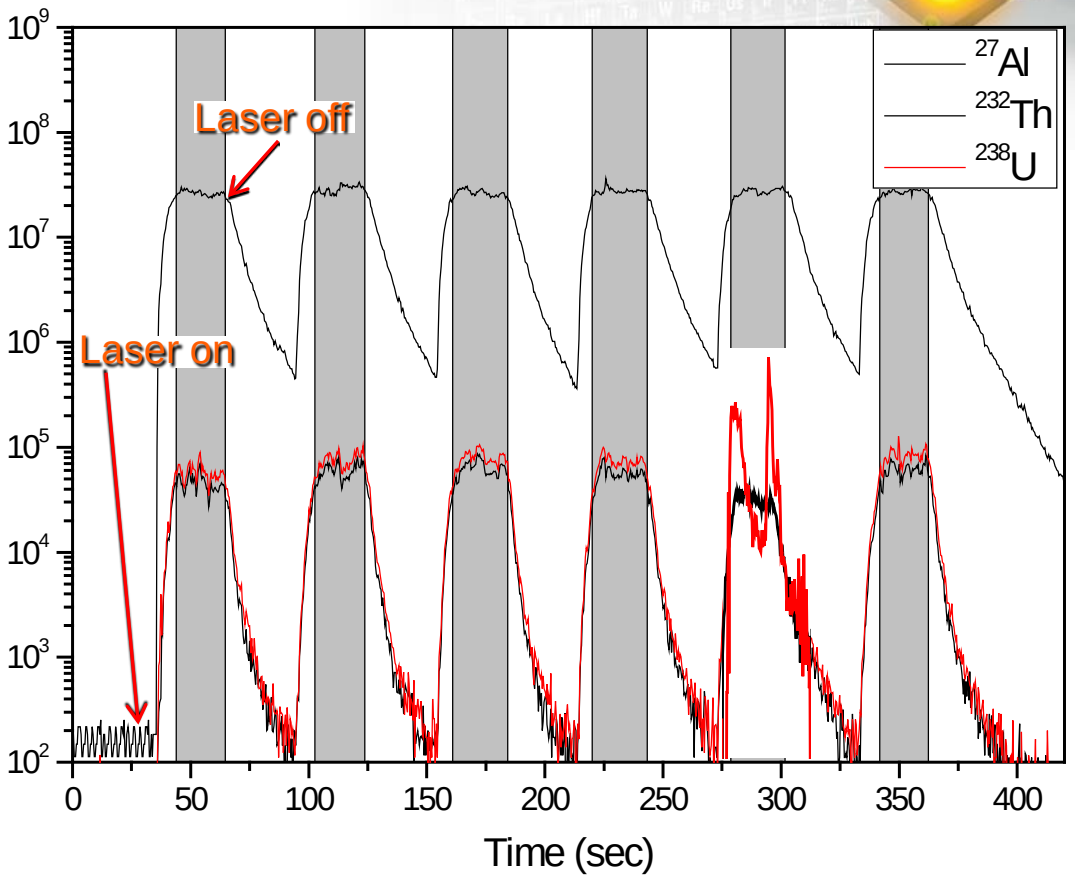
High repetition LA-ICPMS

Glass samples

2 mm
(30 s)





Concentration of ^{232}Th, ^{238}U – 37 µg/g

Laser repetition rate – 20 kHz (λ=343 nm)

Stage moving speed – 20 mm/s

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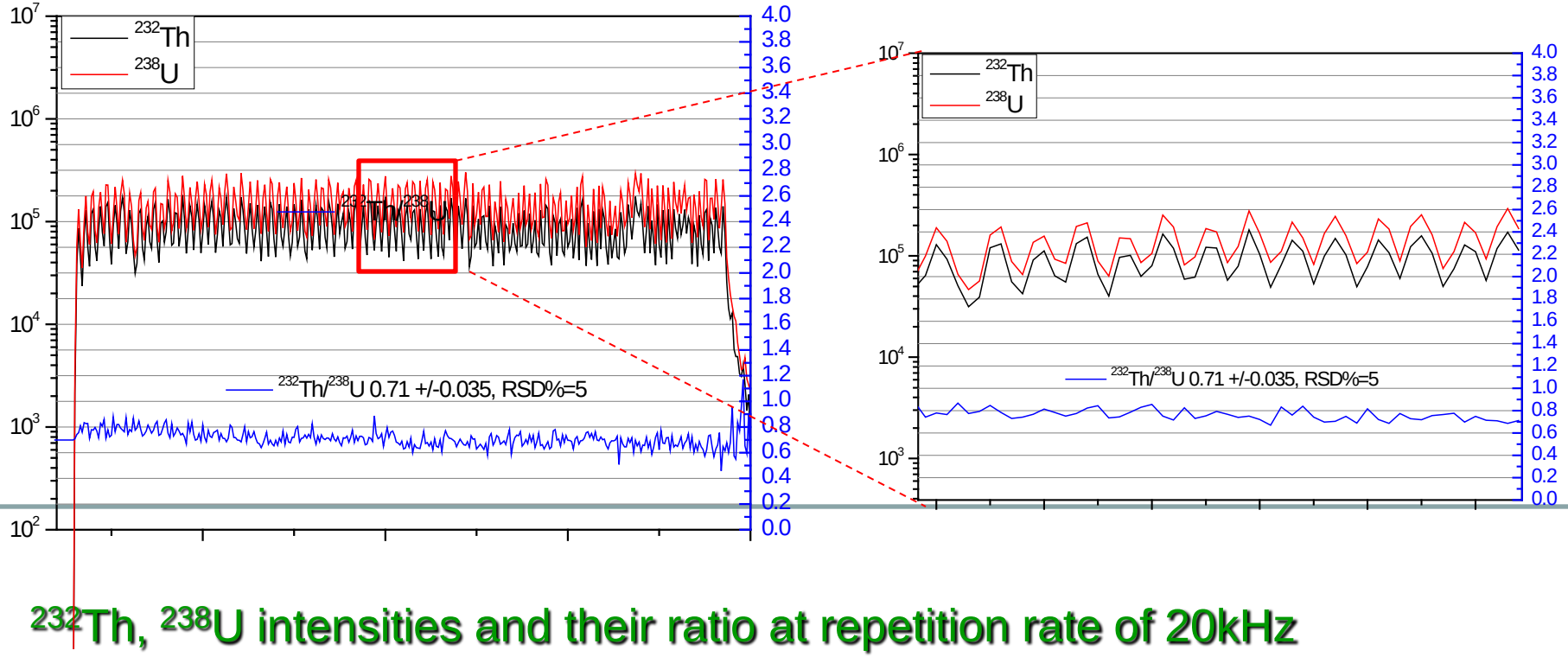
Quasi-continuous LA scanning



232Th, 238U intensities and their ratio at repetition rate of 20kHz

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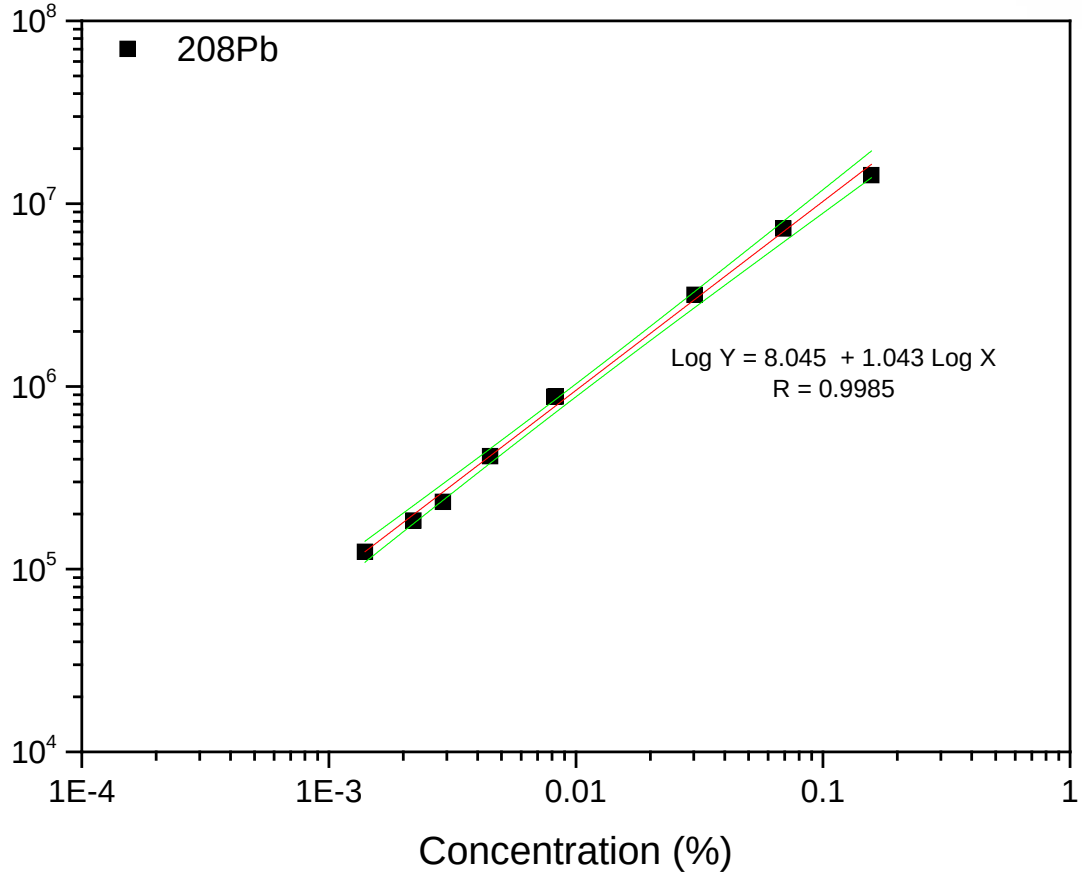
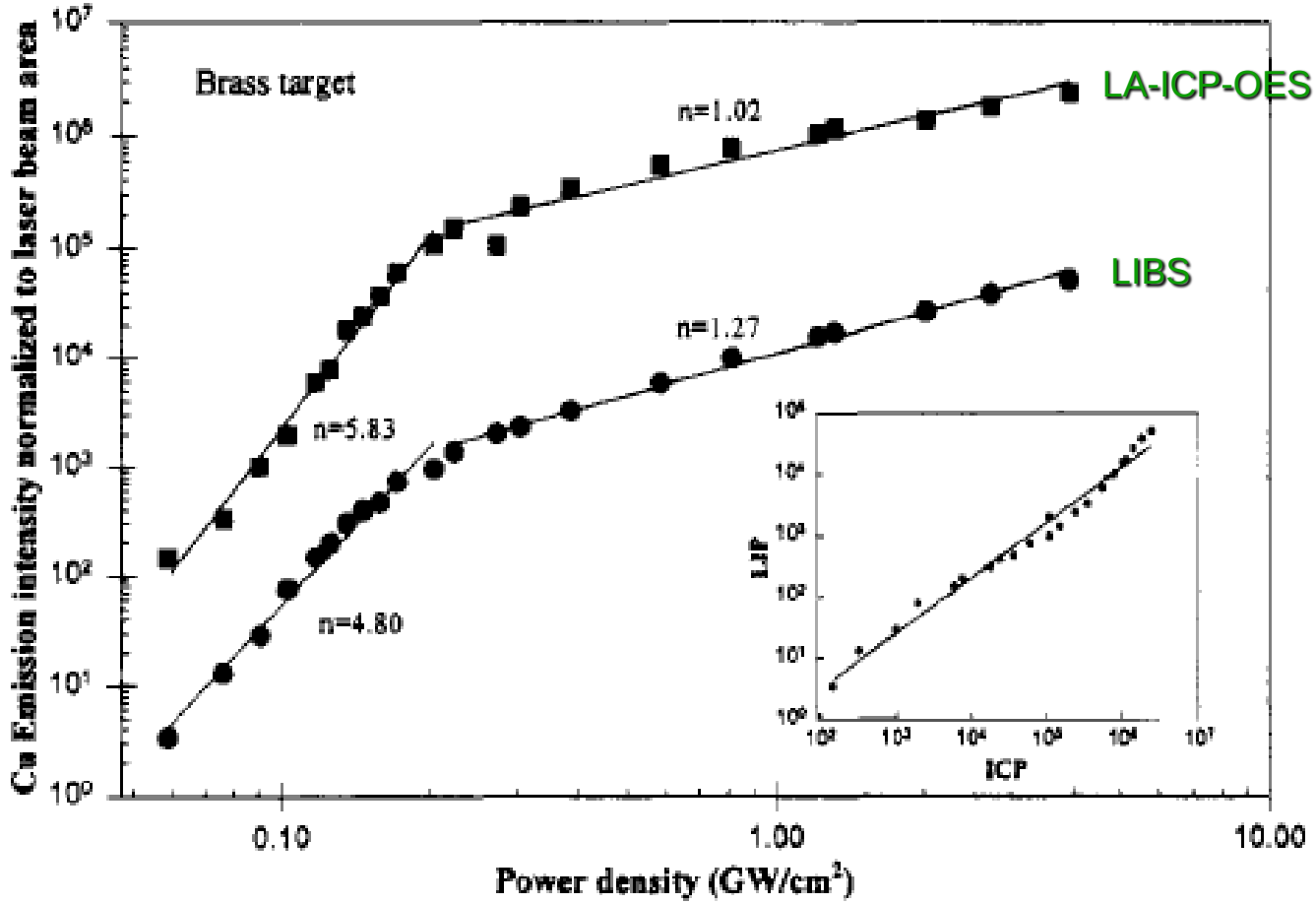
Quantitative LA-ICPMS results



- Lead in zinc alloys
- Linear calibration

λ = 343nm
Laser energy ~0.1 mJ
Fluence ~20 J/cm²
Spot size ~ 25μm
Repetition rate 0.1 kHz
Scan speed – 0.1 mm/s

Correlation of LIBS and LA-ICP



A. Fernandez, X.L Mao, W.T. Chan, M.A. Shannon, R.E. Russo, "Correlation of spectral emission intensity in the inductively coupled plasma and laser-induced plasma during laser ablation of solid samples" – 1995

Conclusion

- Fast (seconds)
- Sensitive (ppm, ppb)
- No sample prep
- Elemental, isotopic
- Organic and inorganic
- Universal for any sample
- Lateral and depth profiling →
- Commercially available models

LIBS, LA-ICP-MS in tandem

~3 μm; ~10 nm
electronics
optical devices
protective coatings
pharmaceutical coatings
micro-mechanical, MEMS
new modified materials

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Thank you

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