INTERACTION OF LASER RADIATION WITH SOLIDS

Viktor Kanicky

**Laboratory of Atomic Spectrochemistry,
Department of Analytical Chemistry
Faculty of Science, Masaryk University, Brno,
Czech Republic**

PACI

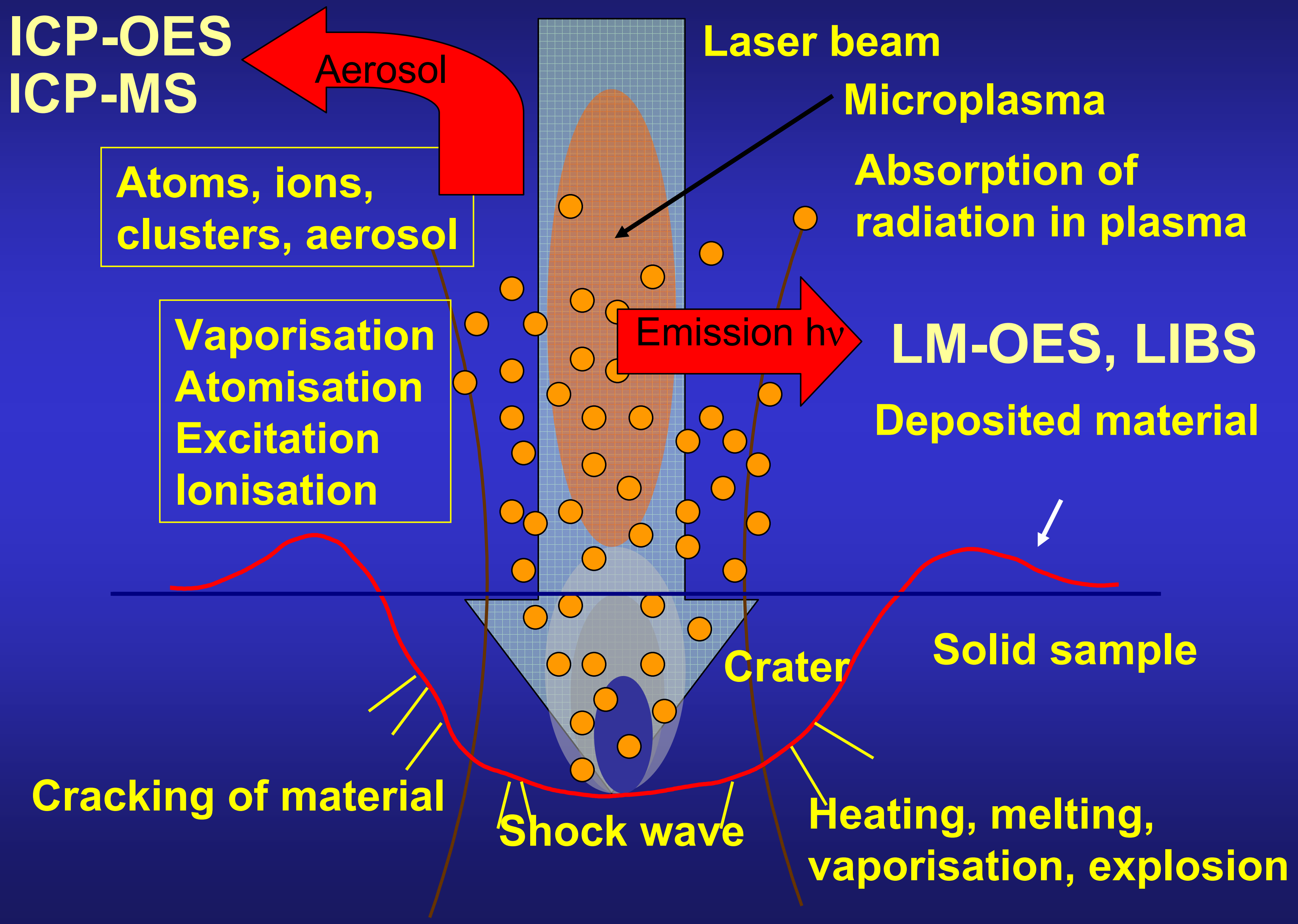
Laboratory of Atomic Spectrochemistry

viktork@chemi.muni.cz

UNIVERSITAS MASARYKIANA BRUNENSIS

- Principles and instrumentation
- Applications
  - Imaging of spatial distribution of elements
  - Determination of average composition (bulk analysis)

Laser Ablation



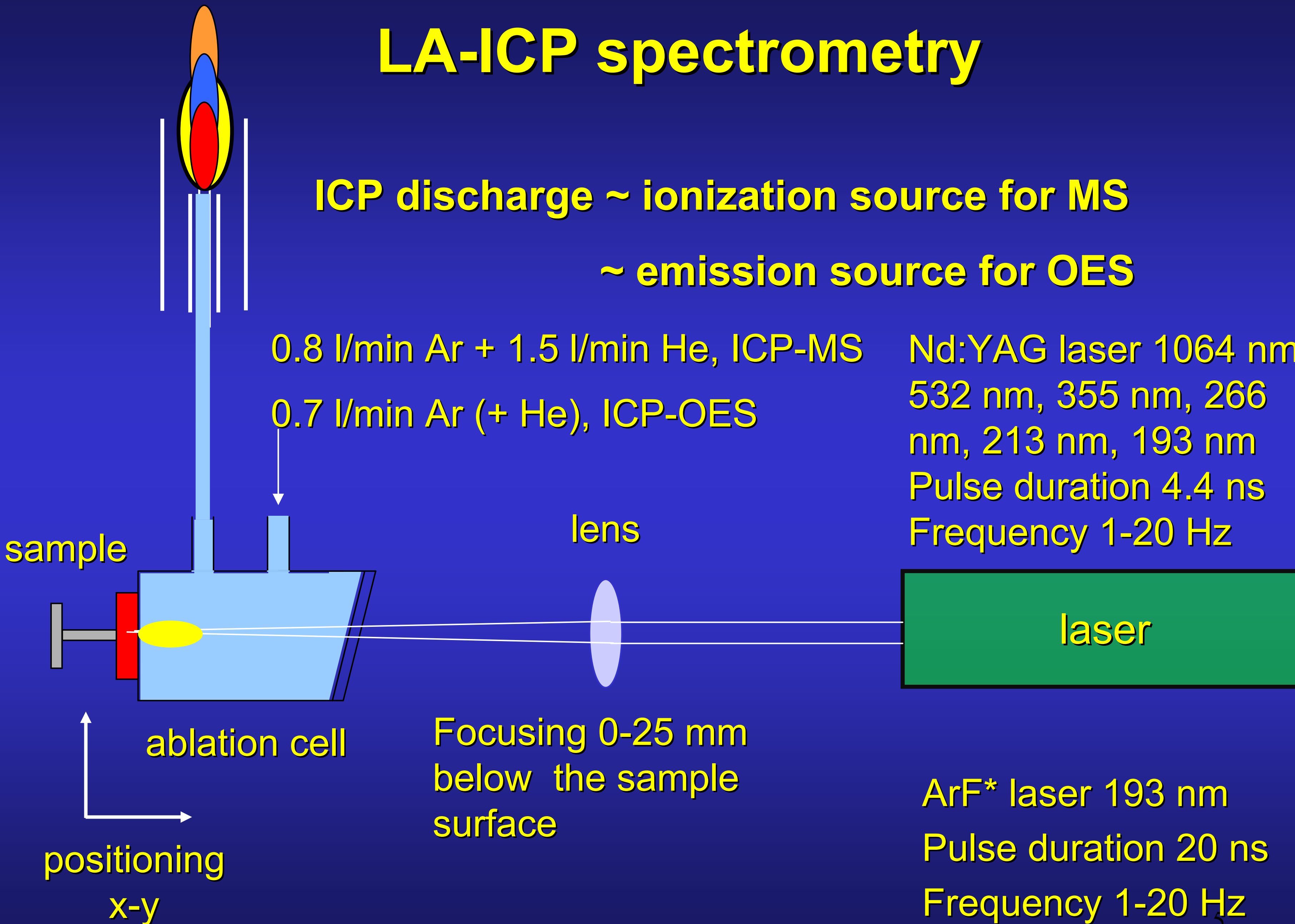
Laser assisted plasma spectroscopy

- Optical Emission Spectroscopy in Laser-Induced Plasma: LM-OES, LIPS, LIBS
- Optical Emission Spectroscopy in Inductively Coupled Plasma with Laser Ablation: LA –ICP- OES
- Mass Spectroscopy in Inductively Coupled Plasma with Laser Ablation: LA-ICP-MS

LA-ICP spectrometry

ICP discharge ~ ionization source for MS

~ emission source for OES

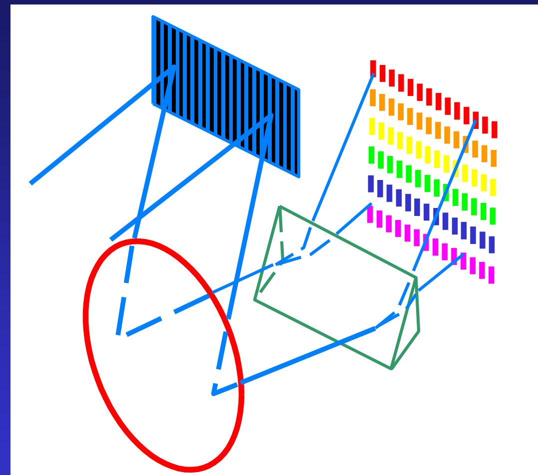


Nd:YAG laser 1064 nm, 532 nm, 355 nm, 266 nm, 213 nm, 193 nm
Pulse duration 4.4 ns
Frequency 1-20 Hz

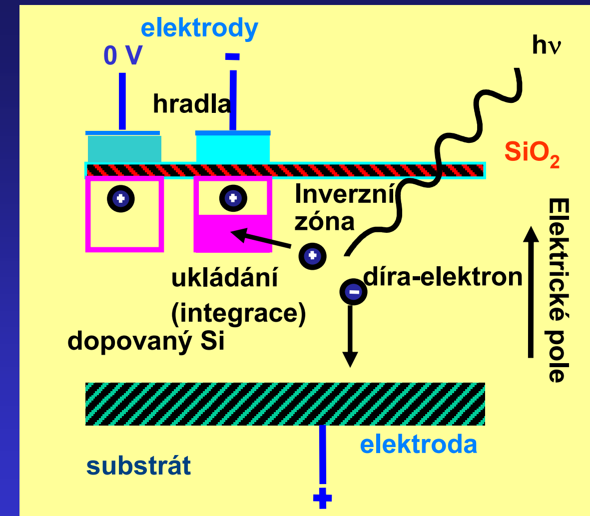
Focusing 0-25 mm below the sample surface

ArF* laser 193 nm
Pulse duration 20 ns
Frequency 1-20 Hz

ICP-OES



Echelle+cross dispersion



CCD detector

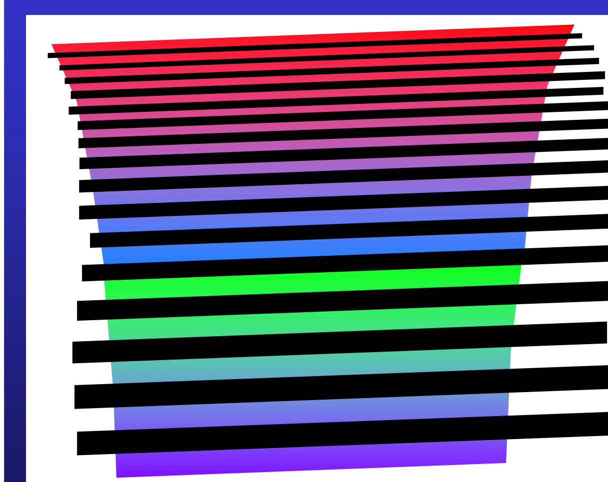
Echellogramme

aerosol

Laser ablation

Atomic and ionic line spectrum

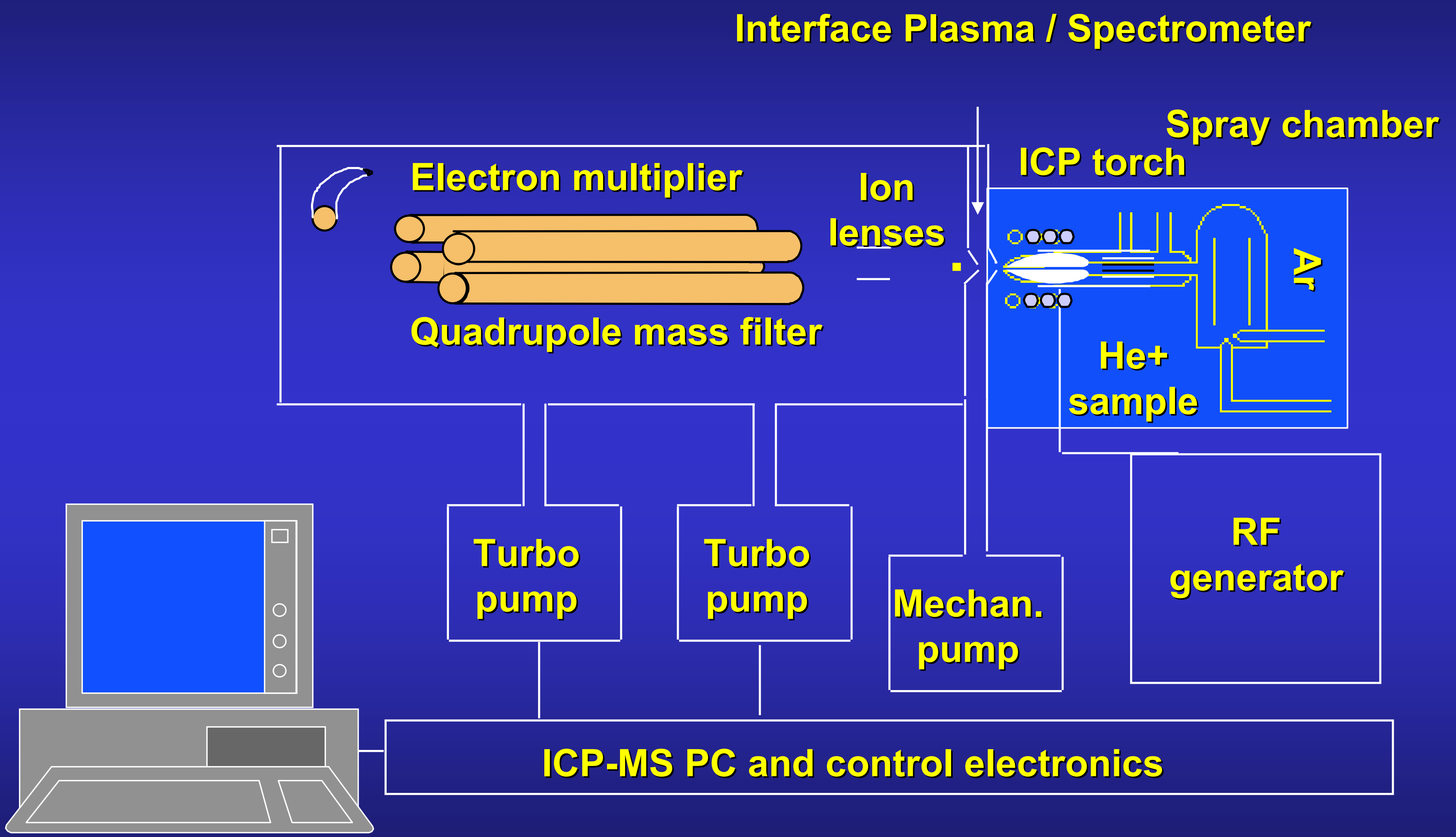
order



wavelength

Carrier gas (Ar, He)

ICP-QMS


Interface Plasma / Spectrometer
Spray chamber
ICP torch
Electron multiplier
Ion lenses
Ar
Quadrupole mass filter
He+ sample
Turbo pump
Turbo pump
Mechan. pump
RF generator
ICP-MS PC and control electronics

Laser-assisted analysis of solids

- **Features of laser ablation based techniques**
  - **<u>Elimination</u> of decomposition for solution analysis**
  - **<u>Elimination</u> of water, O, N, S, Cl from acids; resulting species cause spectral interferences in ICP-MS**
  - **<u>Non-destructive</u>: material removing from the area 10 μm^2 to 1mm^2 to the depth cca 0.01-0.1μm/laser pulse**
  - **<u>2D-3D „speciation”:</u> preserves information on spatial distribution of elements**

Priorities of laser-assisted plasma spectroscopy

1) Analysis of surfaces and coatings: xy - local analysis, microanalysis, areal mapping (mineralogical sections, inhomogeneities in steel)
2) Depth profiling of multi-layer advanced materials or natural structured objects (xyz resolution)
3) Bulk analysis:
   - Compact samples (steel, alloys, glass, ceramics)
   - Powdered samples:
     - pressed pellets with or without a binder,
     - cast pellets with e.g. epoxy resin, polyurethane … ,
     - melted with fusing agents for XRF $\Rightarrow$ cast pearls

Influencing parameters

- Laser wavelength.
- Pulse energy.
- Focus position relative to surface.
- Laser repetition rate.
- Crater diameter/depth (aspect ratio).

Effect of laser wavelength

- ✓ Infrared laser: Nd:YAG 1064 nm
  - ✓ Strongly absorbing microplasma, long interaction ⇒ thermal effects ⇒ selective volatilisation, fractionation
- ✓ Ultraviolet laser: ArF* 193 nm, Nd:YAG 266 nm or 193 nm
  - ✓ Short interaction, minimum thermal effects, minimum fractionation

Critical parameters of LA

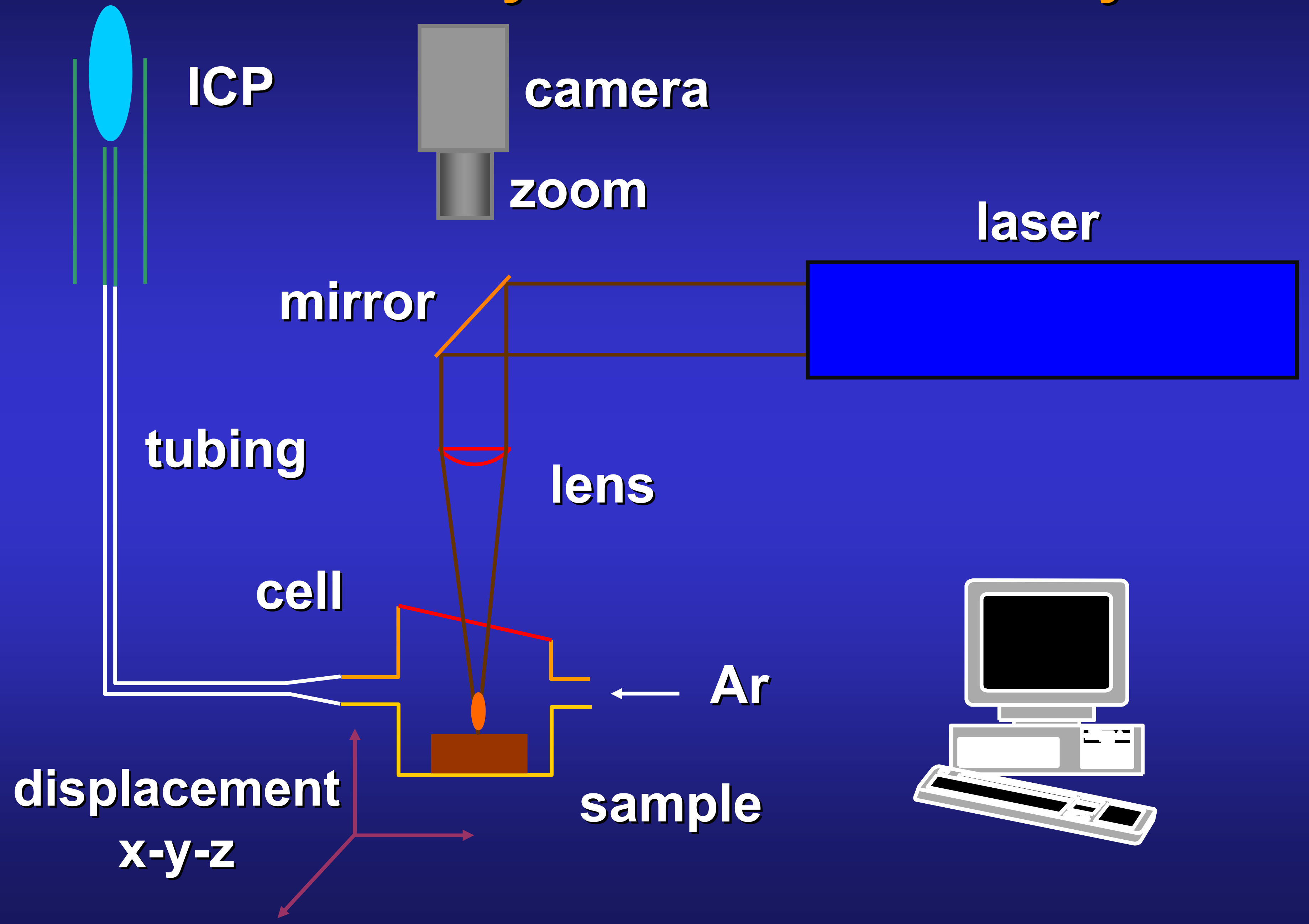
- **Wavelength (UV$\times$IR) *vs* fractionation**
- **Pulse duration (fs$\times$ns) *vs* fractionation**

Features important for paticular tasks

- Depth profiling, mapping, local analysis:
  - Laser beam profile, spot size, aspect ratio,
- Bulk analysis:
  - Powders: pellet preparation, cohesion and homogeneity, easy calibration
  - Compacts: no preparation, homogeneity, lack of calibration samples

I. Depth profiling and surface mapping

Localized analysis: laser ablation system



Laser assisted plasma spectroscopy: A tool for spatially resolved elemental analysis of solids ?

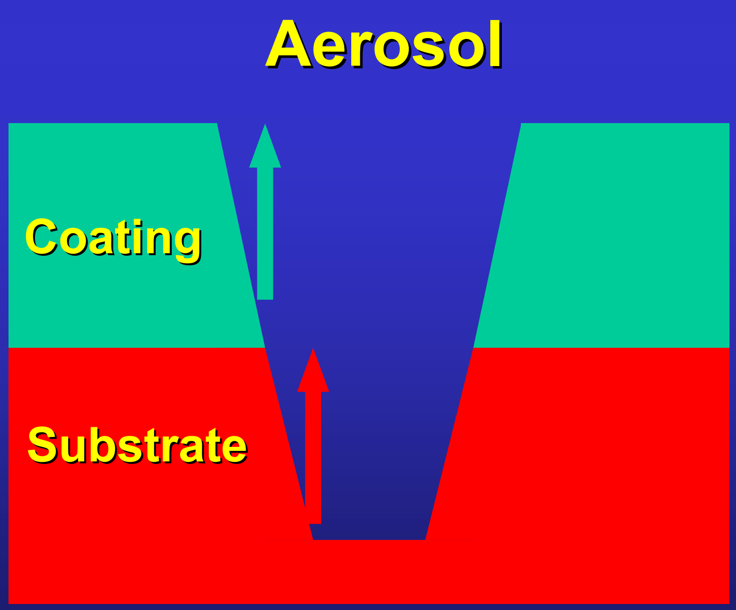
- <u>Local analysis</u>: single spot directed beam
- <u>Surface mapping</u>: beam scanning or sample translation (xy)
- <u>Depth profiling ?</u>:
  - Thermal effects $\Rightarrow$ elemental fractionation
  - Crater shape effect $\Rightarrow$ overlap of signals originating from individual layers

Influence of beam profile on crater shape

Untreated beam

Conical craters

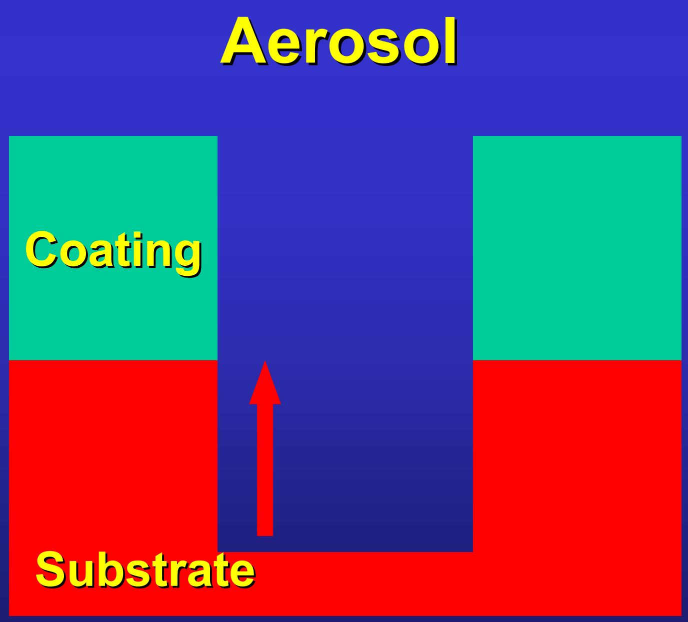
$\Rightarrow$ signal mixing



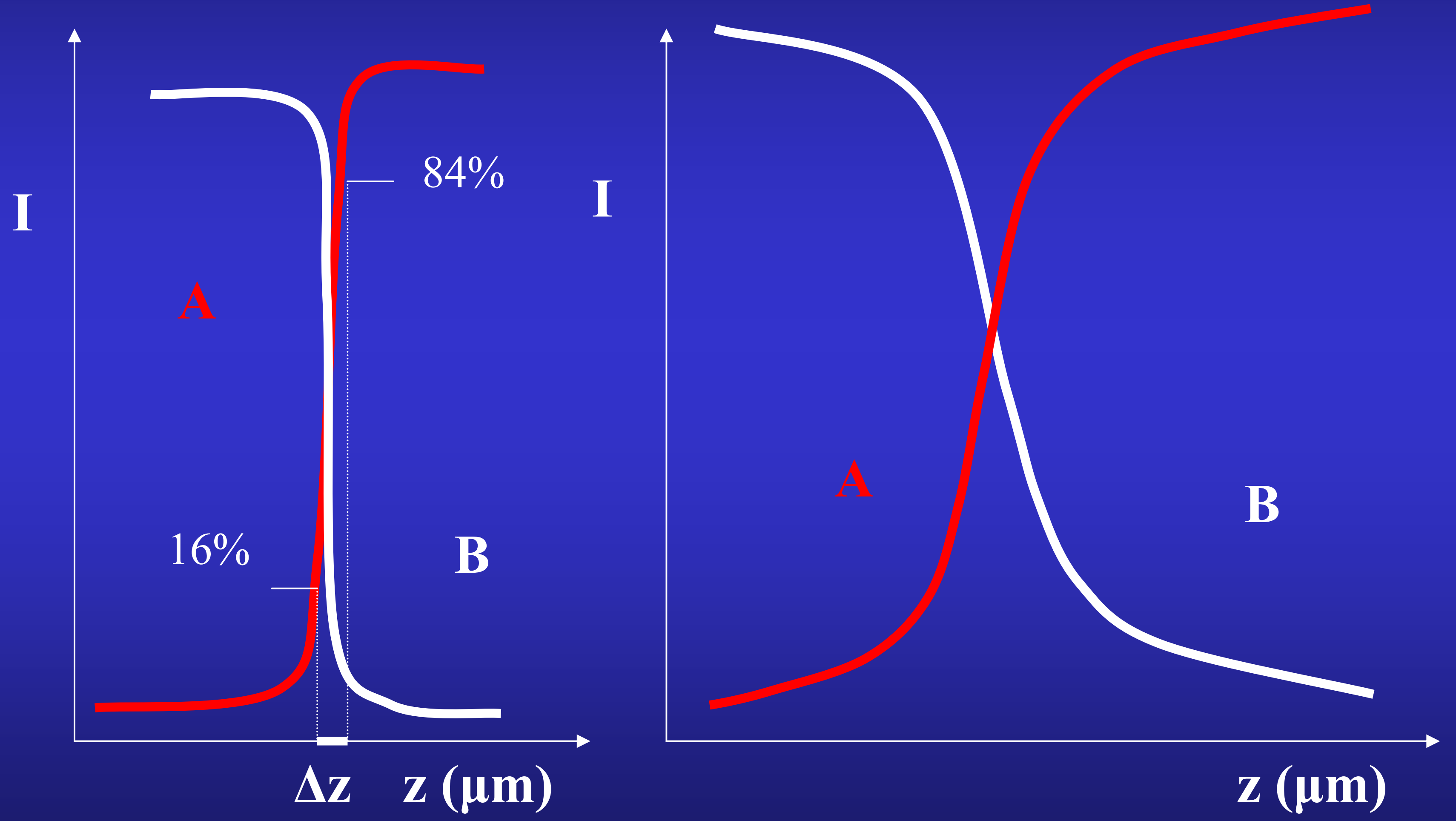
Homogenized beam

Flat-top beam profile

$\Rightarrow$ cylindrical craters



Depth resolution



Coating materials

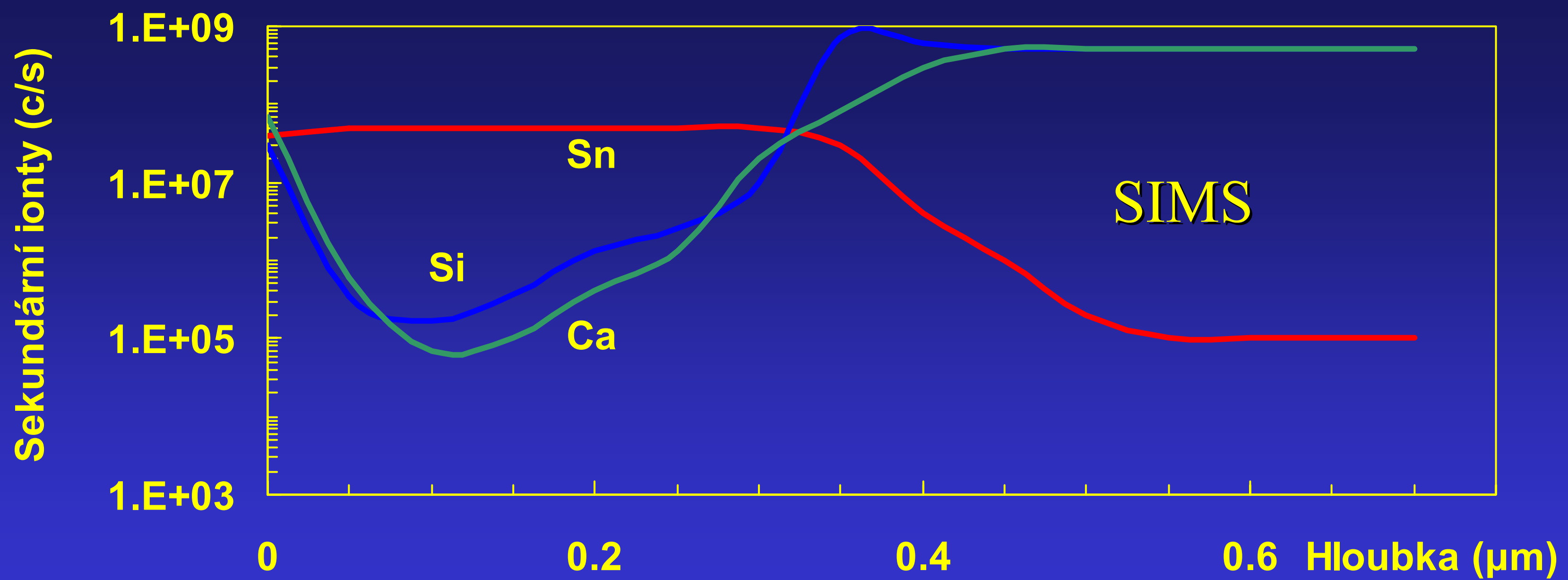
- 1-μm Sn coating on float glass
- 3-μm ZrTiN, ZrN, TiN coatings on HS steel,
- 10 – 30-μm thick Zinc coatings on steel sheets
- 200 – 300 Thick ceramic coatings: glazed wall tiles with or w/o 100-μm engobe

1-μm thick Sn coating on float glass

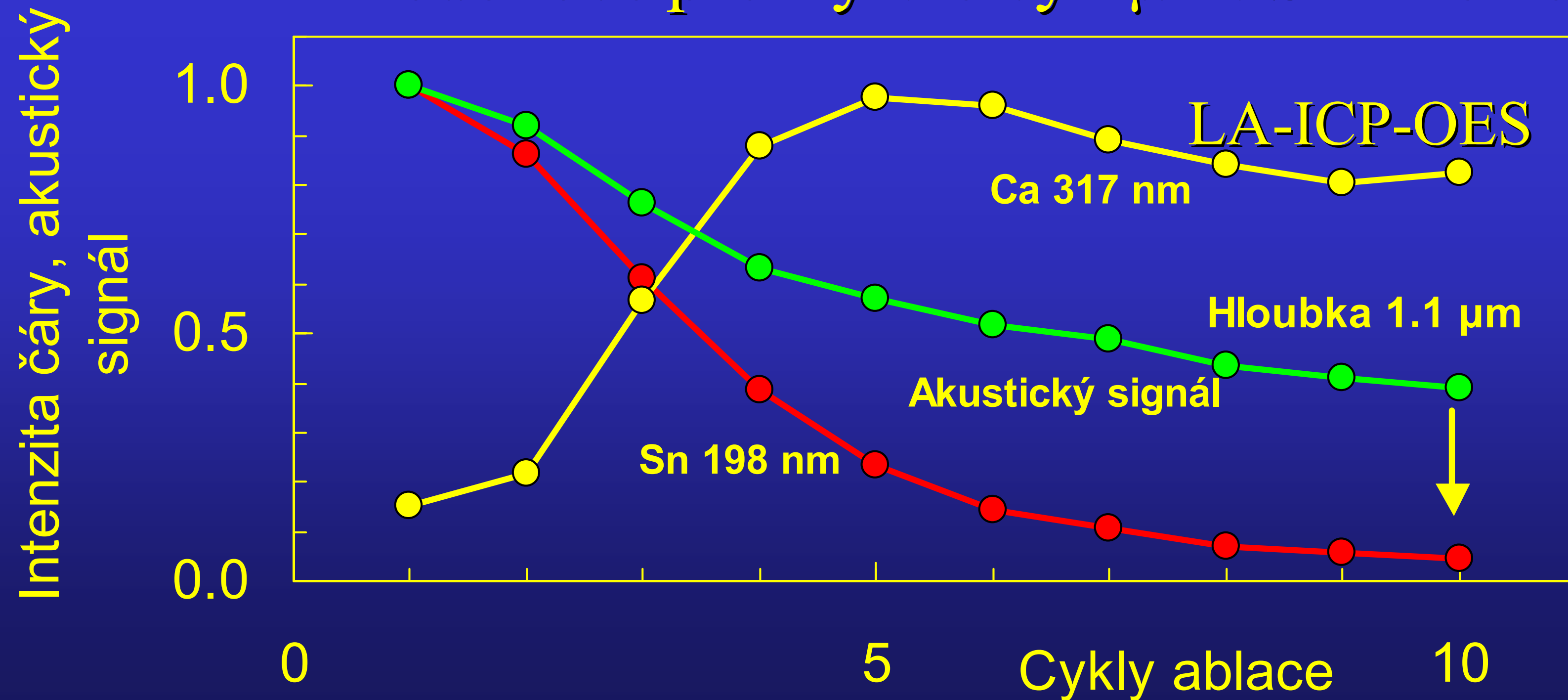
Nd:YAG laser, 266 nm, 1 mJ/pulse, 10 Hz,

Sample xy-translated at ablation (raster)

ICP-AES Optima (echelle grating, SCD detector)



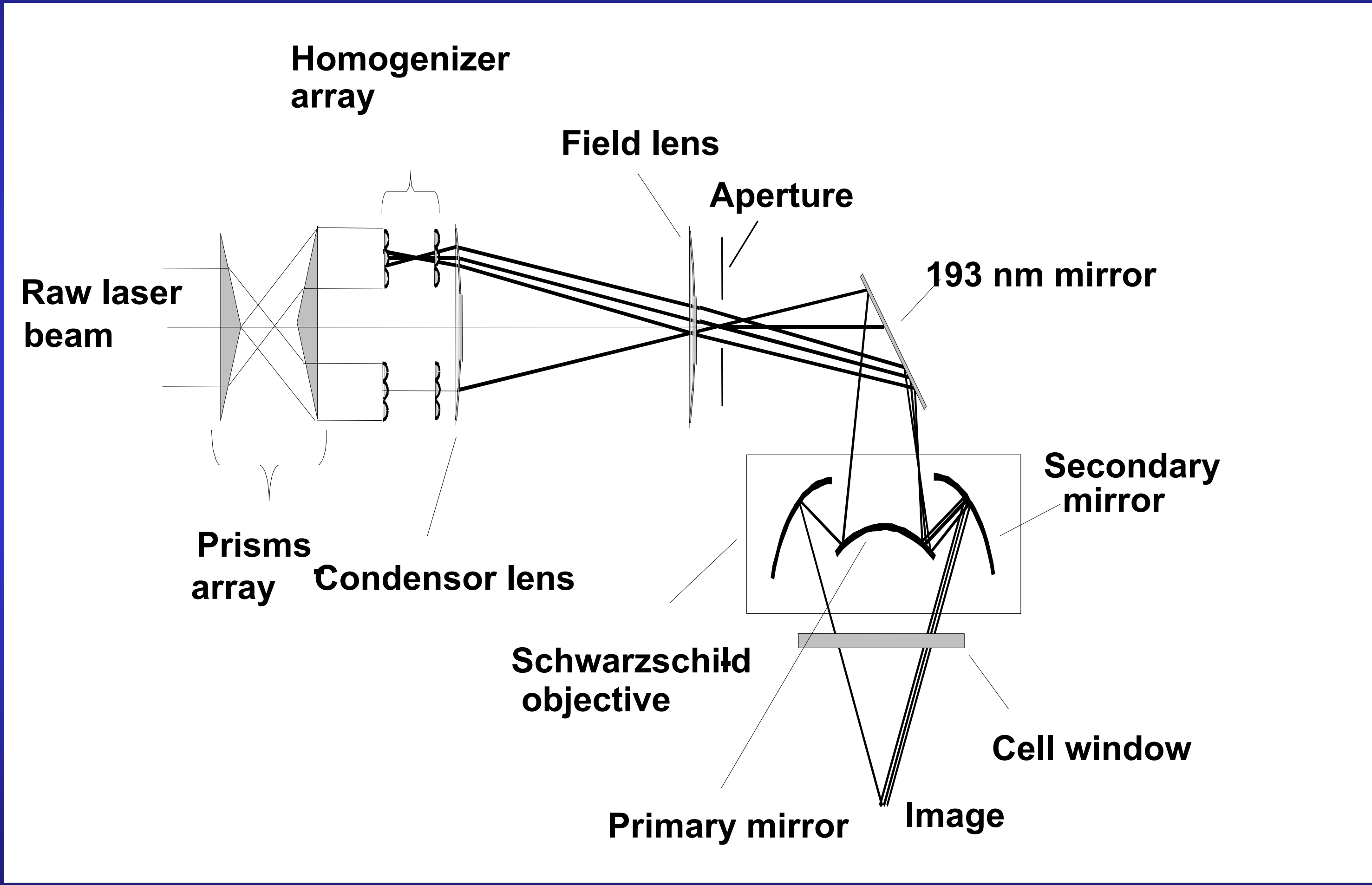
Hloubkové profily vrstvy 1 μm: Sn na skle



3-μm thick ZrTiN, ZrN, TiN coatings on HS steel, physical vapour deposition

- Nd:YAG 355 nm, ICP-AES
- ArF*193 nm, ICP-QMS

ArF* ablation system (Geolas) with beam homogenizer



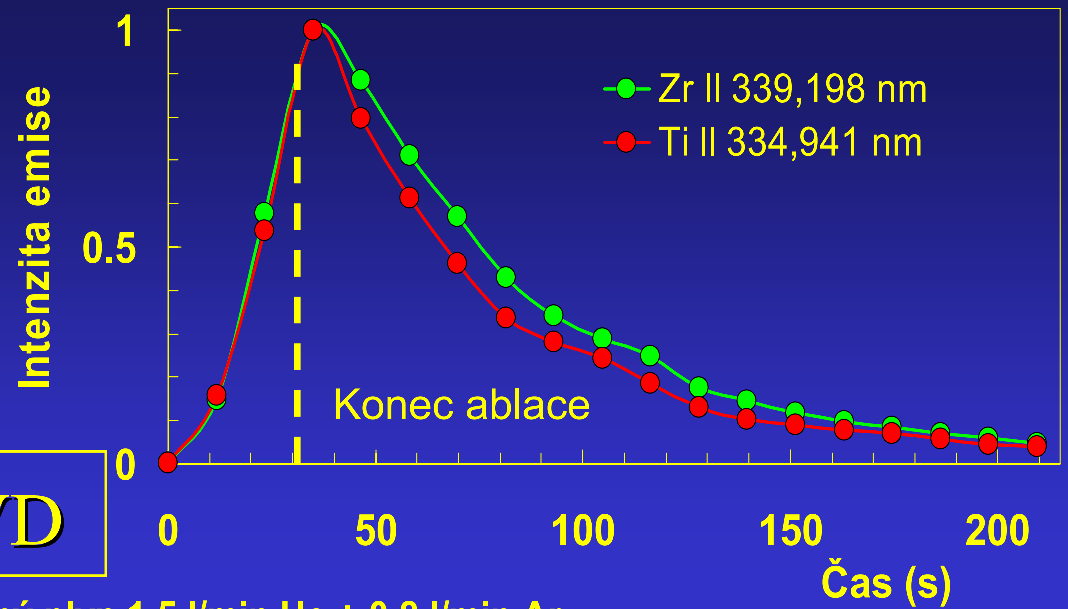
D. Günther et al., J. Anal. At. Spectrom. 12 (1997) 939-944.

GeoLas (Microlas) ArF* (Lambda Physik)

Petrographic microscope (Axioplan, Zeiss)

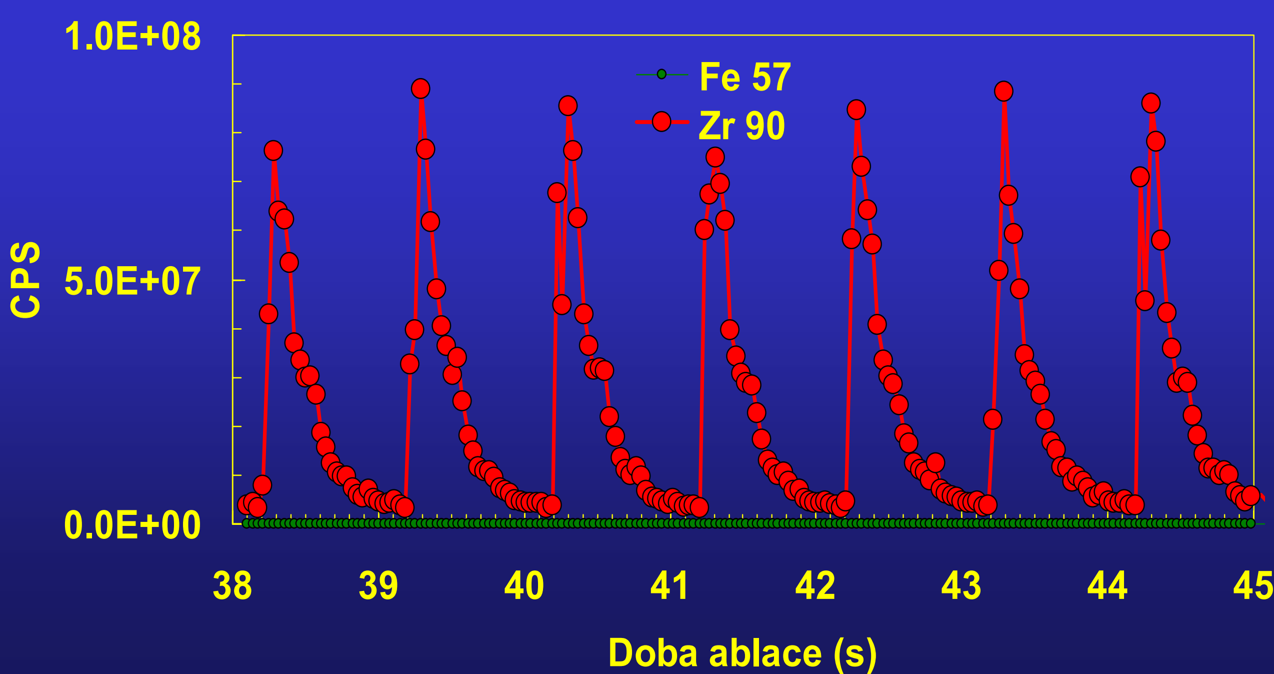
GeoLas ablation system + ICP-QMS (Elan 6000 DRC)

Nd:YAG 10 Hz
355 nm, 5 mJ
Pohyb vzorku: rastr 15 mm, 1 mm/s, 1 vrstva=
2 cykly, Ablační cela 140 cm^3
ICP-OES SPECTROFLAME



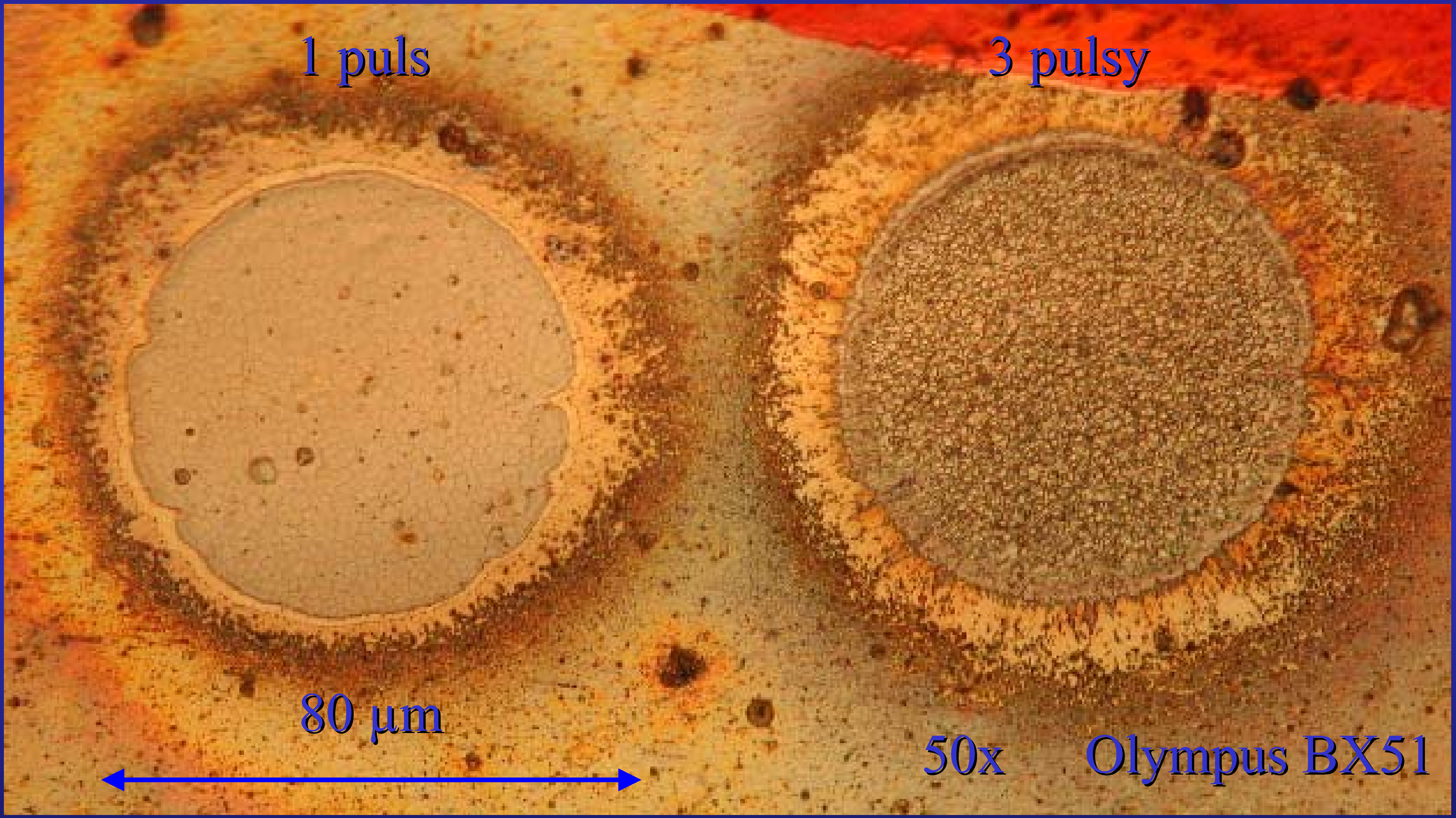
ZrTiN 3µm povlak PVD

PVD vrstva 0,003 mm ZrN, nosný plyn 1,5 l/min He + 0,8 l/min Ar, průměr kráteru 0,040 mm

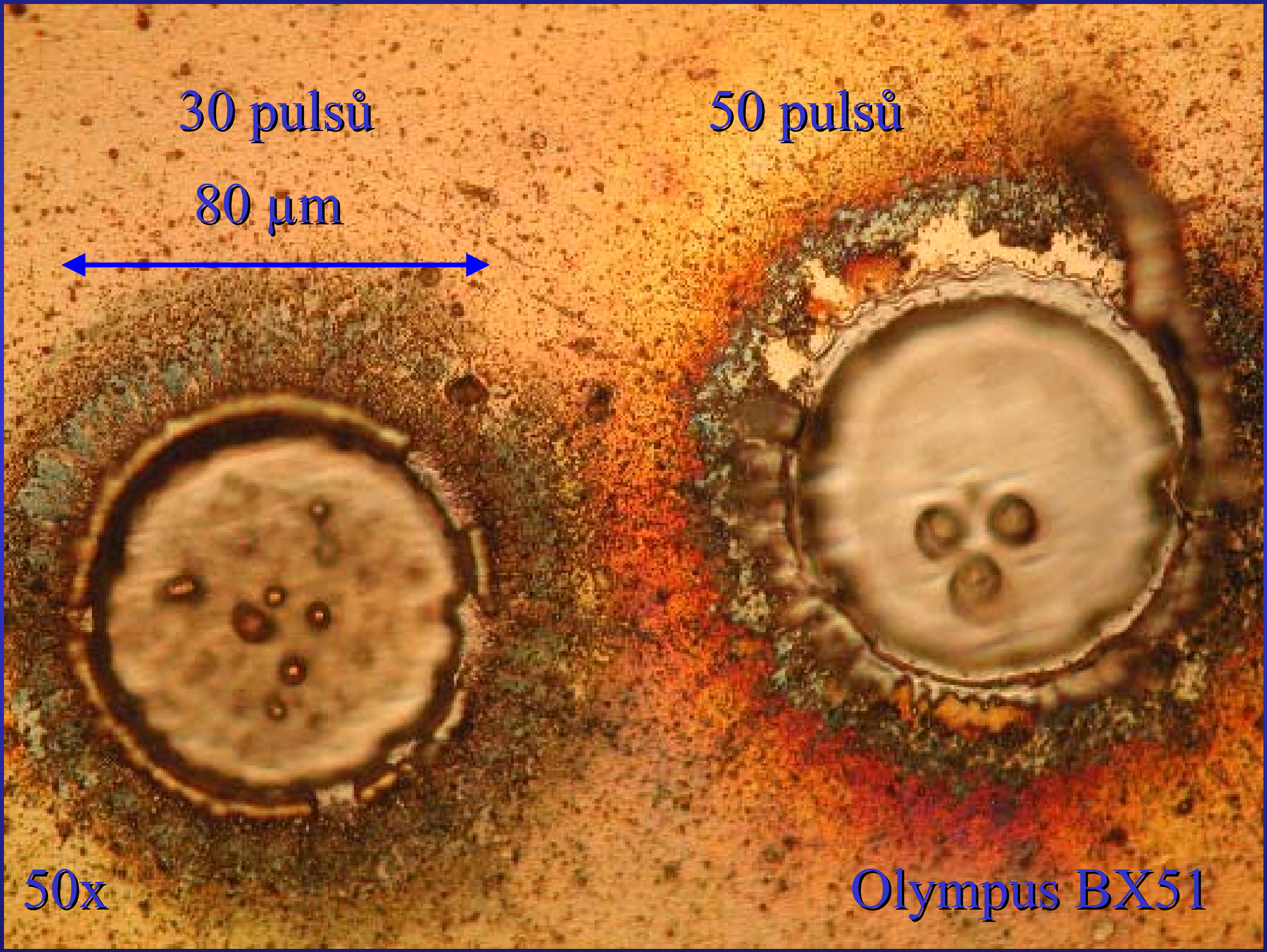


ICP-QMS Agilent
Laser ArF*193 nm, 134 mJ, 1 Hz, „beam homogenizer 9x9 lens“, objem ablační cely 1 cm^3

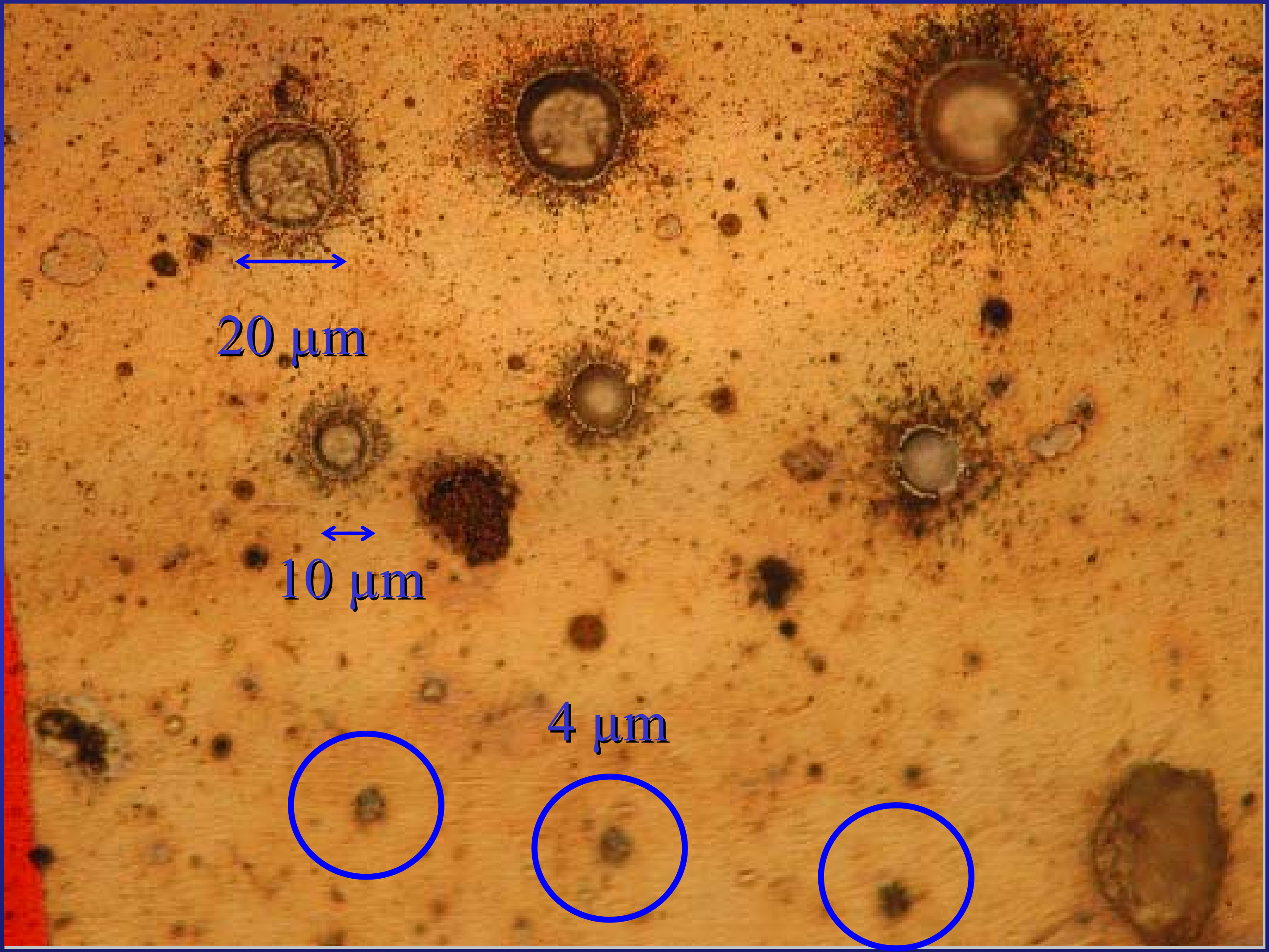
Zr/Ti nitrid, 74% Zr,1 % Ti, povlak 3 µm, laser ArF* 193 nm, 1 Hz, 132 mJ, beam homogenizer, ICP-QMS Agilent 7500, He+Ar



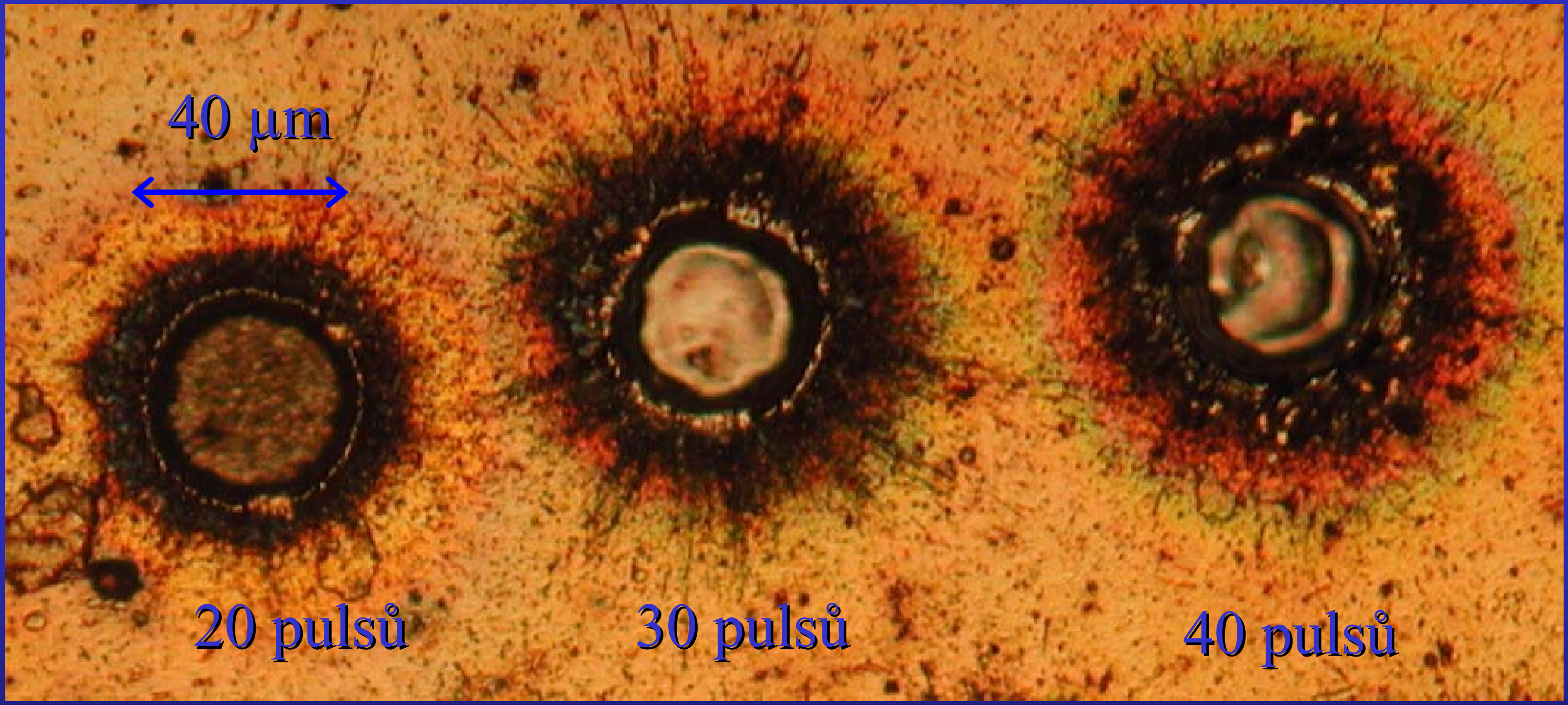
Zr/Ti nitrid, 74% Zr,1 % Ti, povlak 3 μm, laser ArF* 193 nm, 1 Hz, 132 mJ, beam homogenizer, ICP-QMS Agilent 7500, He+Ar



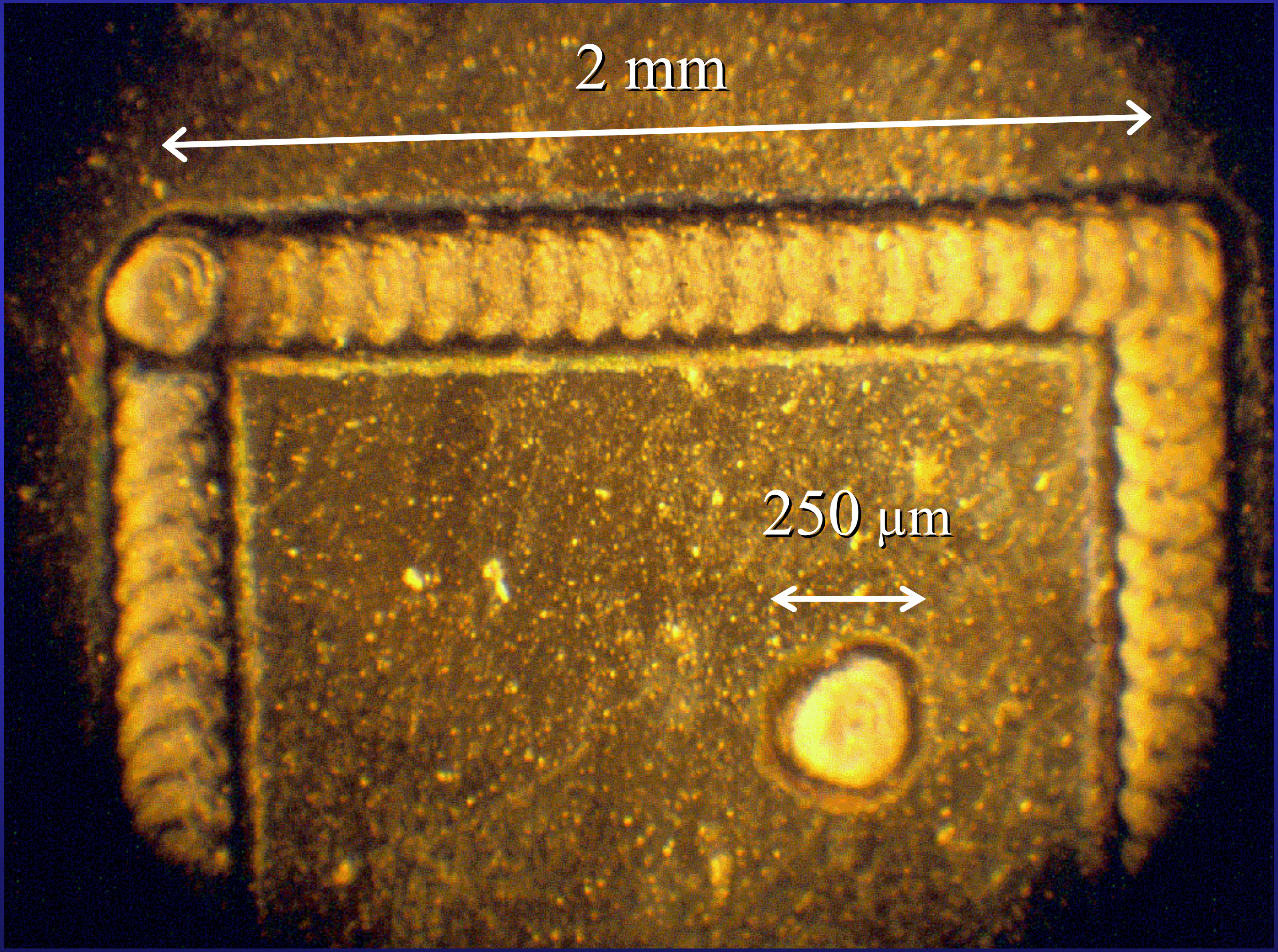
Zr/Ti nitrid, 74% Zr,1 % Ti, povlak 3 μm, laser ArF* 193 nm, 1 Hz, 132 mJ, beam homogenizer, ICP-QMS Agilent 7500, He+Ar



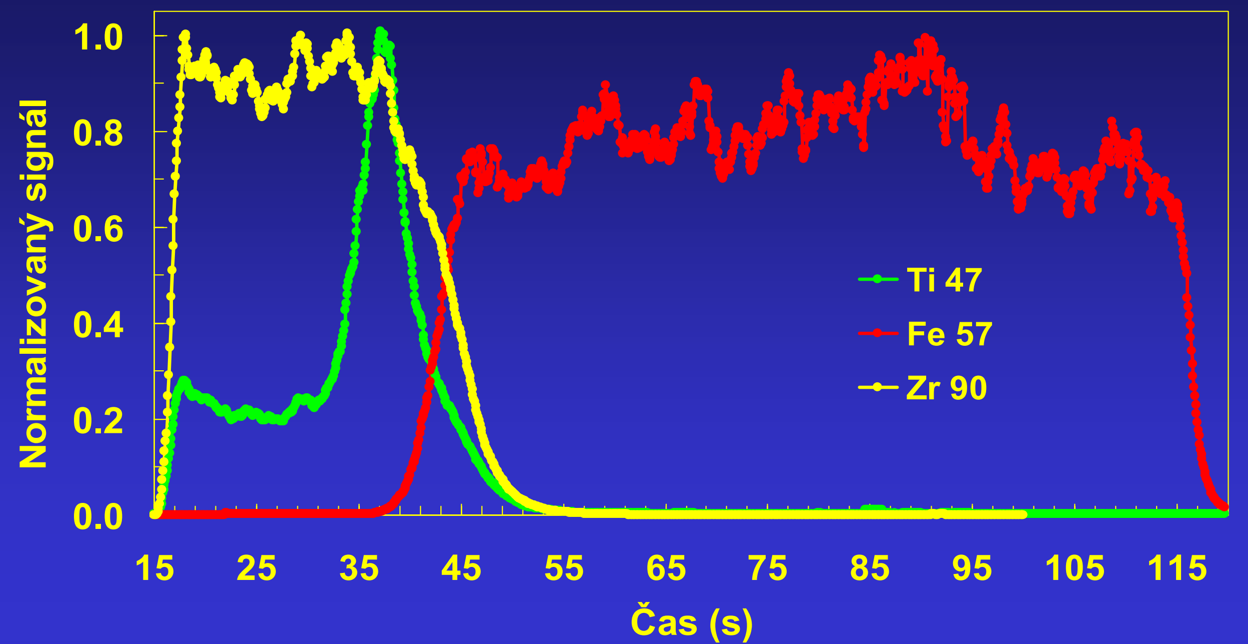
Zr/Ti nitrid, 74% Zr,1 % Ti, povlak 3 μm, laser ArF* 193 nm, 1 Hz, 132 mJ, F = 4×10^{11} W/cm^2, beam homogenizer, ICP-QMS Agilent 7500, He+Ar



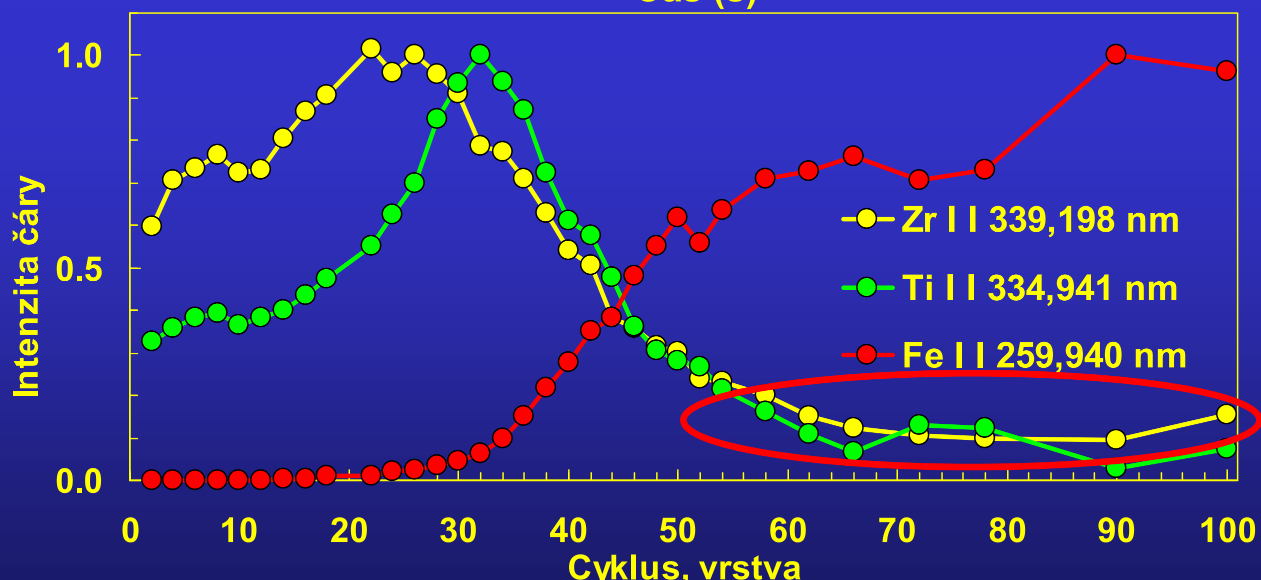
Zr/Ti nitrid, 69 % Zr, 6 % Ti, povlak 3 μm, laser Nd:YAG 355 nm, 10 Hz, 5 mJ, $F=5x10^9$ W/cm^2, trajektorie 2x2 mm, rychlost posunu 1mm/s, 5 cyklů, rychlost ablace 0,1 μm/cyklus, ICP-OES Spectro D



PVD Zr/Ti nitrid, 76% Zr, 1 % Ti, tloušťka povlaku 3 µm



ArF* 1 Hz
193 nm, 134 mJ,
Ablace do bodu spojitě
40 µm Ø kráteru
„beam homogenizer“
9x9 čoček, cela 10 cm^2
ICP-MS Agilent 7500,
nosný, plyn 0,8 Ar
+ 1,5 He (l/min),



Nd:YAG 10 Hz
355 nm, 5 mJ
Pohyb vzorku: rastr,
1 mm/s, 1 vrstva =
2 cykly, ICP-OES
Spectroflame D:
2 monochromátory

Zn-based coatings on steel sheets thickness 10-30 μm

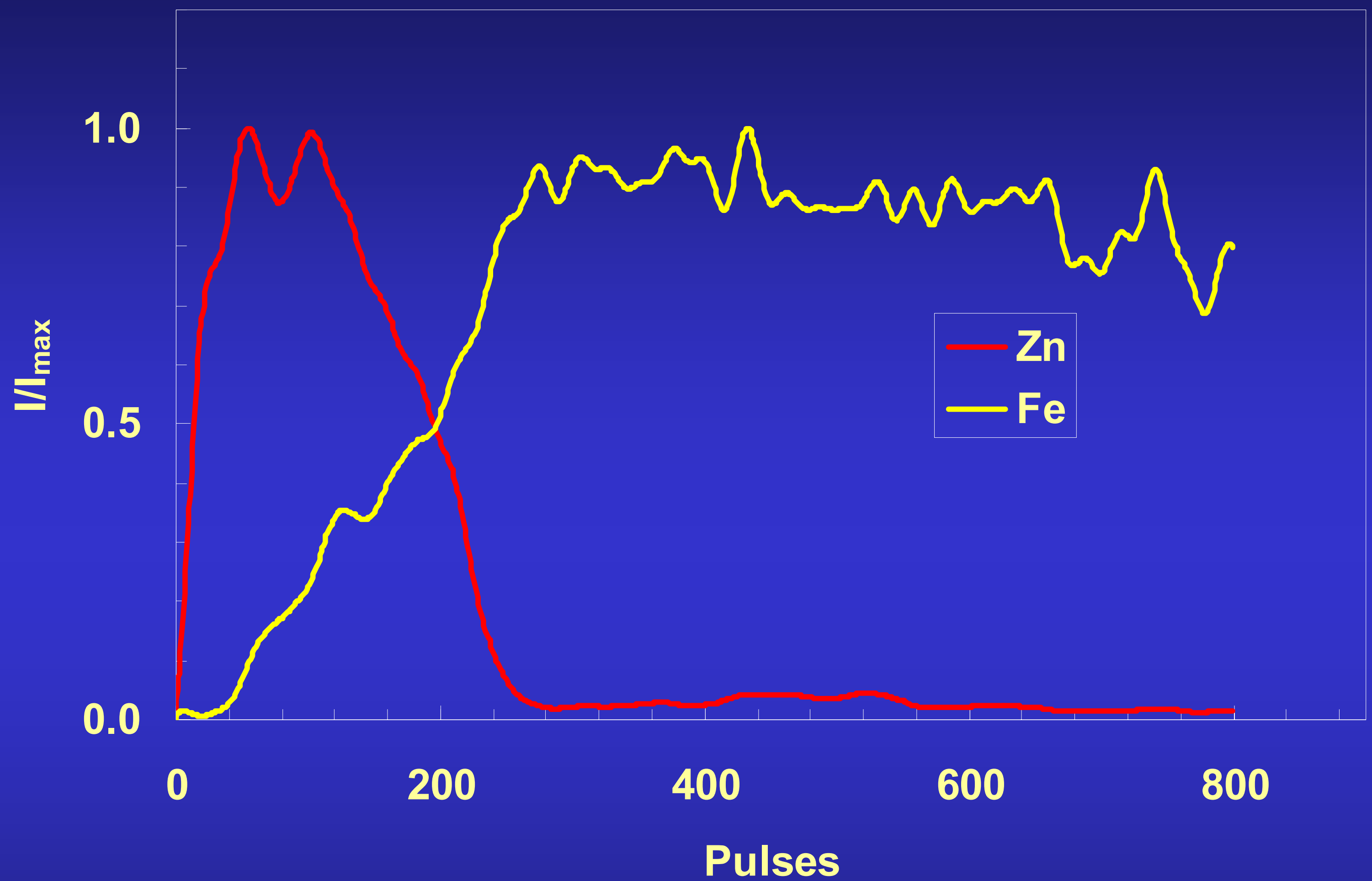
- **Hot-dipped Zn (Hoesch Stahl)**
- **Hot–dipped ZnNi (Sollac)**
- **Electroplated Zn (Sollac)**

Zn: melting temperature 419.5 °C, boiling temp. 906.2°C

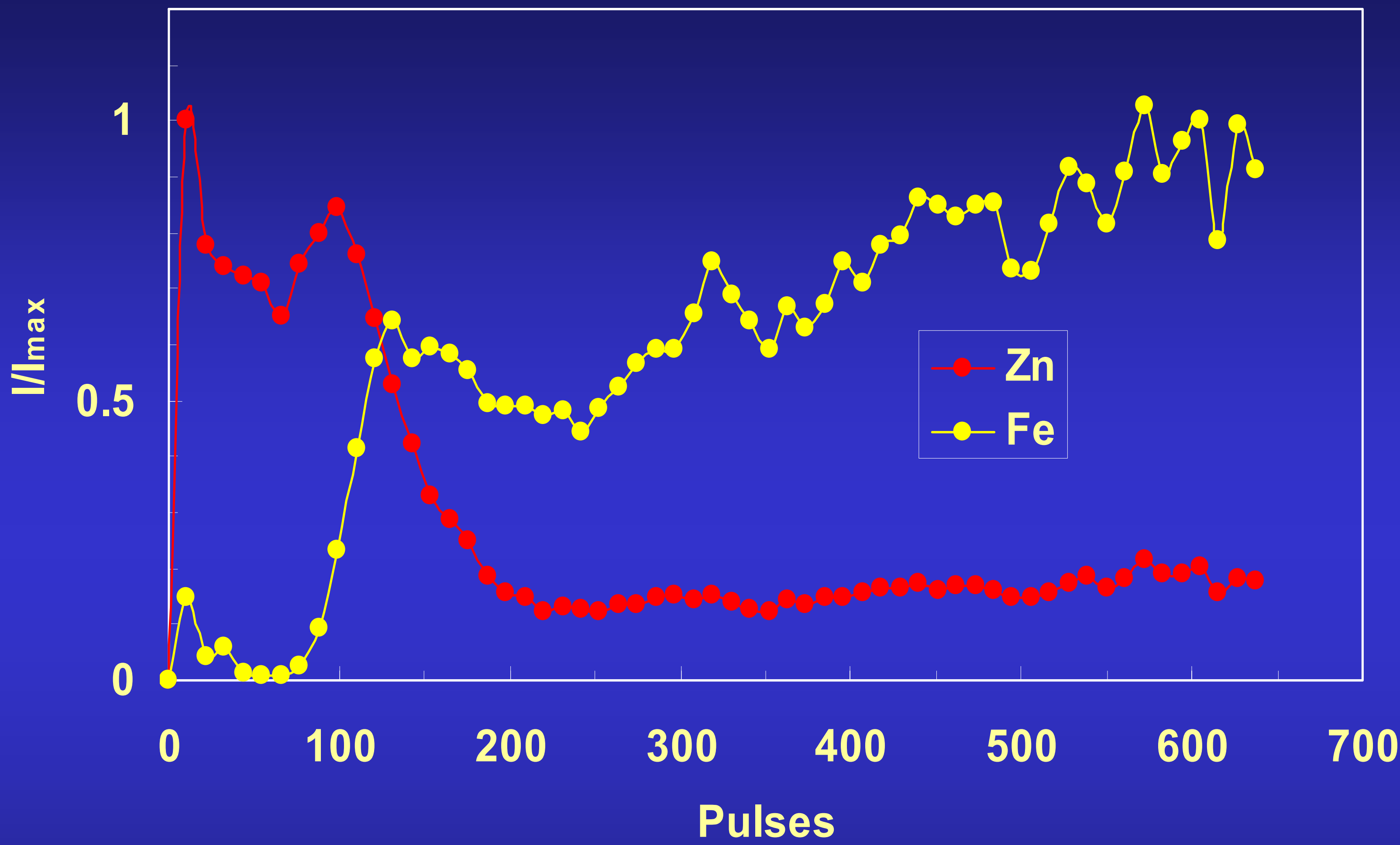
Imaging and depth measurement with EMPA device SX-100 by CAMECA

dc-GD-OES (SA-2000 by LECO) profiles taken with permission of Dr. Zdeněk Weiss from:

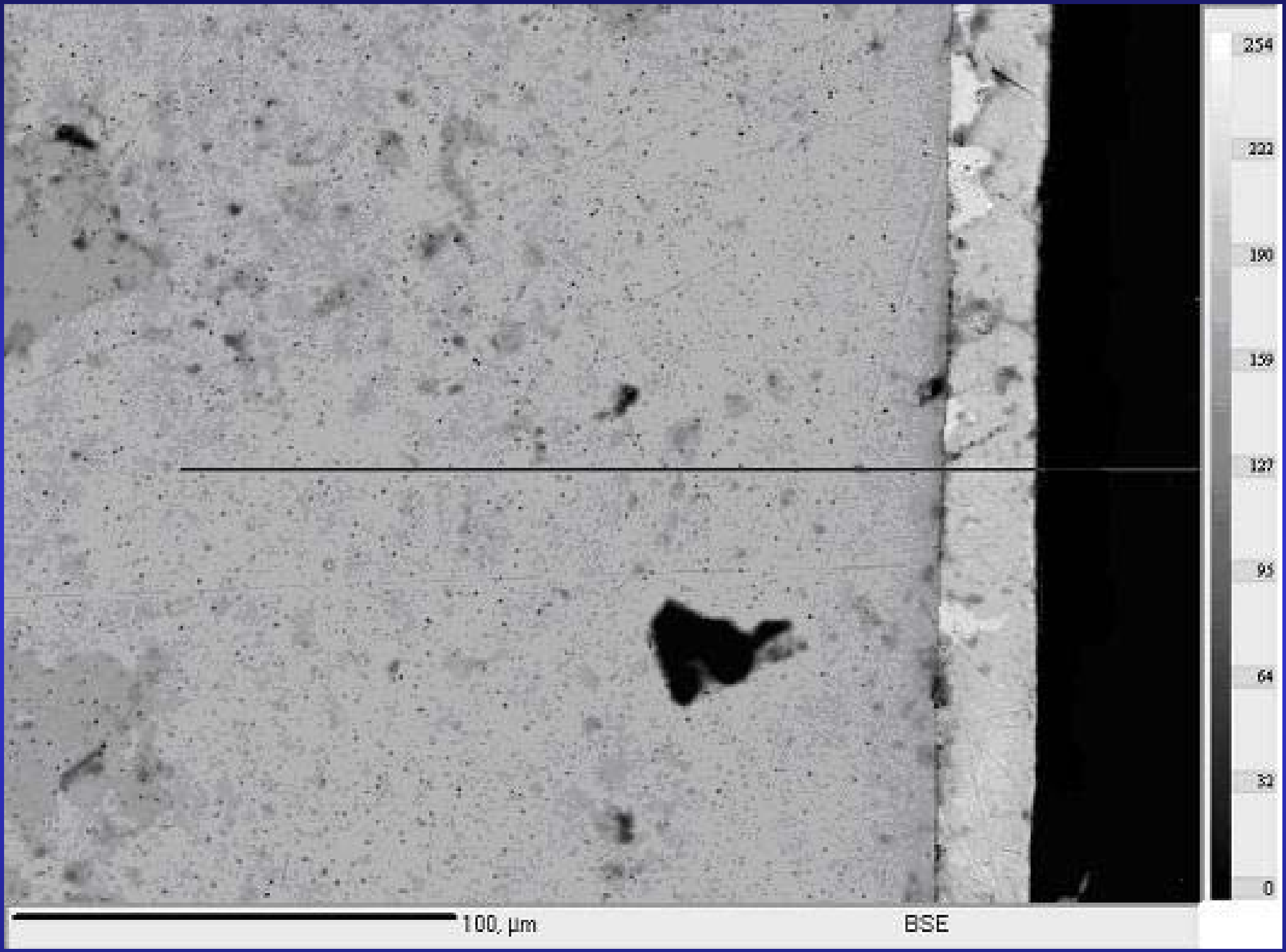
Z. Weiss, Analysis of Zn based coatings on steel, GD-Emission spectrometry systems, Application report 98-7P, LECO Pilsen CZ



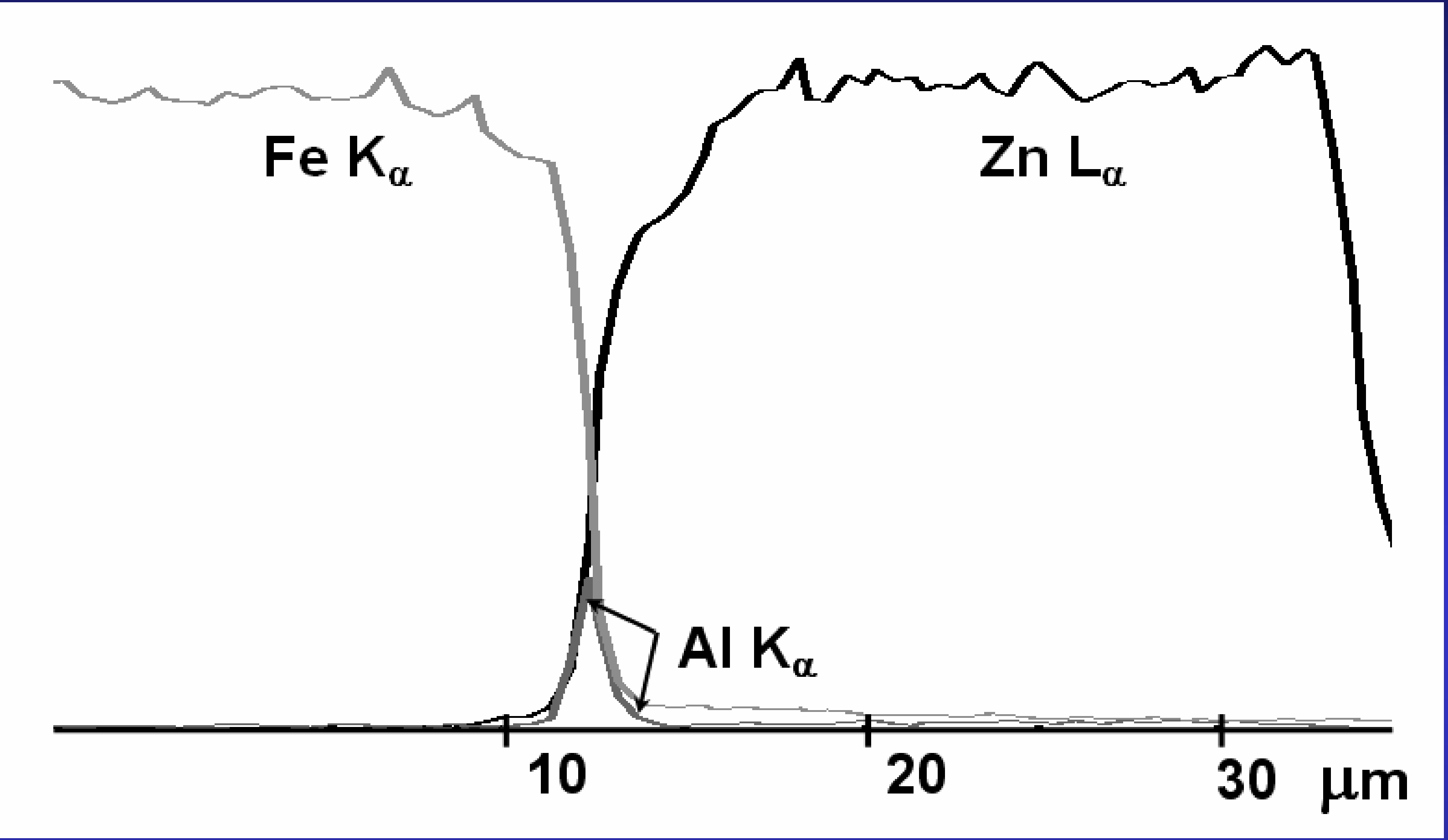
Electroplated Zn, thickness 10 µm, E= 40 mJ, ∅ crater 120 µm, Geolas ArF* 193 nm, FWHM 15 ns, f = 5 Hz, ICP-QMS Elan 6000 DRC, dwell time 10 ms, isotopes: Zn 68, Fe 57



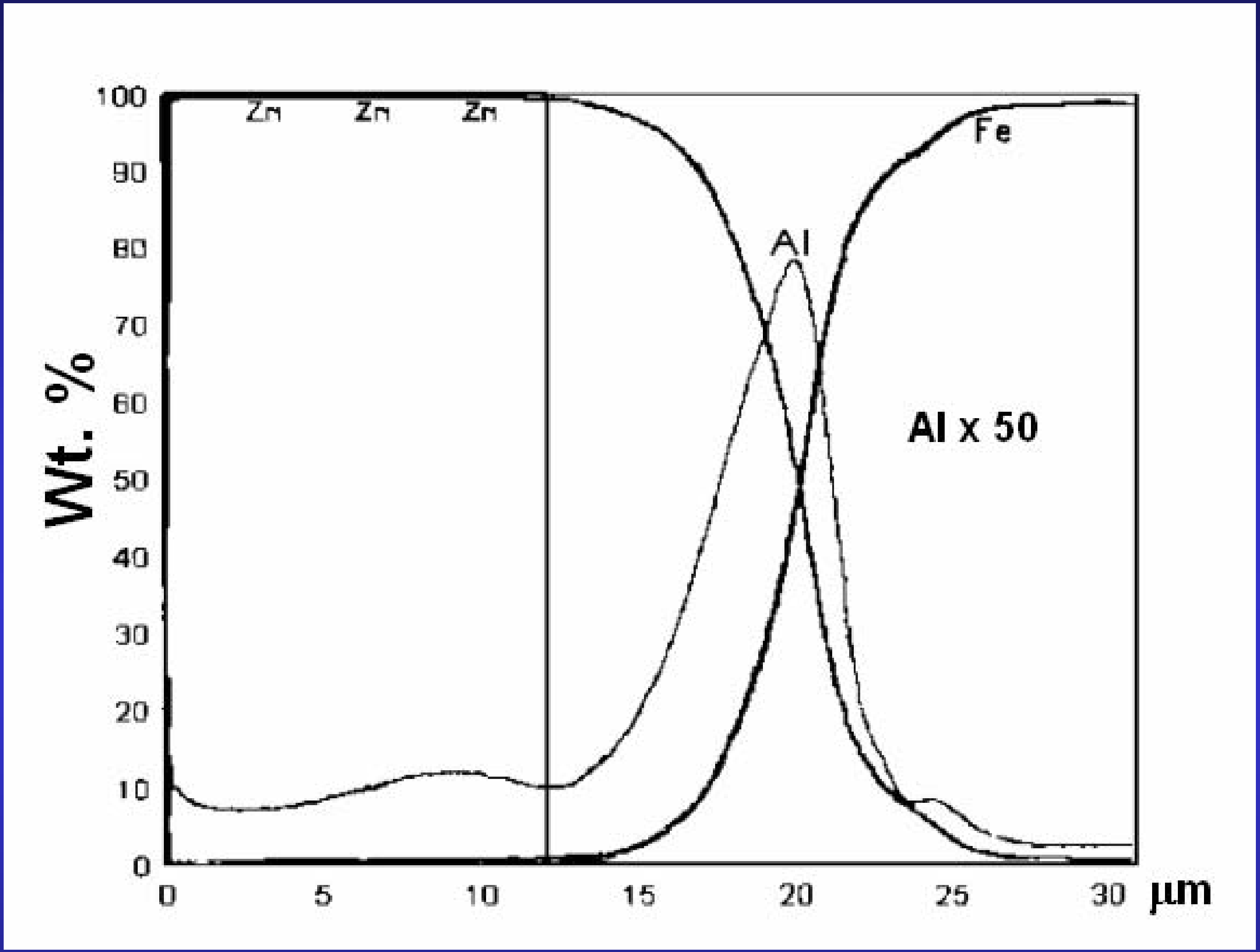
Electroplated Zn, thickness 10 µm, E= 58 mJ, ∅ crater 0.9 mm, Nd:YAG 1064 nm, f = 10 Hz, pulse FWHM 4,4 ns, focusing -25 mm,without beam masking, ICP-OES 170 Ultrace JY Horiba,int. time 0.5 s, 1 replicate 1.1 s, lines poly. [nm]: Zn I 213.86, Fe II 259.944



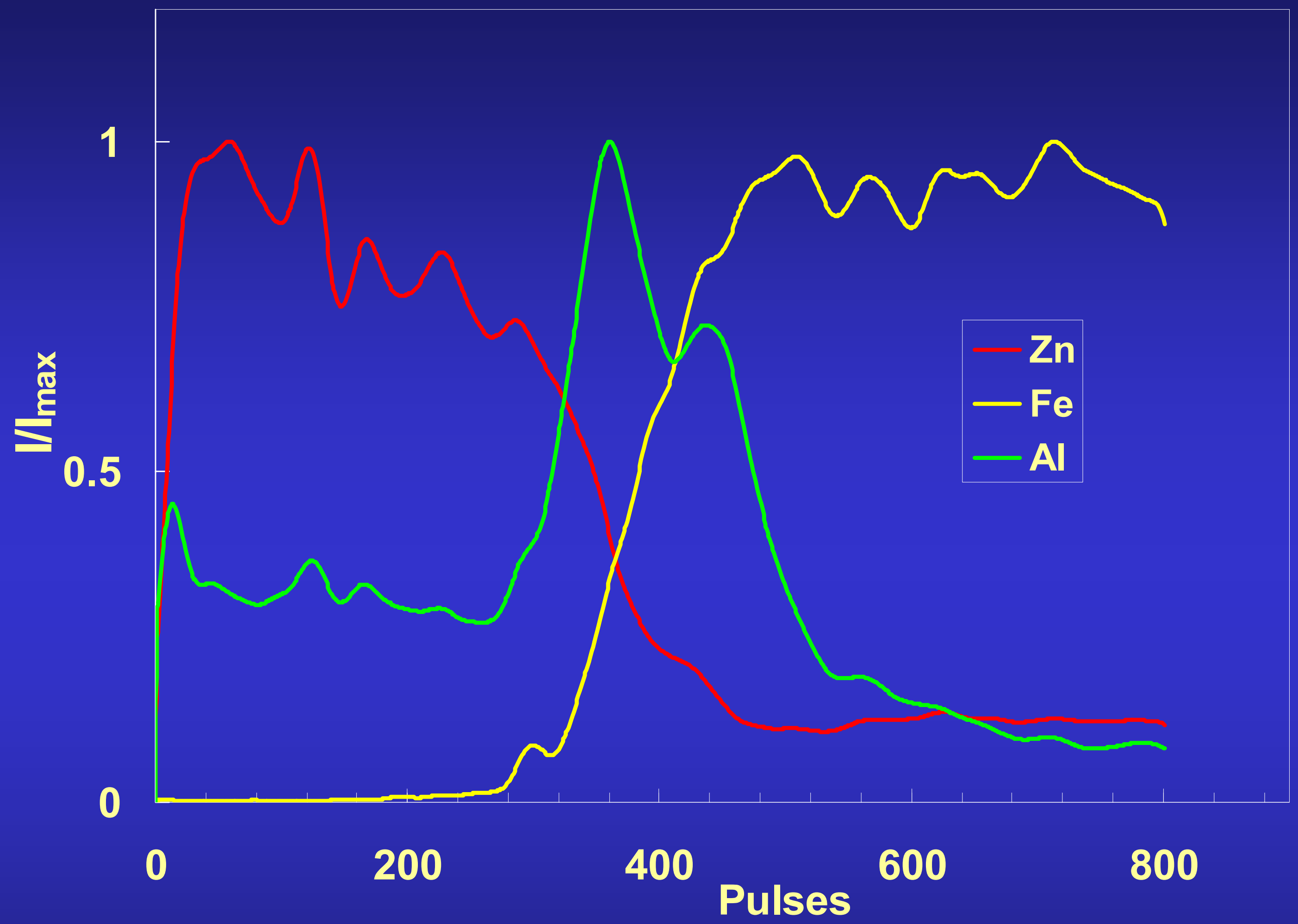
Hot dipped Zn profile – an image in backscattered electrons (BSE). The line indicates the path of EDX measurement



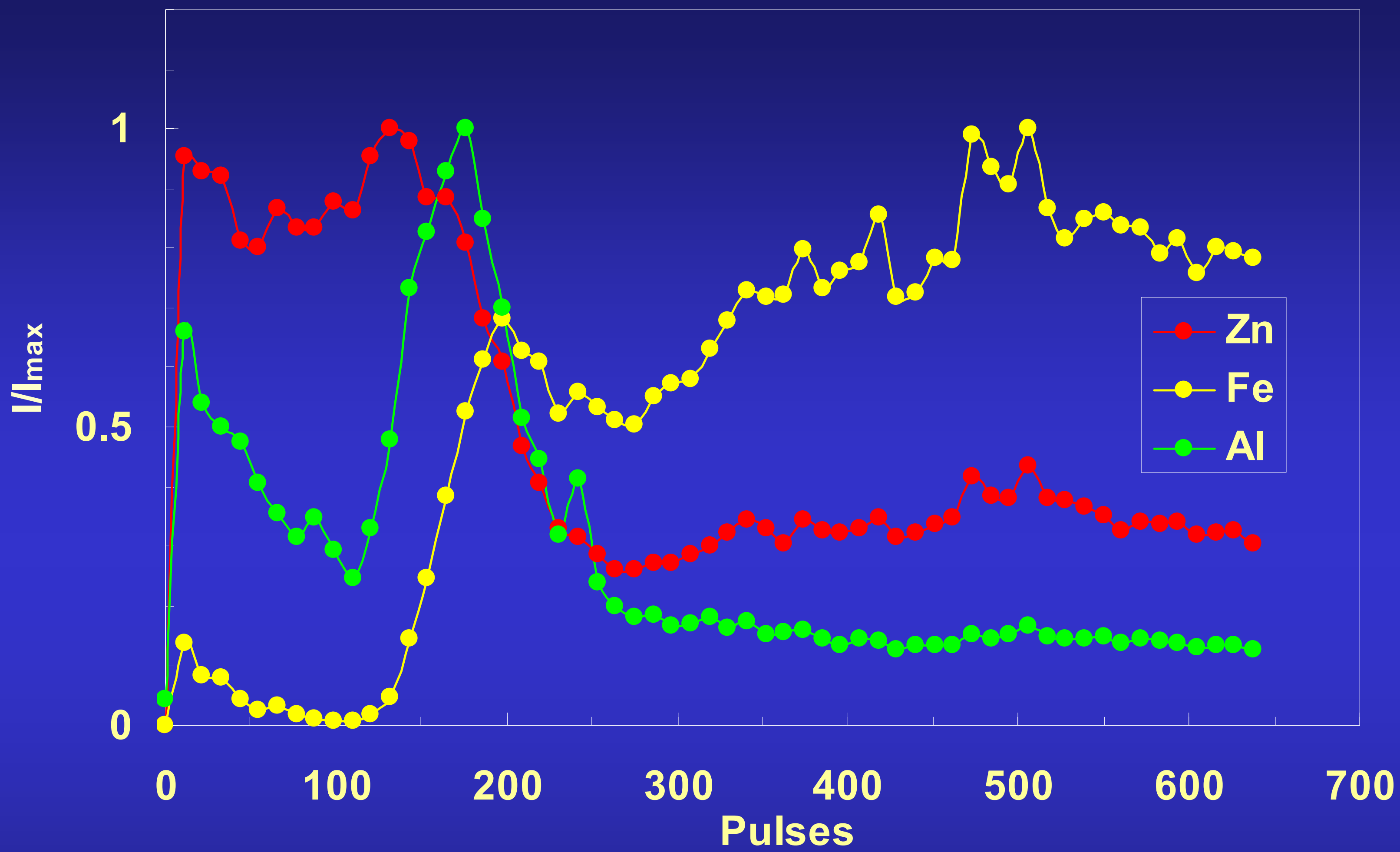
EMPA: Hot dipped Zn profile: The Al peak appears just in the crossing point



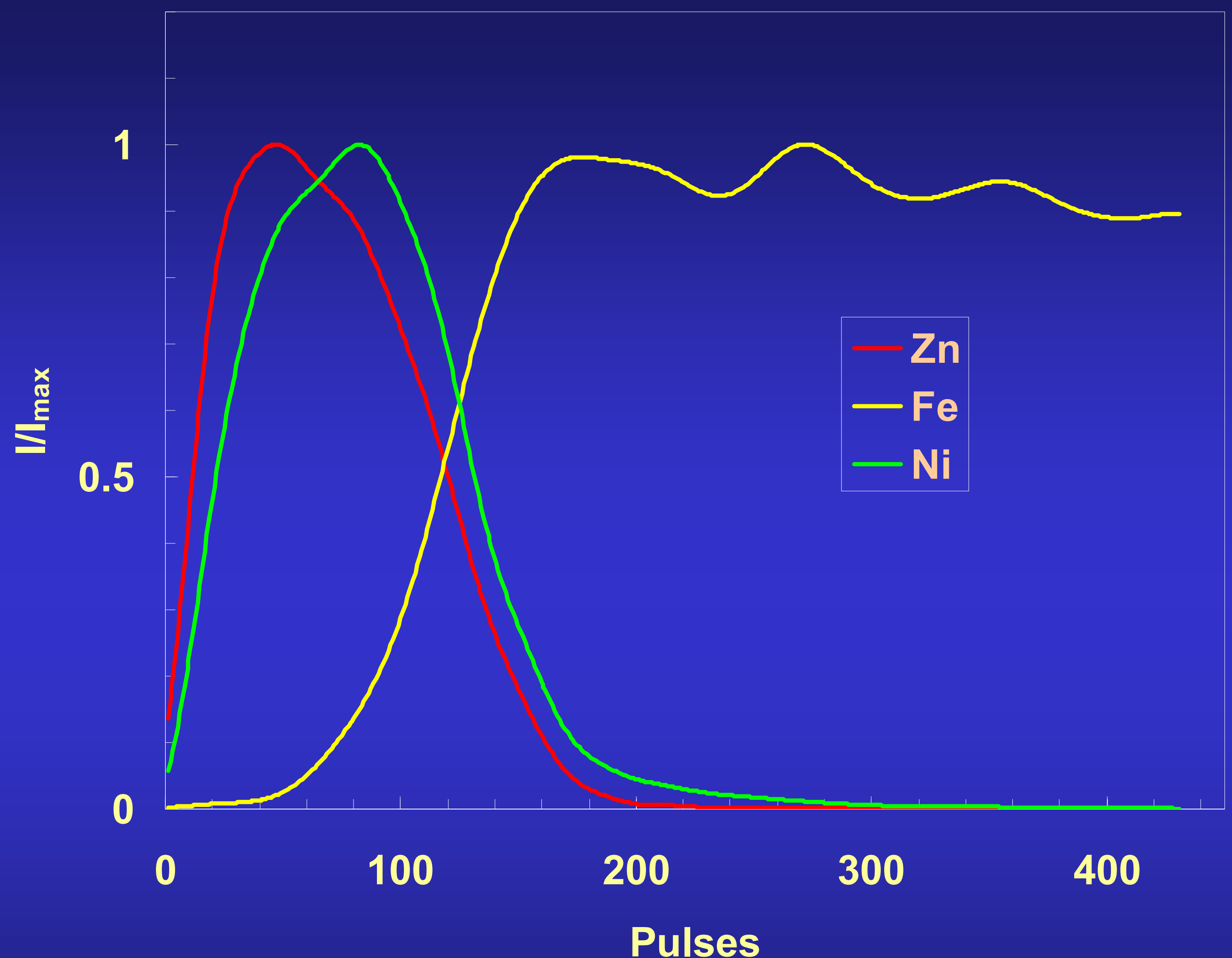
dc-GD-OES: Hot dipped Zn, thickness 20 µm



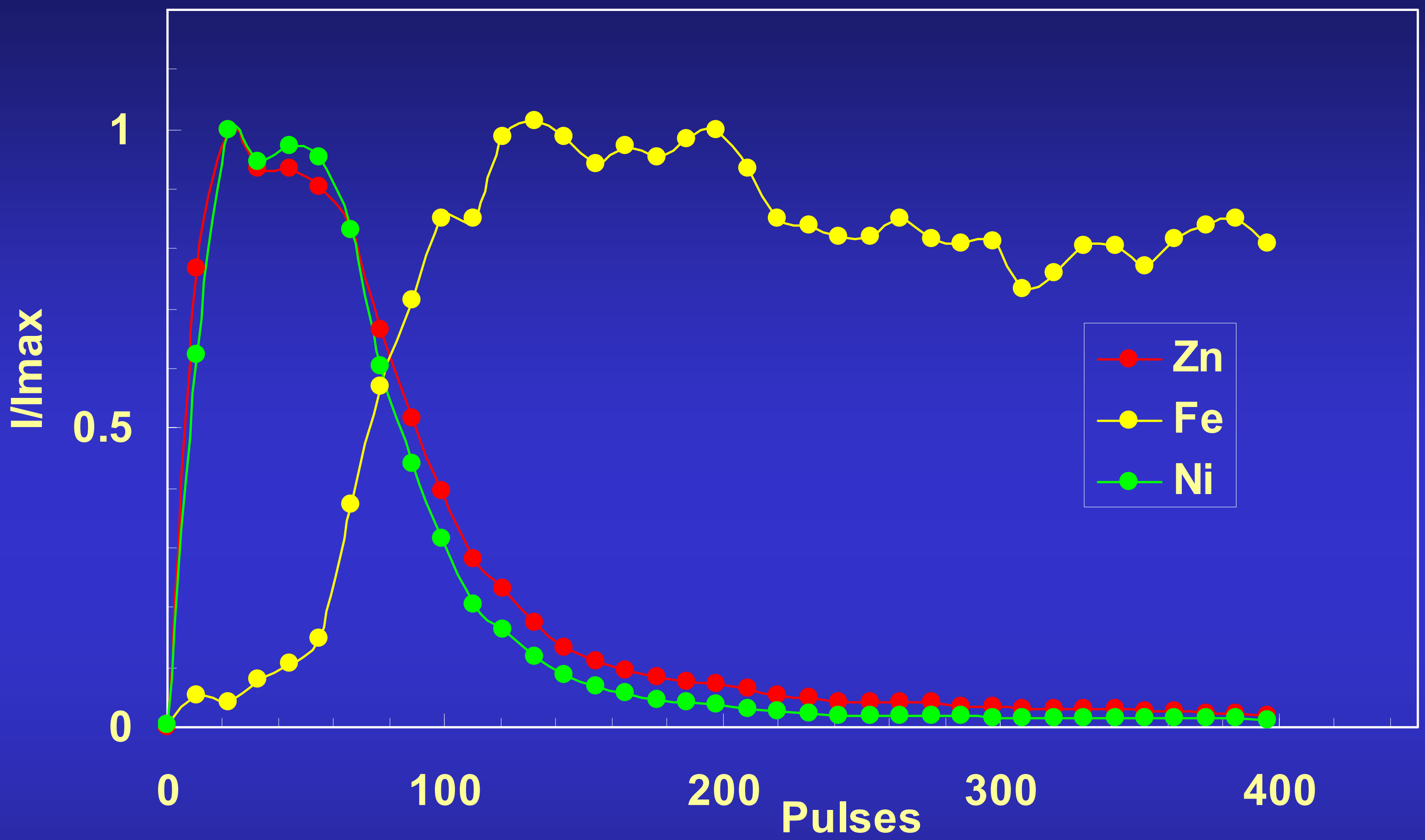
Hot dipped Zn, thickness 20 µm, E= 40 mJ, ∅ crater 120 µm, Geolas ArF* 193 nm, FWHM 15 ns, f = 5 Hz, ICP-QMS Elan 6000 DRC, dwell time 10 ms, isotopes: Zn 68, Fe 57, Al 27



Hot dipped Zn, thickness 20 µm, E= 58 mJ, ∅ crater 0.9 mm, Nd:YAG 1064 nm, f = 10 Hz, pulse FWHM 4.4 ns, focusing -25 mm, without beam masking, ICP-OES 170 Ultrace JY Horiba, int. time 0.5 s, 1 replicate 1.1 s, lines poly. [nm]: Zn I 213.86, Al I 308.220, Fe II 259.944



Electroplated ZnNi, max. Zn 88 wt%, Ni 12 wt% in layer, layer thickness 7.5 µm, E= 40 mJ, ∅ crater 120 µm, Geolas ArF* 193 nm, FWHM 15 ns, f = 5 Hz, ICP-QMS Elan 6000 DRC, dwell time 10 ms, isotopes: Zn 68, Fe 57, Ni 60



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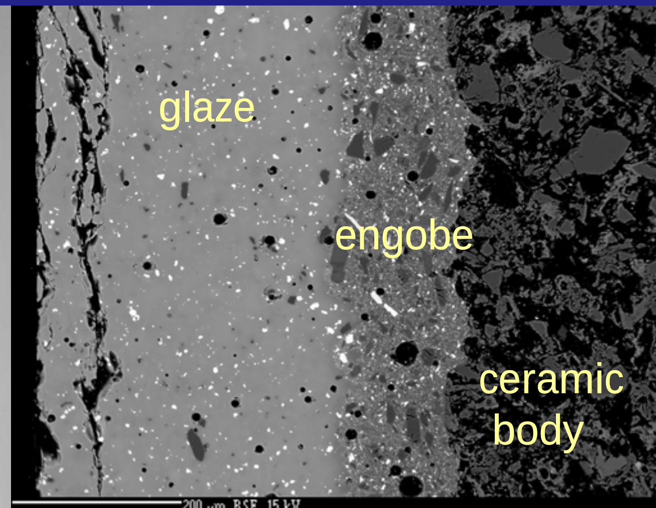
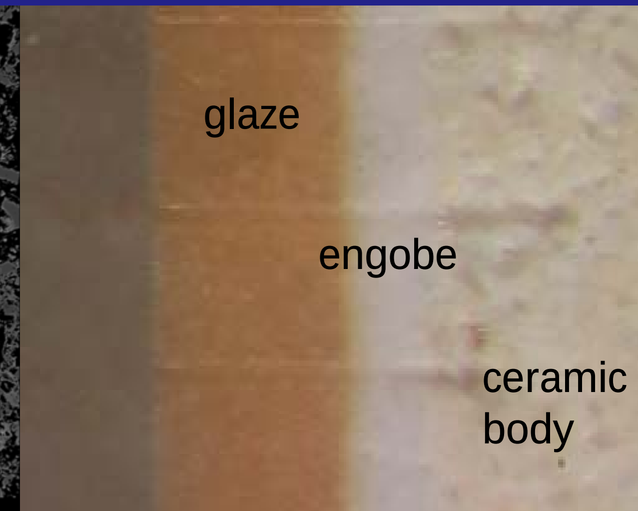
1) Ceramic tiles (HOB, Lasselsberger)





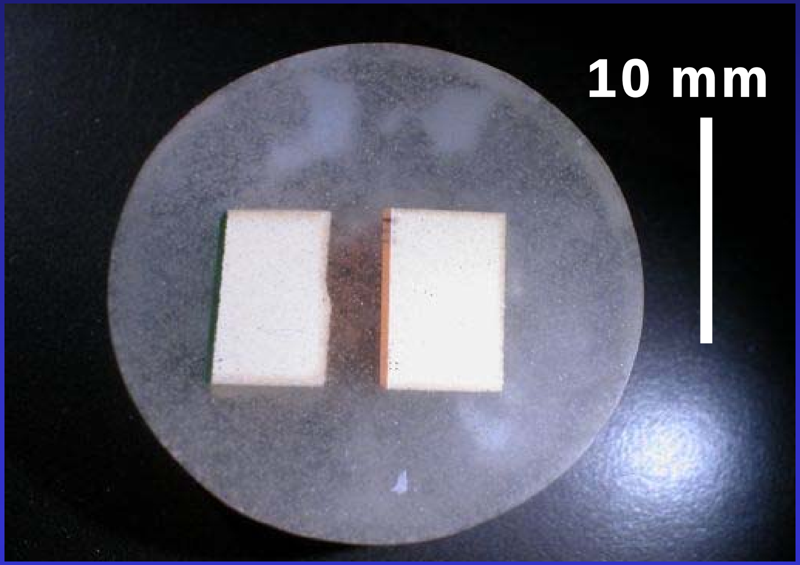
m/m %, Orange tile

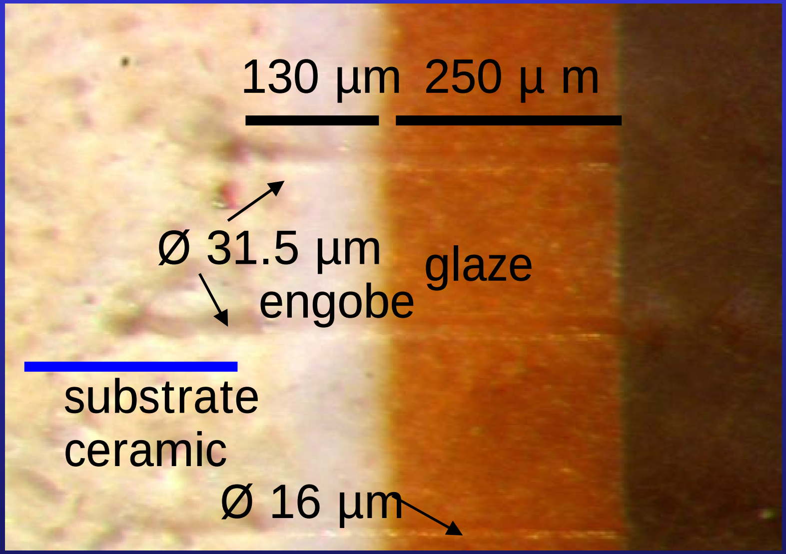
Compound	glaze	engobe	body
Al2O3	7.87	12.90	16.70
CaO	5.99	3.79	8.61
Fe2O3	0.27	0.29	1.08
PbO	7.74	0.07	0.00
TiO2	0.10	0.22	0.60
ZrO2	4.85	15.50	0.00
SiO2	58.60	57.08	66.11

a) LA-ICP-MS, section scanning (mapping)

GEOLAS Q CETAC
Agilent 7500 ICP-QMS

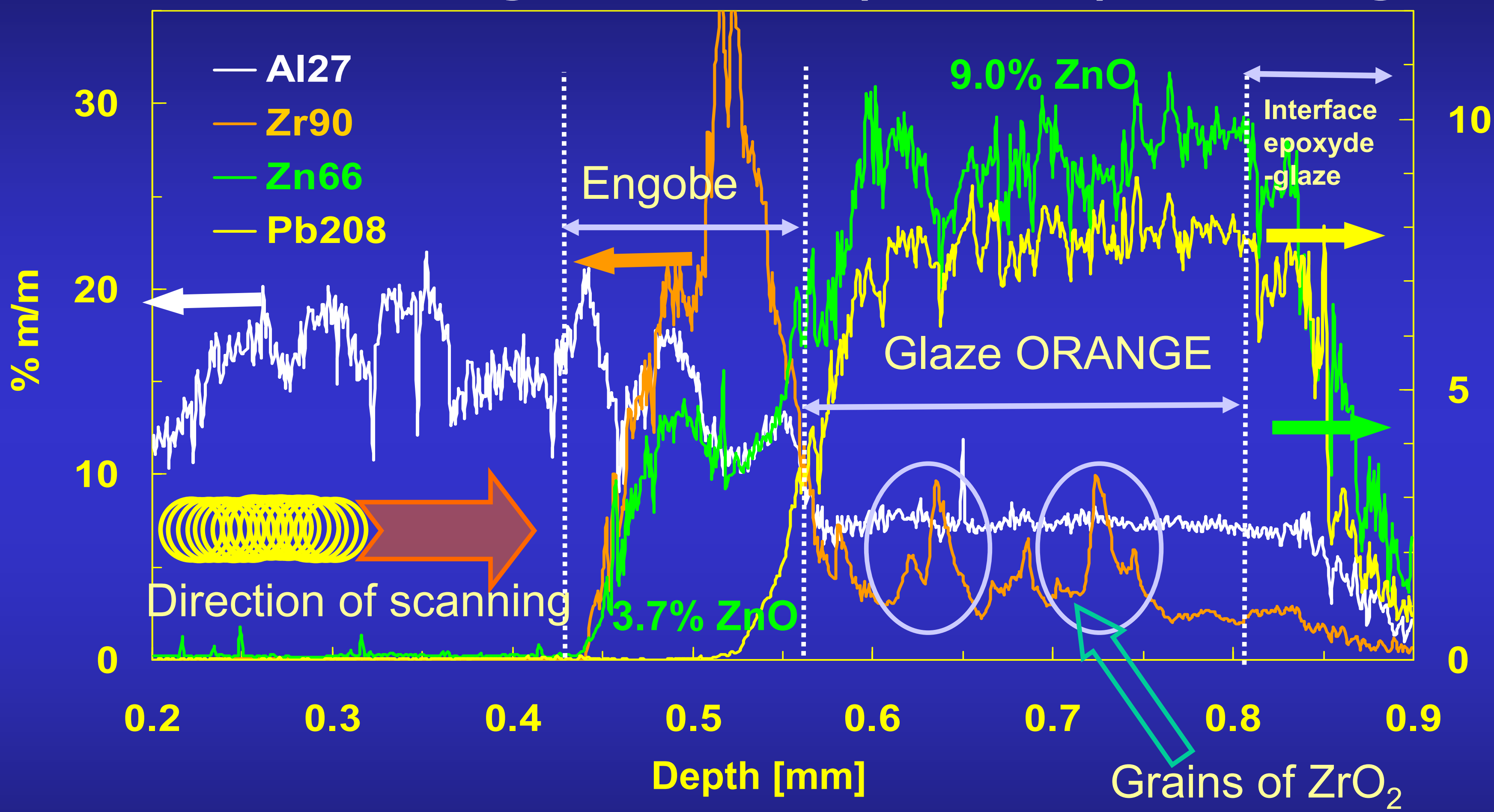
Laser ArF* with beam homogenizer
Ablation linear scan, speed 10 µm/s
Spot Ø 31.5 µm, 16 µm
Repetition rate 10Hz
Pulse energy 2.5 µJ/imp
Carrier gas (1.0 He + 0.80 Ar) L/min





GEOLAS Q CETAC Agilent 7500 ICP-QMS

Lateral scanning – surface (section) mapping



Scan speed 5 μm/s; spot Ø 31.5 μm; repetition rate 10Hz; energy / pulse 2.5 μJ/pulse; carrier gas (1.0 He + 0.80 Ar) L/min, internal standard – Si 29

b) LA-ICP-OES, depth profiling

LINA Spark™

Surelite (Continuum)

Q switched Nd:YAG

1064 nm

Pulse energy: 23 – 90 mJ

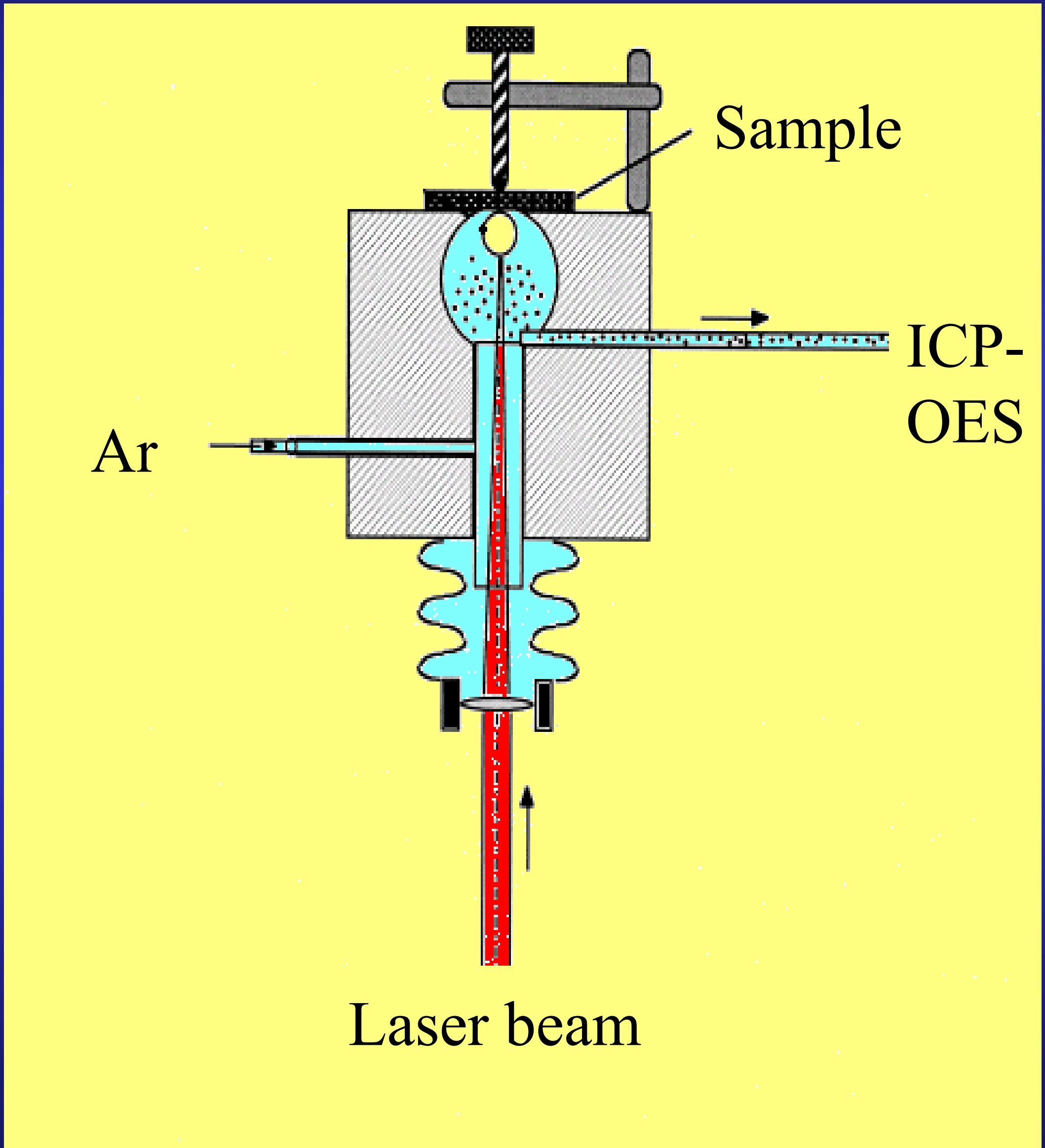
Repetition rate: 10 Hz

Laser spot diameter

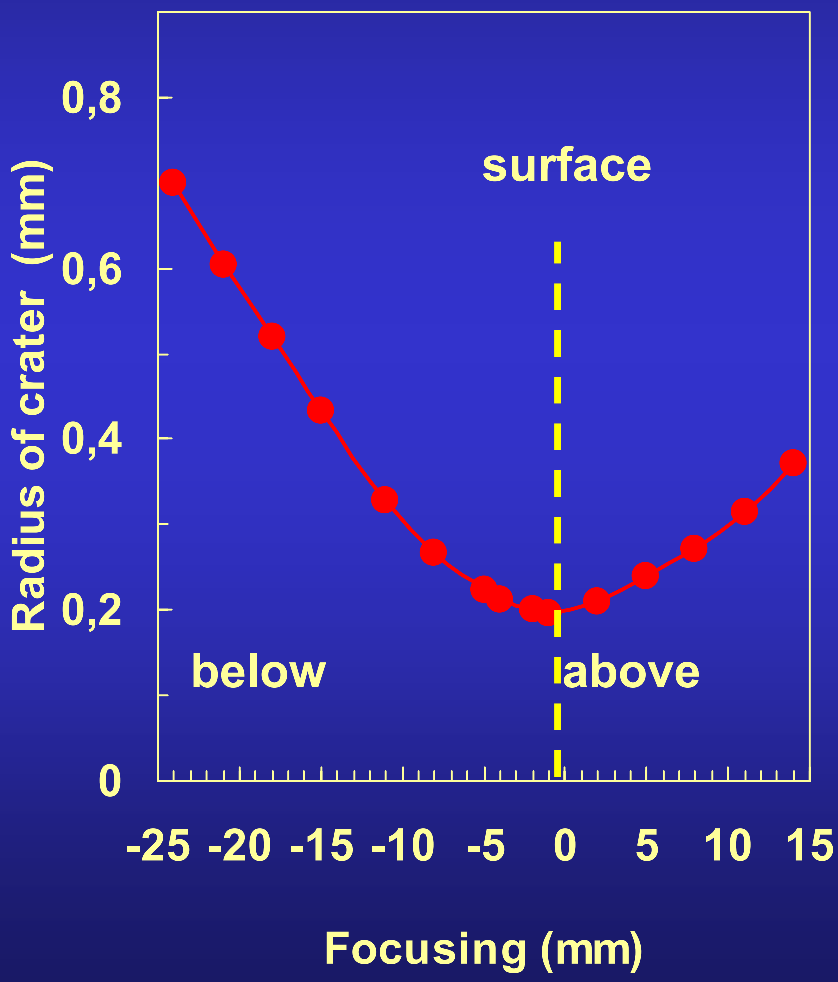
approx. 1mm

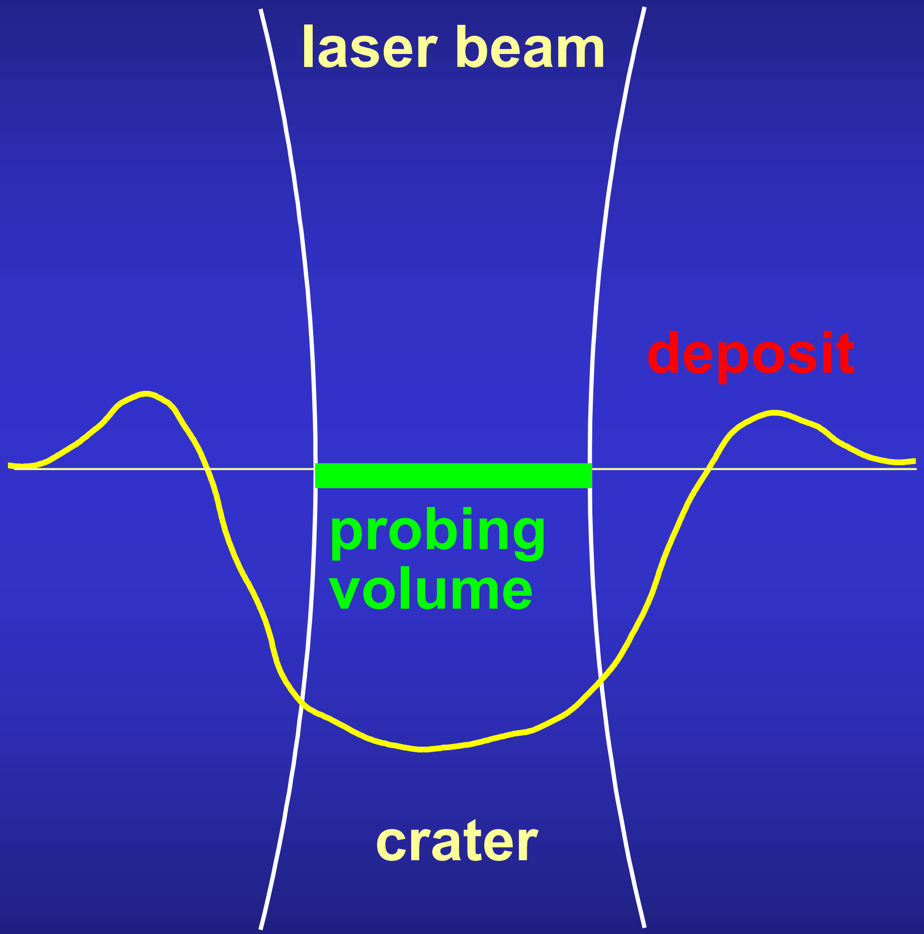
Duration of ablation:

3 min.



LINA Spark focusing

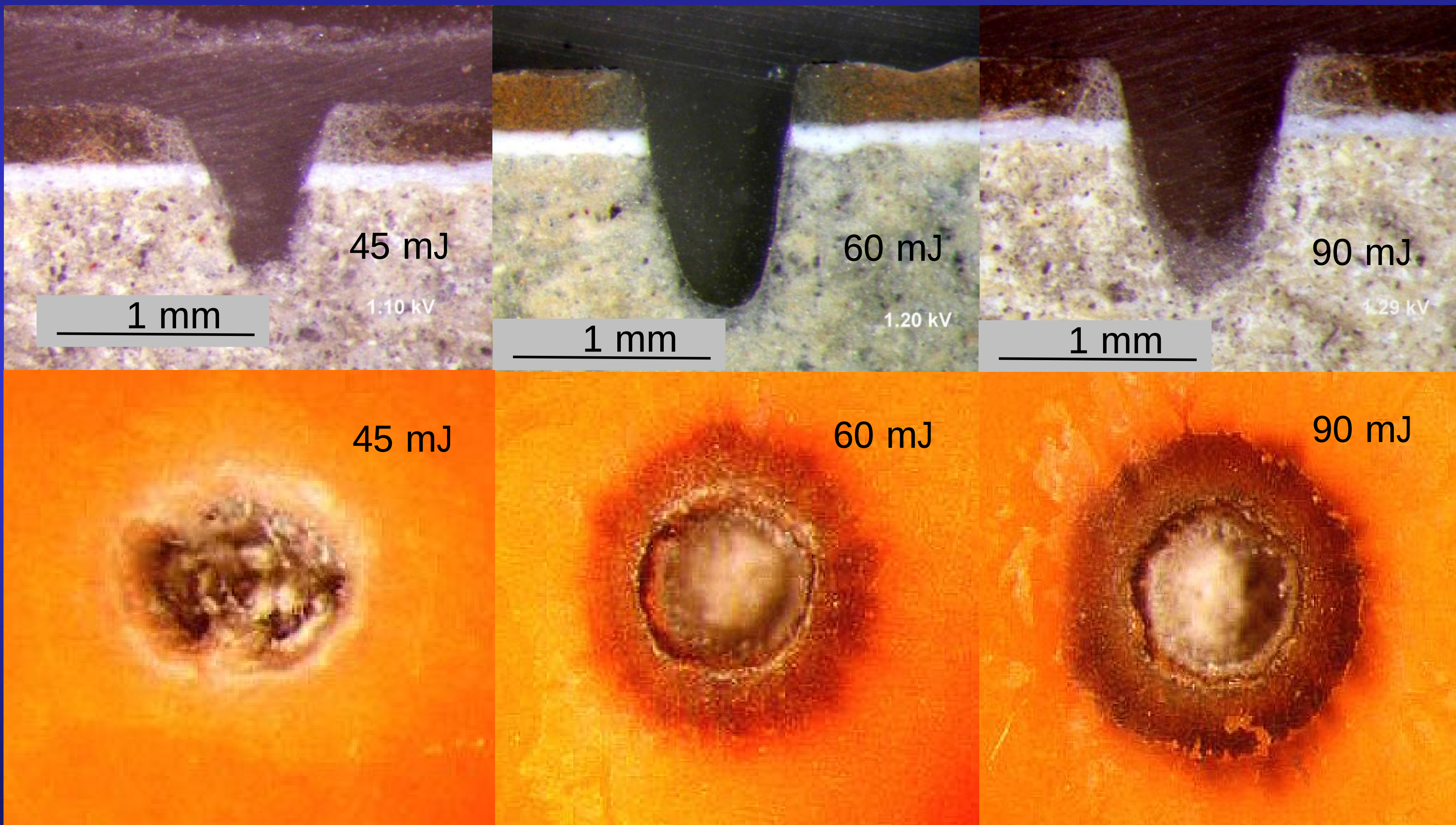




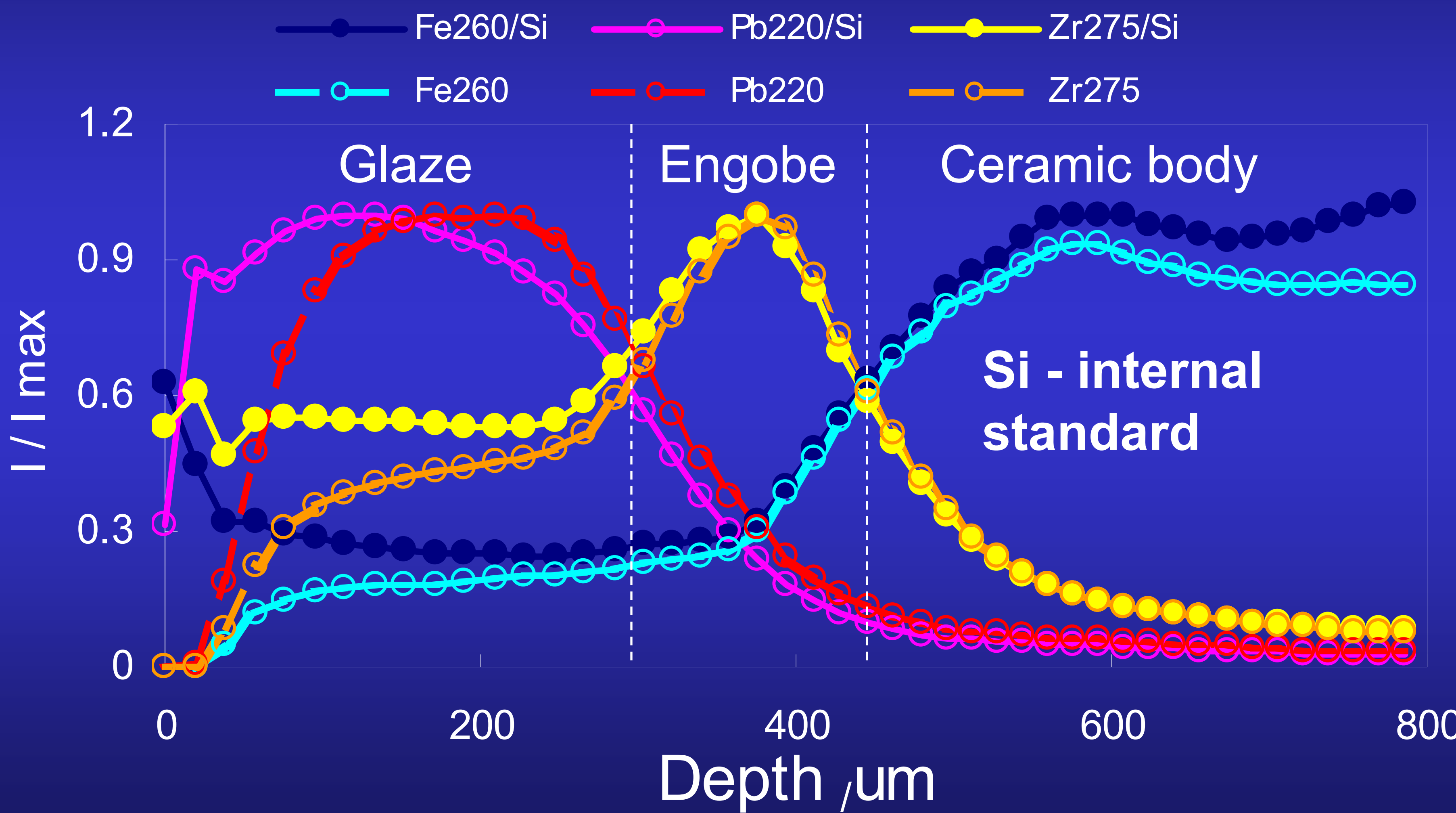
LINA Spark – VISTA Pro

Fixed spot ablation, ceramic tile sections and crater views

Energy influence

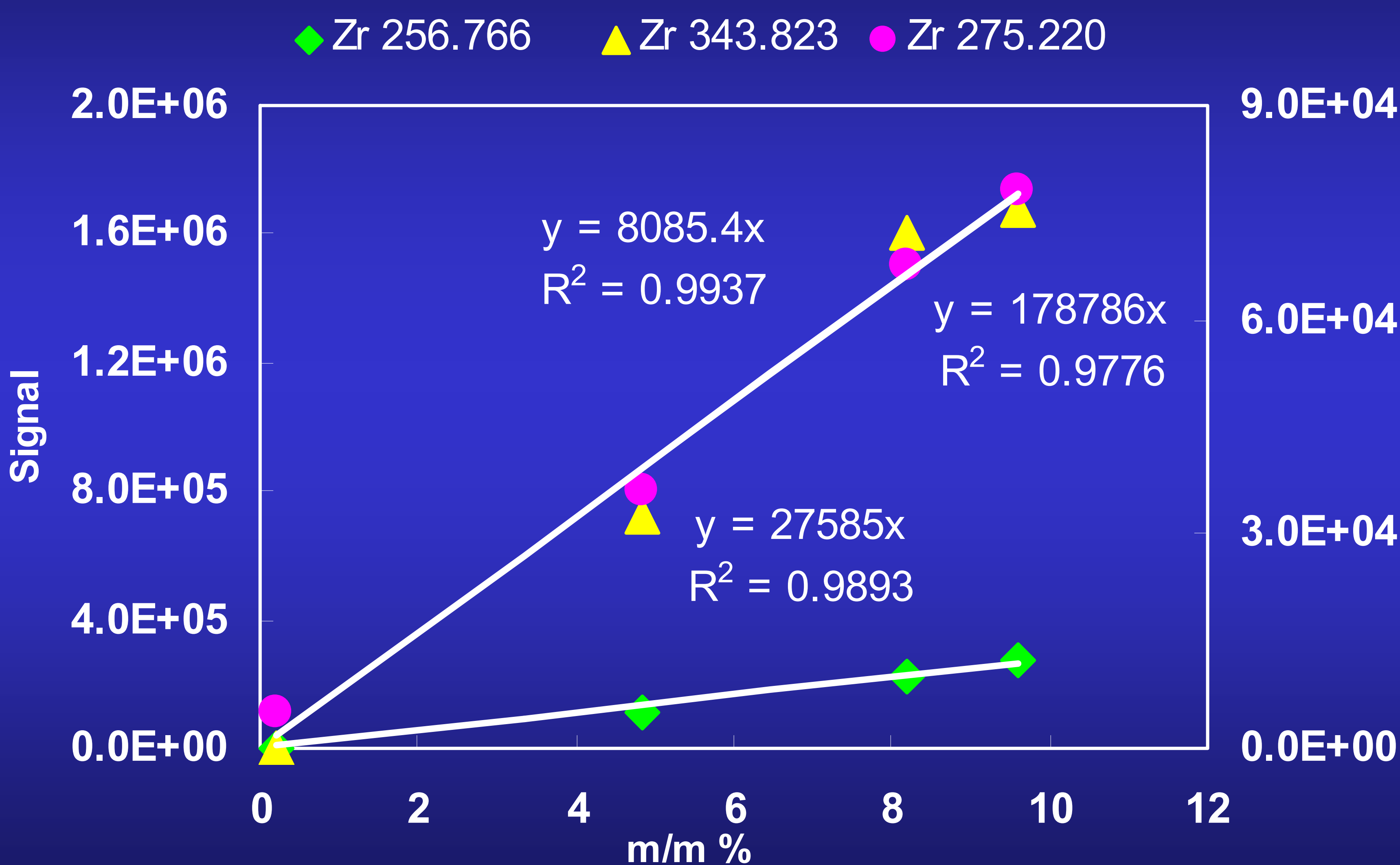


LINA-Spark, Vista Pro ICP-OES

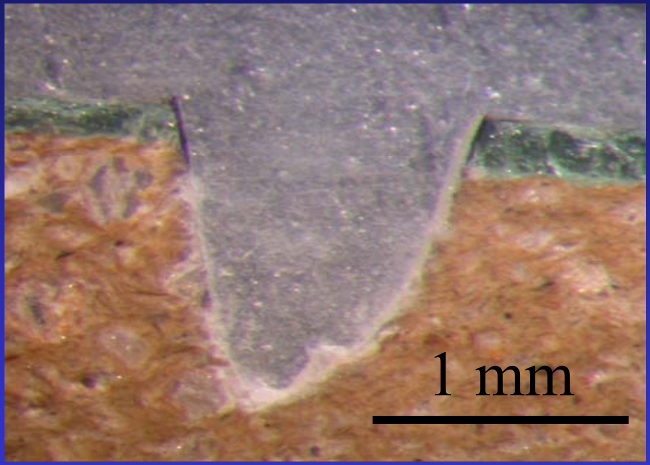


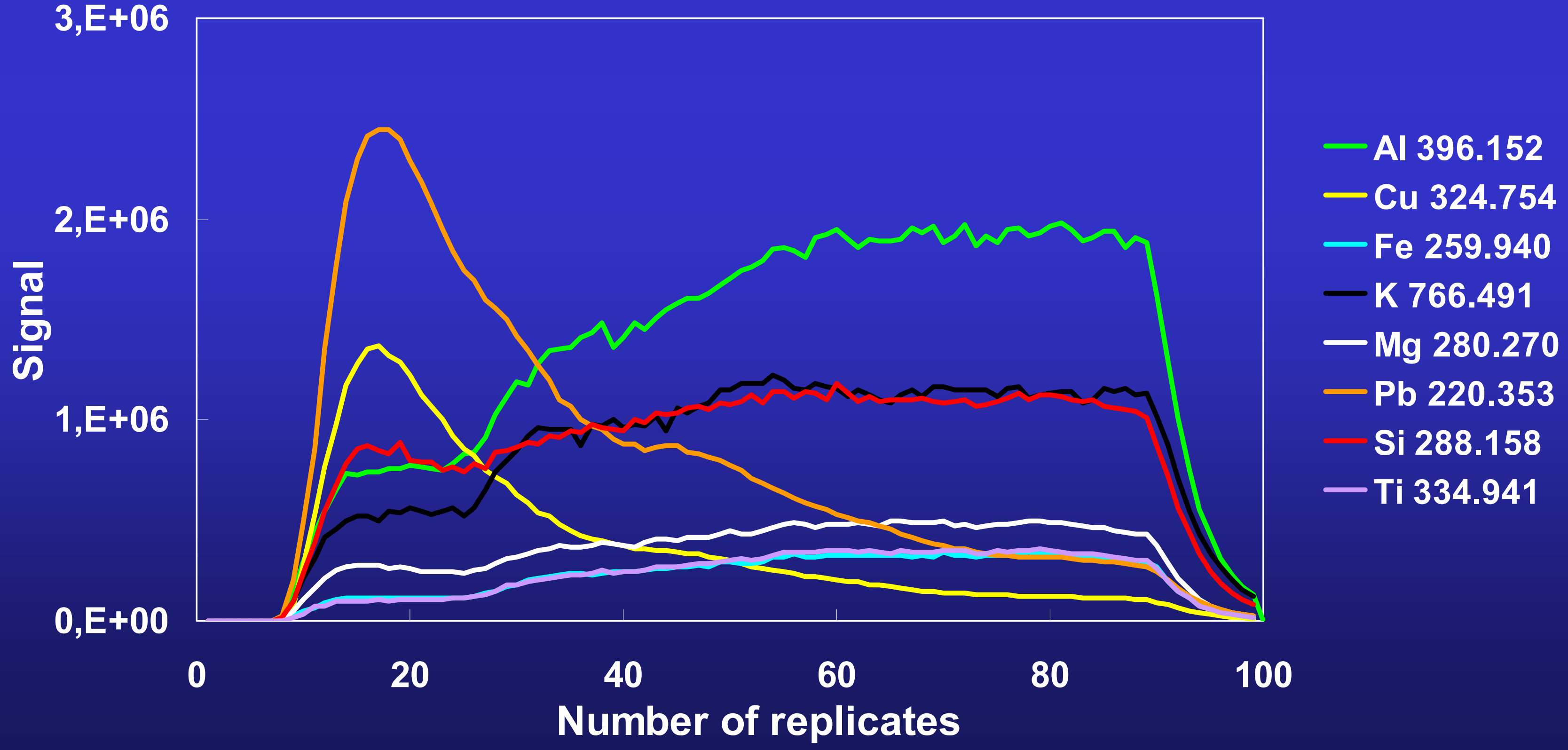
Calibration for zirconium

Various glazes and engobes



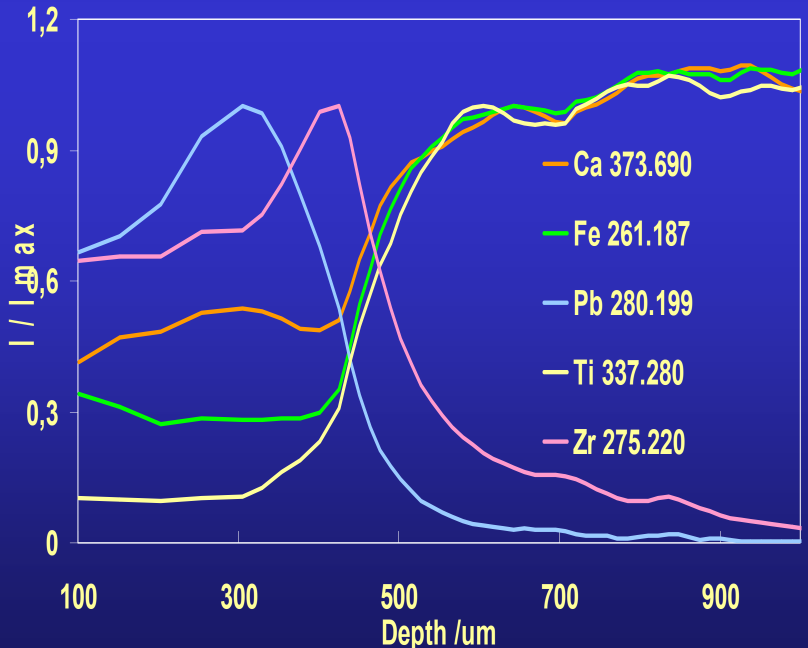
Application in archaeology

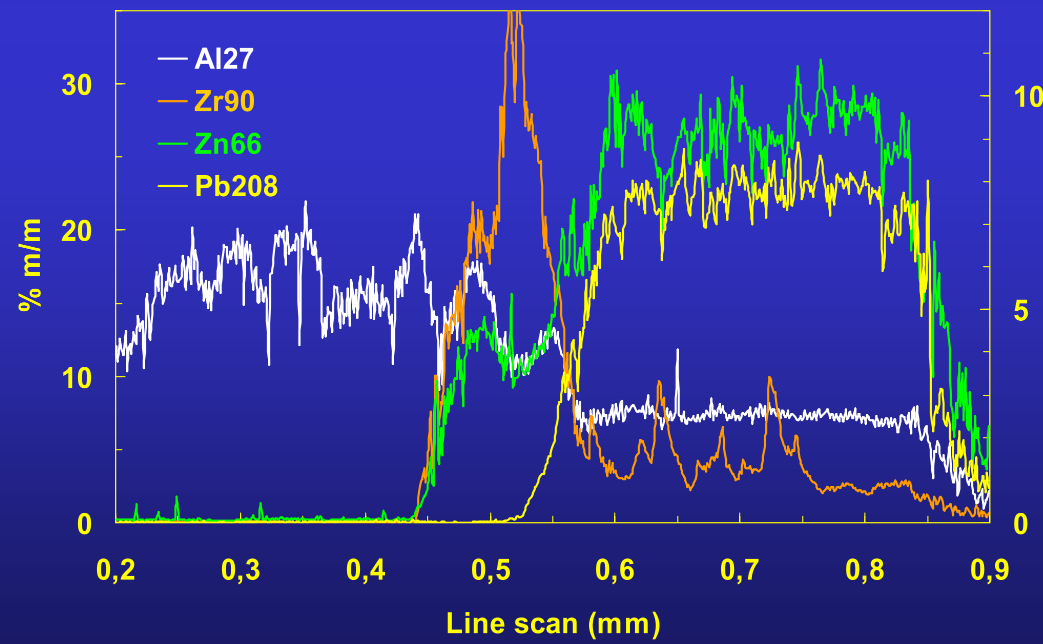




Conclusion - thick heterogeneous coatings

„Bulk“ depth profile	Microstructure depth profile
LA-ICP-OES	LA-ICP-MS
Defocused beam	Focused beam
Depth profiling	Linear Scanning





Zinc coatings 17 µm

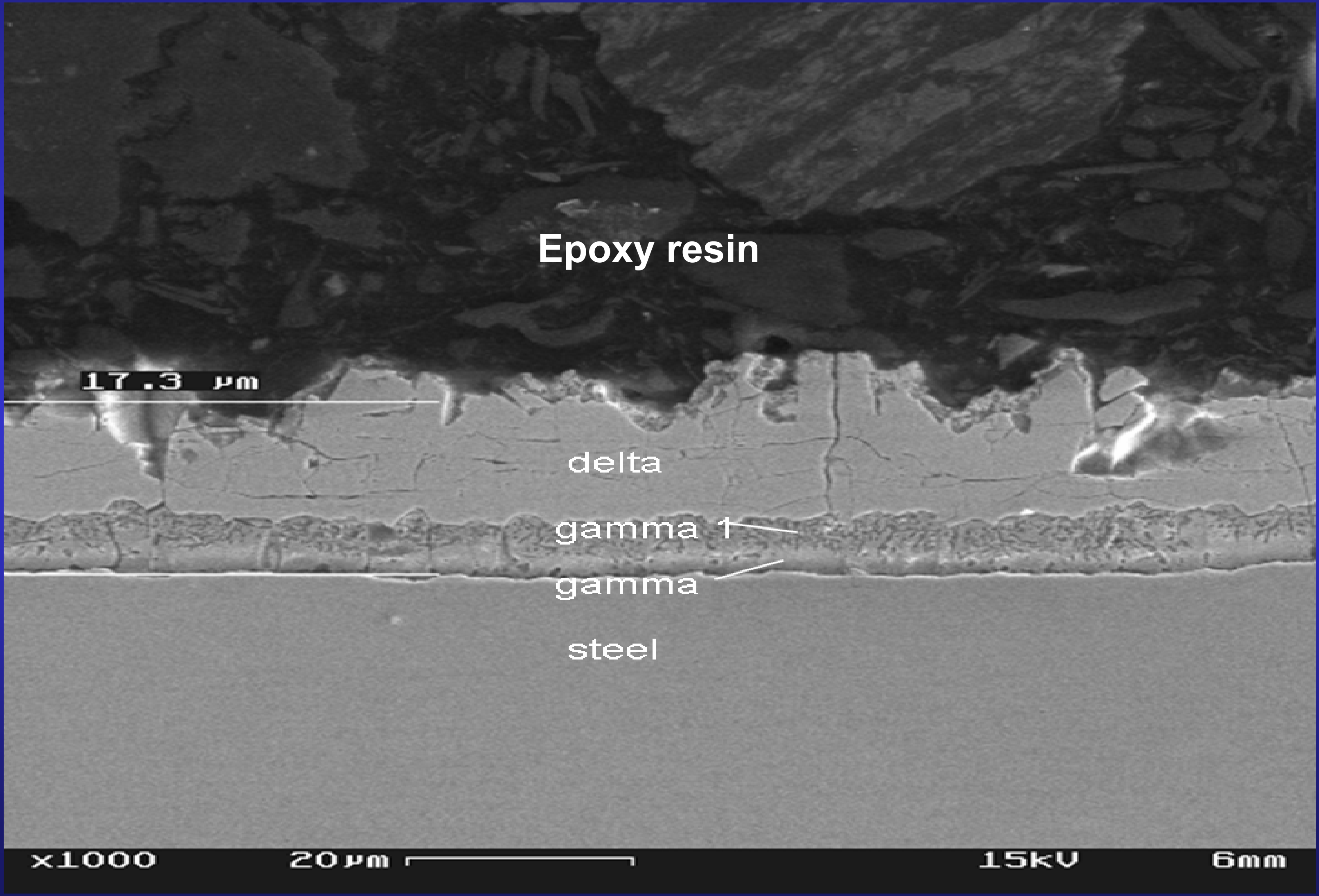
Intermetallic phases

Intermetallic phases

- Additional annealing of hot dipped zinc on steel creates by thermal diffusion intermetallic phases with different crystal structure in following order:
- Pure Zn, Zeta $FeZn_{13}$, Delta $FeZn_{10}$, Gamma 1 Fe_5Zn_{21}, Gamma Fe_3Zn_1, steel [1, 2] are determined by EPXMA and Mössbauer spectroscopy [3]
- 1064 nm and 266 nm and Nd:YAG-LA-ICP-OES with Gaussian beam and 193 nm ArF* flat top beam (UVF)-LA-ICP-QMS were employed.

1. F. C. Porter: Zinc handbook, Marcel Dekker, New York 1991.
2. J. Mackowiak, N. R. Short: Metallurgy of galvanised coatings, Int. Metals Reviews 1, 1979.
3. M. Zmrzlý, J. Fiala, O. Schneeweiss, Y Houbaert, Structure of intermetallic phases in Al-free galvannealed zinc coatings, Czechosl. J. Phys. 55 (2005) 923-931

Intermetallic phases in Zn coatings by EPMA



Laser

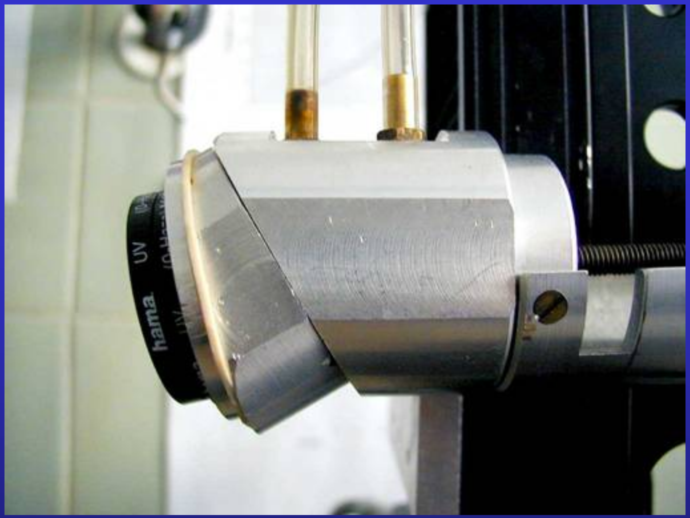
- Nd:YAG laser (Brilliant, Quantel)
- 1064 nm and 266 nm
- frequency: 10 Hz
- pulse duration: 4.4 ns
- power: 0.3 – 2.2 mW

Nd:YAG laser (Brilliant, Quantel) + ablation system

Ablation + transport system

Ar + sample aerosol
to ICP

Ar

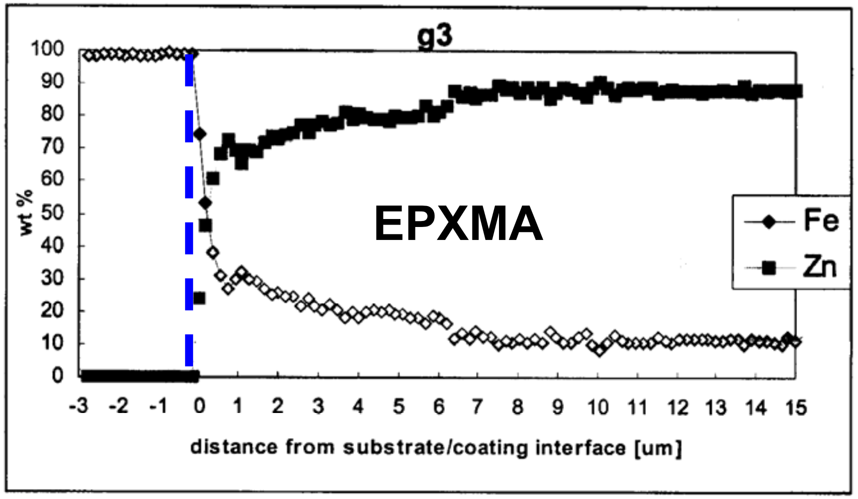


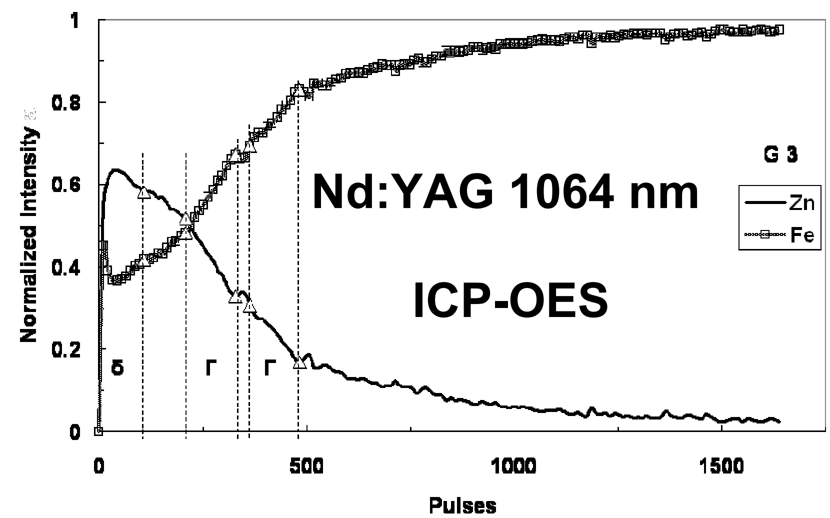
- lens (IR: glass, UV: fused silica)
- ablation cell (lab-made, 15 cm^3, Al)
- translator (displacement X-Y)
- transport tube (internal diameter 4 or 2 mm, length 1.5 m, polyamide)

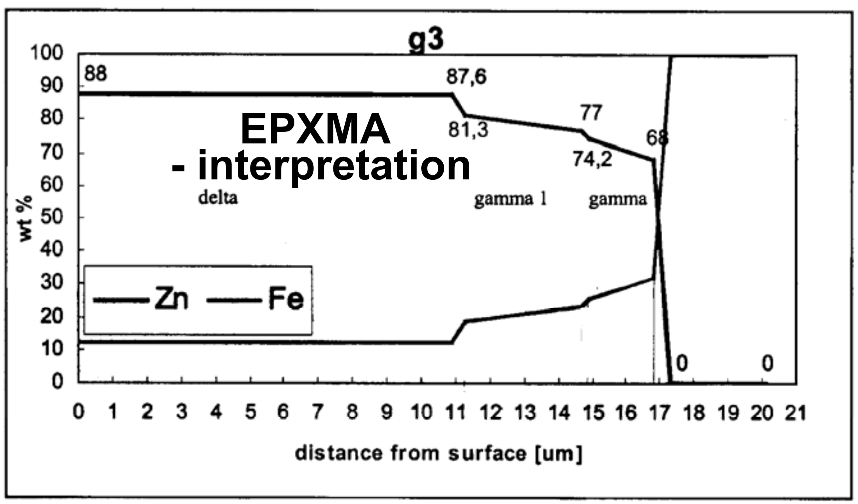
Spectrometer

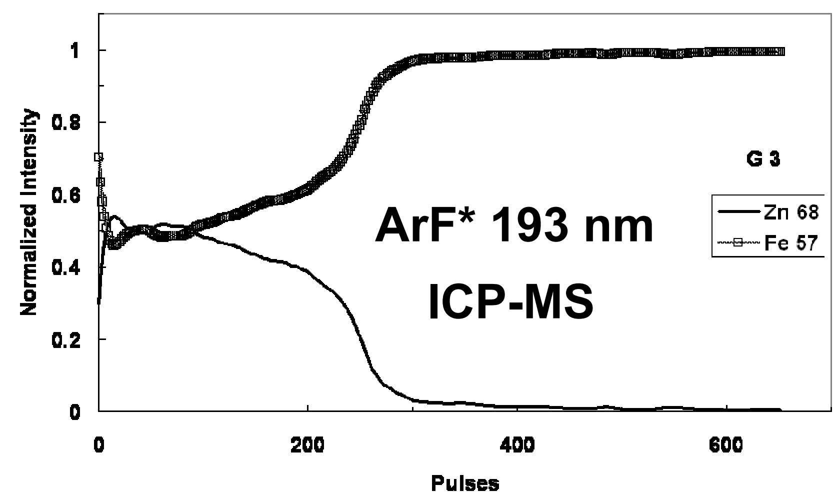
- ICP-OES Jobin Yvon
- generator: 40.68 MHz
- input: 600 – 1200 W
- monochromator: Czerny-Turner
- polychromator: Paschen Runge
- detector: photomultiplier

Intermetallic phases in Zn coatings by EPXMA and 193 nm and 1064 nm lasers







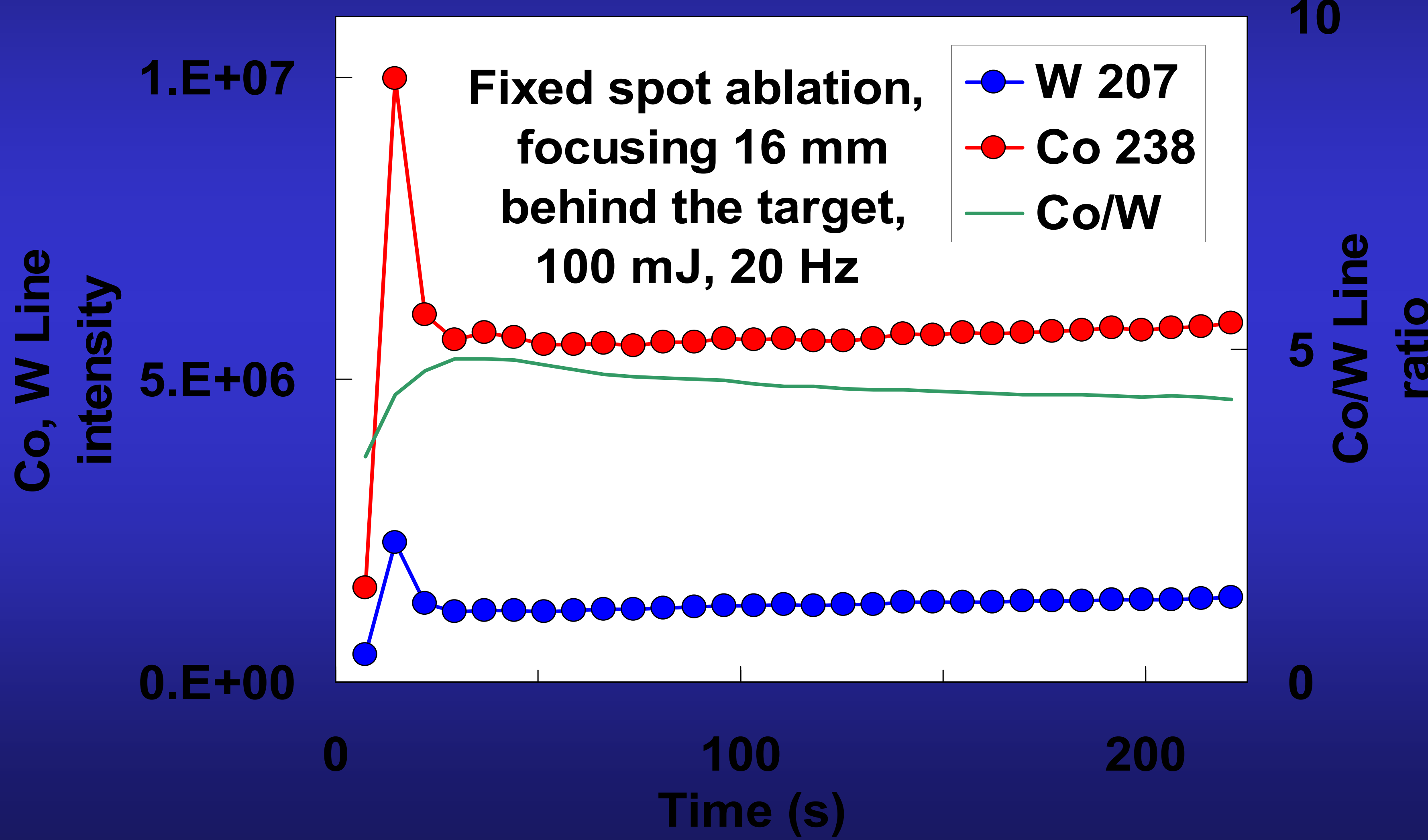


Conclusion Intermetallic phases

- It is possible to distinguish individual layers of intermetallic phases in Zn coating
- For this purpose 1064 nm is suitable because is more sensitive to different properties of the phases in comparison with UV (193 nm)

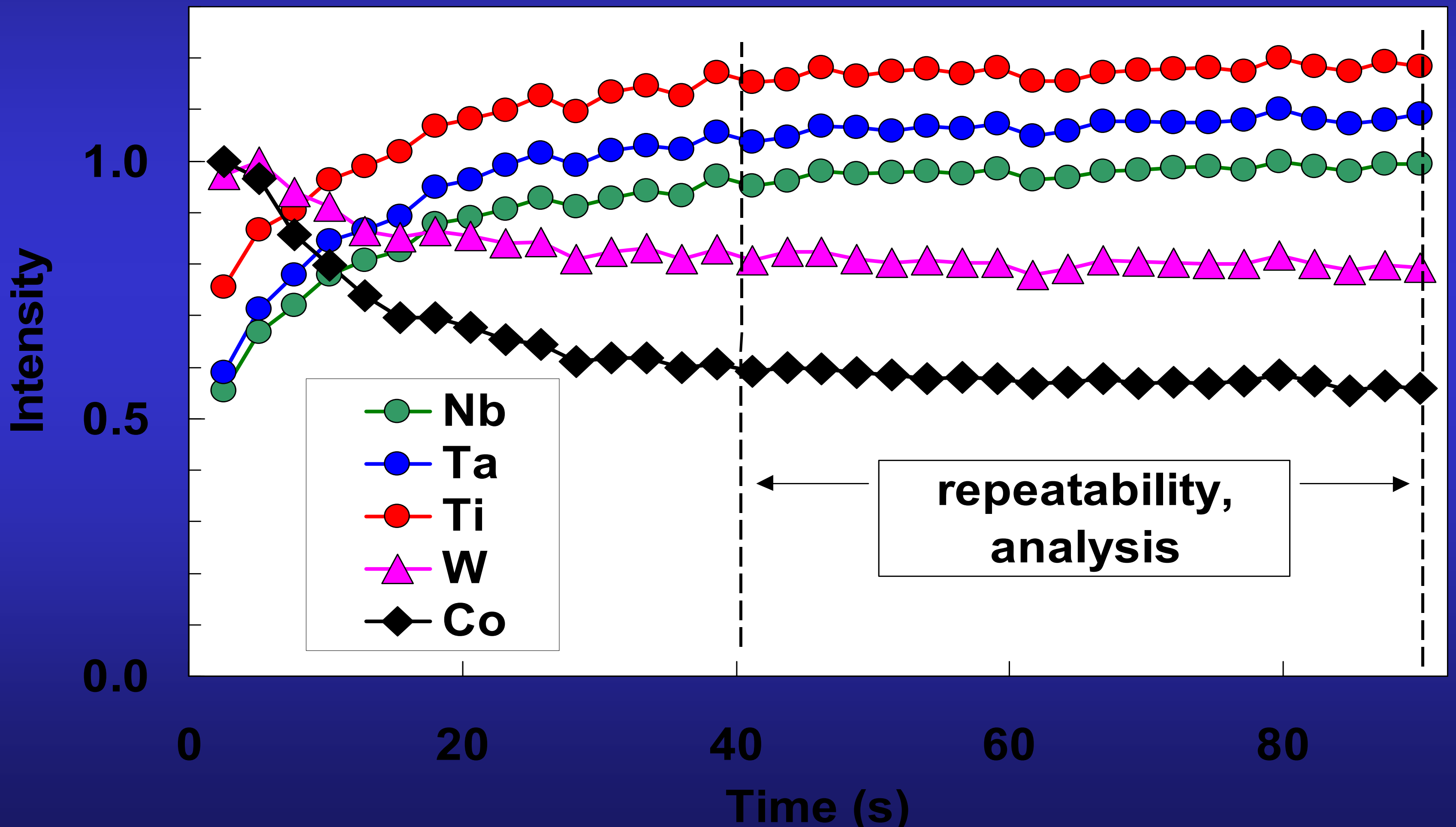
II. Bulk analysis

LINA-Spark Laser 1064 nm, ICP OPTIMA 3000 lateral
Sample: plasma sprayed WC-17%Co coating

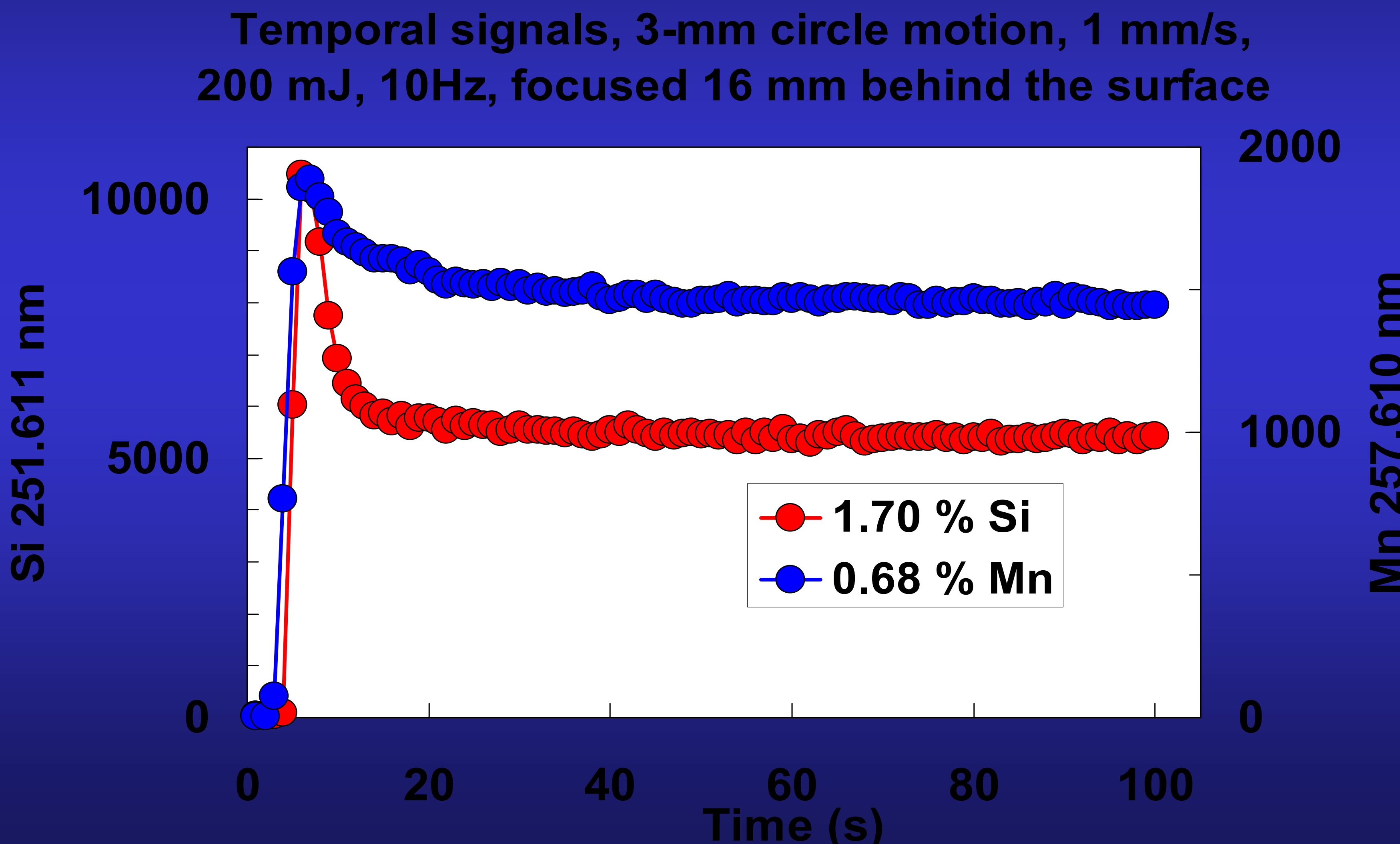


LINA-Spark Laser 1064 nm, ICP OPTIMA 3000 lateral
Sample: Cobalt-cemented sintered WC with Ti, Ta, Nb

Fixed spot, focus 16 mm behind target, 200 mJ, 20Hz, 3.2 GW/cm²

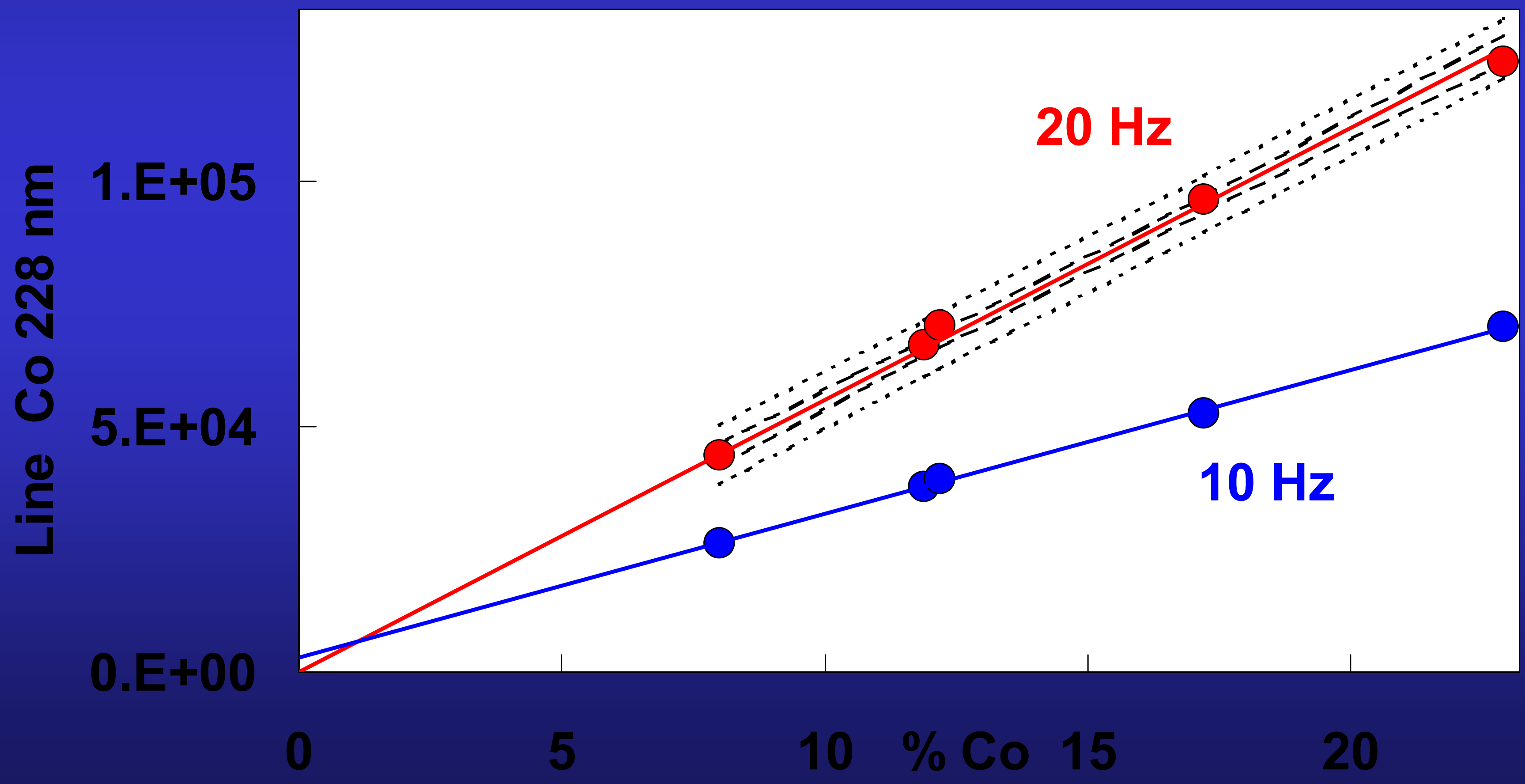


Quantel Brilliant Laser 1064 nm, ICP Jobin-Yvon 170
Ultrace lateral observation, Sample: Steel



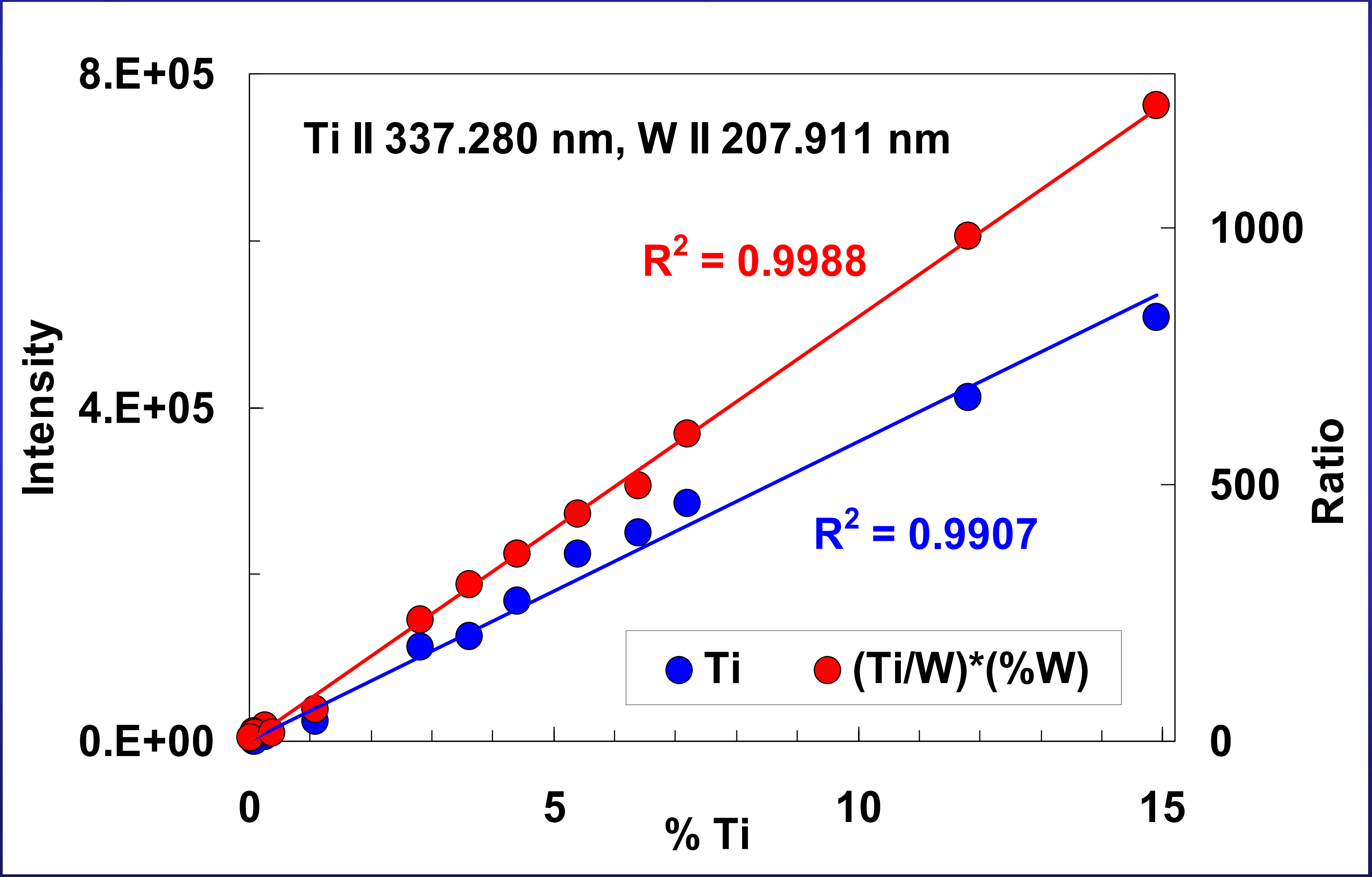
LINA-Spark Laser 1064 nm, ICP OPTIMA 3000 lateral
Sample: plasma sprayed WC-Co coating

Calibration, 3 rep/pt, dashed line- regression band, dotted line - dispersion band (focus -18 mm, 220 mJ, fixed spot)

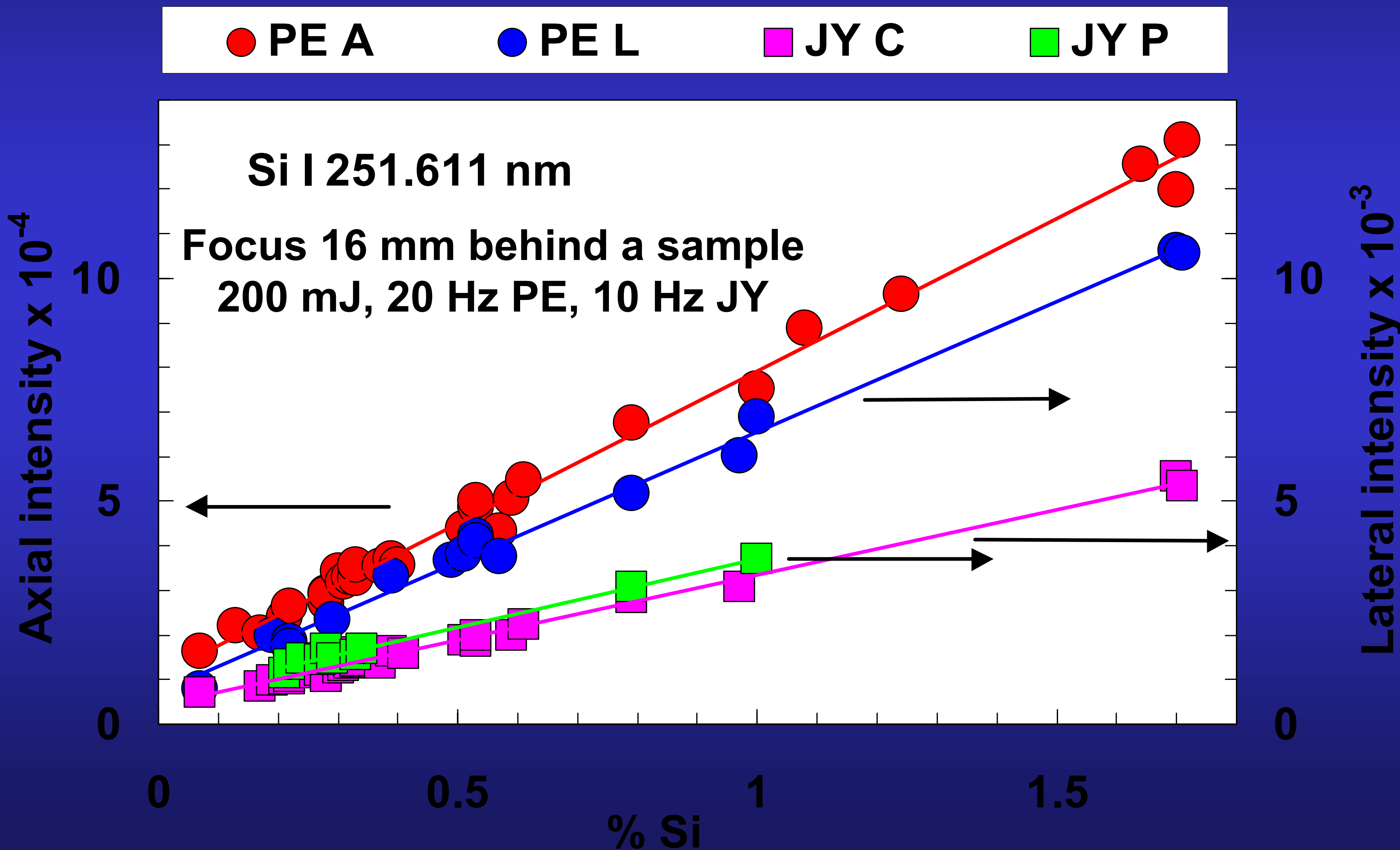


LINA-Spark Laser 1064 nm, ICP OPTIMA 3000 lateral
Sample: Cobalt-cemented sintered WC with Ti, Ta, Nb

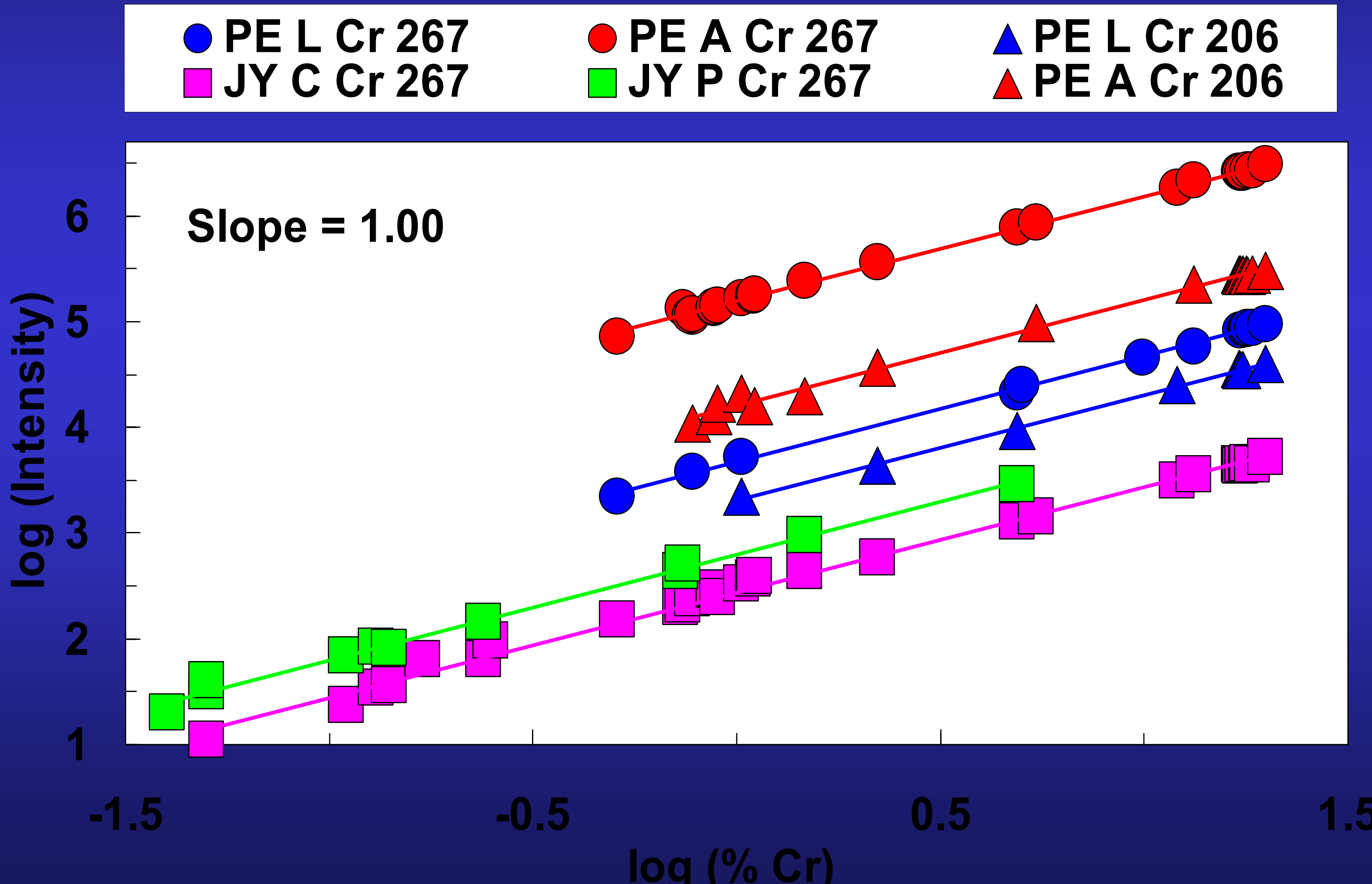
Fixed spot, focus 16 mm behind target, 200 mJ, 20Hz, 3.2 GW/cm^2



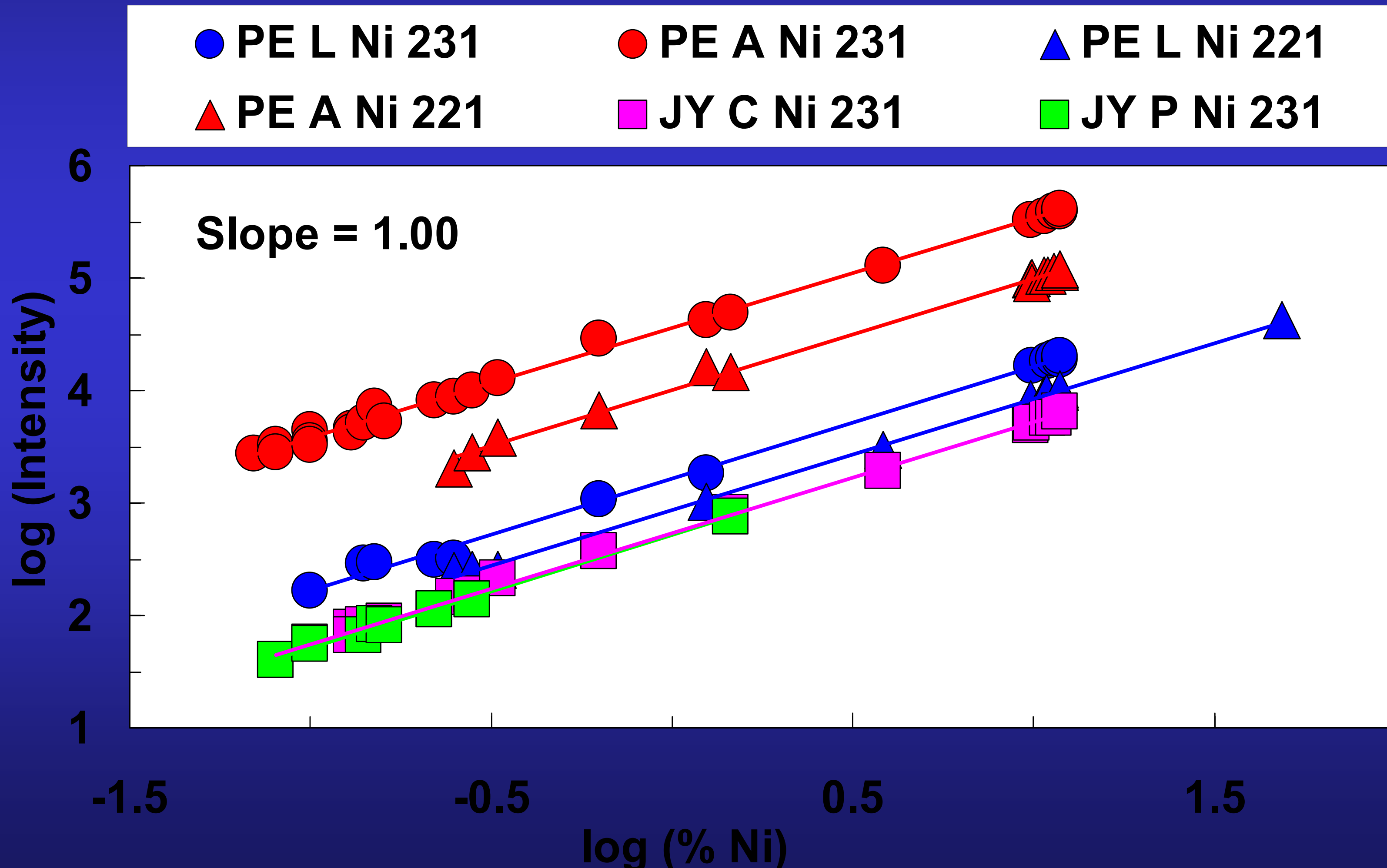
LINA laser 1064 nm, ICP OPTIMA PE Axial, Lateral Quantel Brilliant laser 1064 nm, ICP Jobin-Yvon JY Ultrace, lateral, ablation Circle, Point, Sample: steel



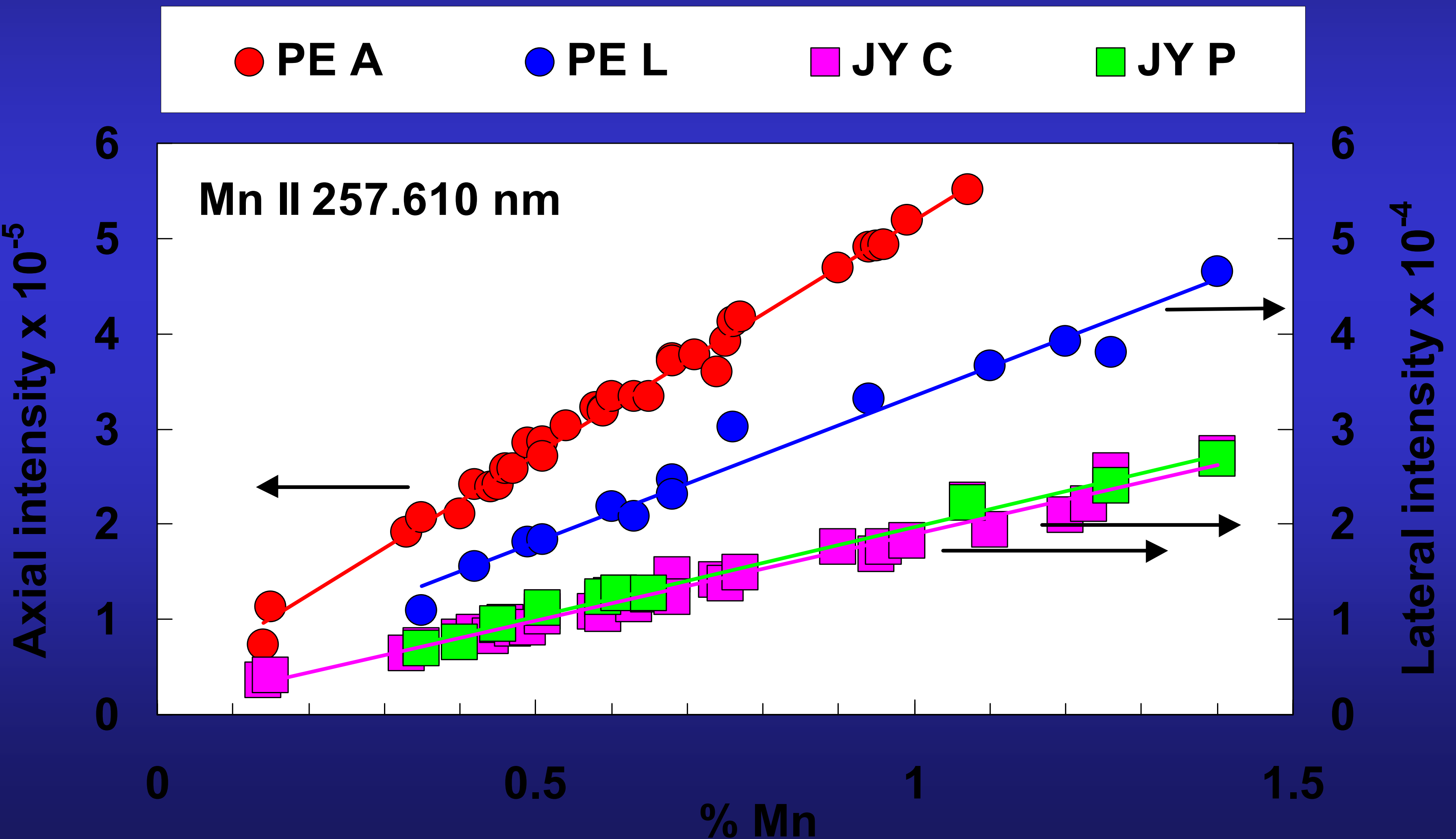
LINA laser 1064 nm, ICP OPTIMA PE Axial, Lateral Quantel Brilliant laser 1064 nm, ICP Jobin-Yvon JY Ultrace, lateral, ablation Circle, Point, Sample: steel



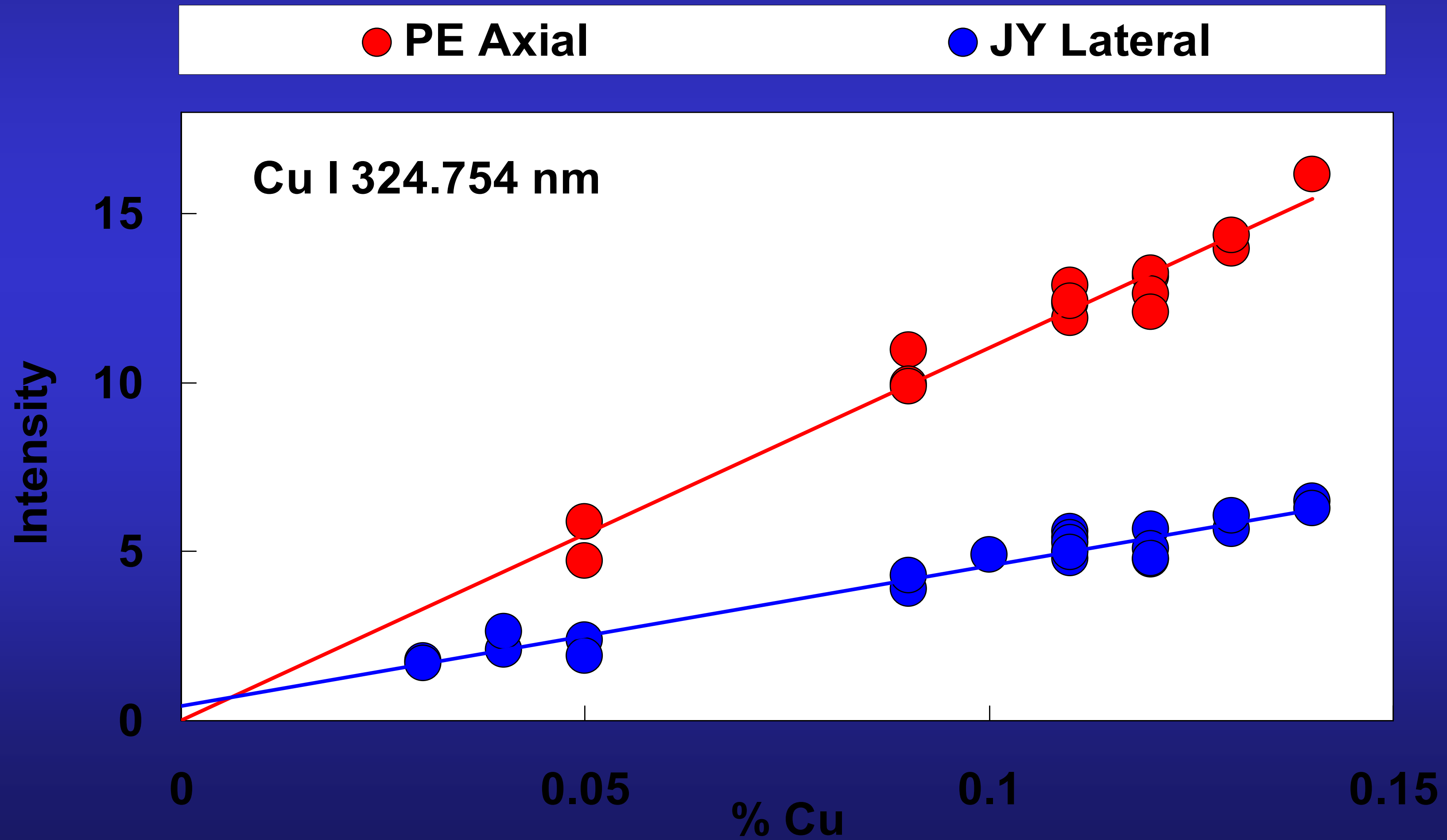
LINA laser 1064 nm, ICP OPTIMA PE Axial, Lateral
Quantel Brilliant laser 1064 nm, ICP Jobin-Yvon JY Ultrace, lateral, ablation Circle, Point, Sample: steel



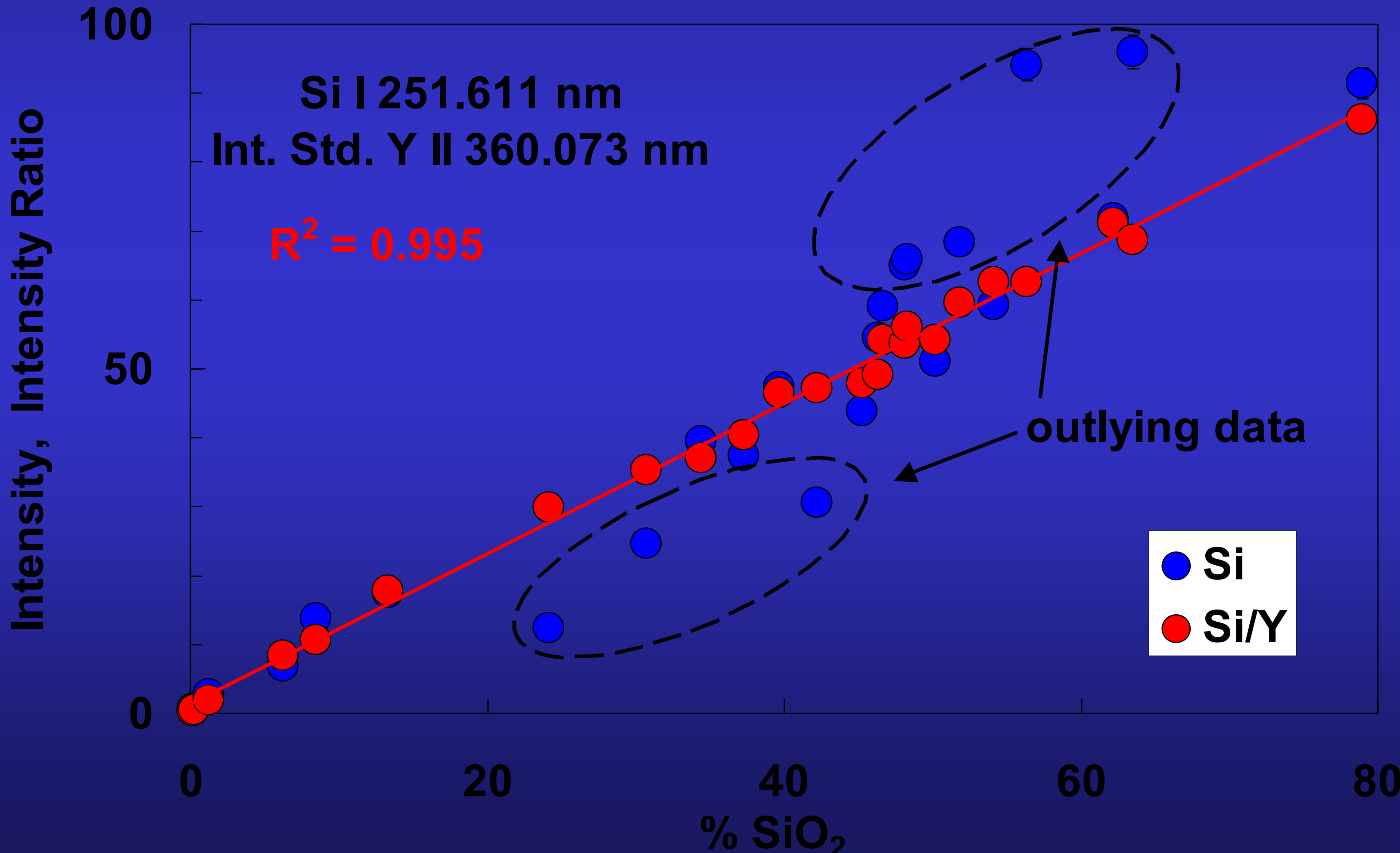
LINA laser 1064 nm, ICP OPTIMA PE Axial, Lateral Quantel Brilliant laser 1064 nm, ICP Jobin-Yvon JY Ultrace, lateral, ablation Circle, Point, Sample: steel



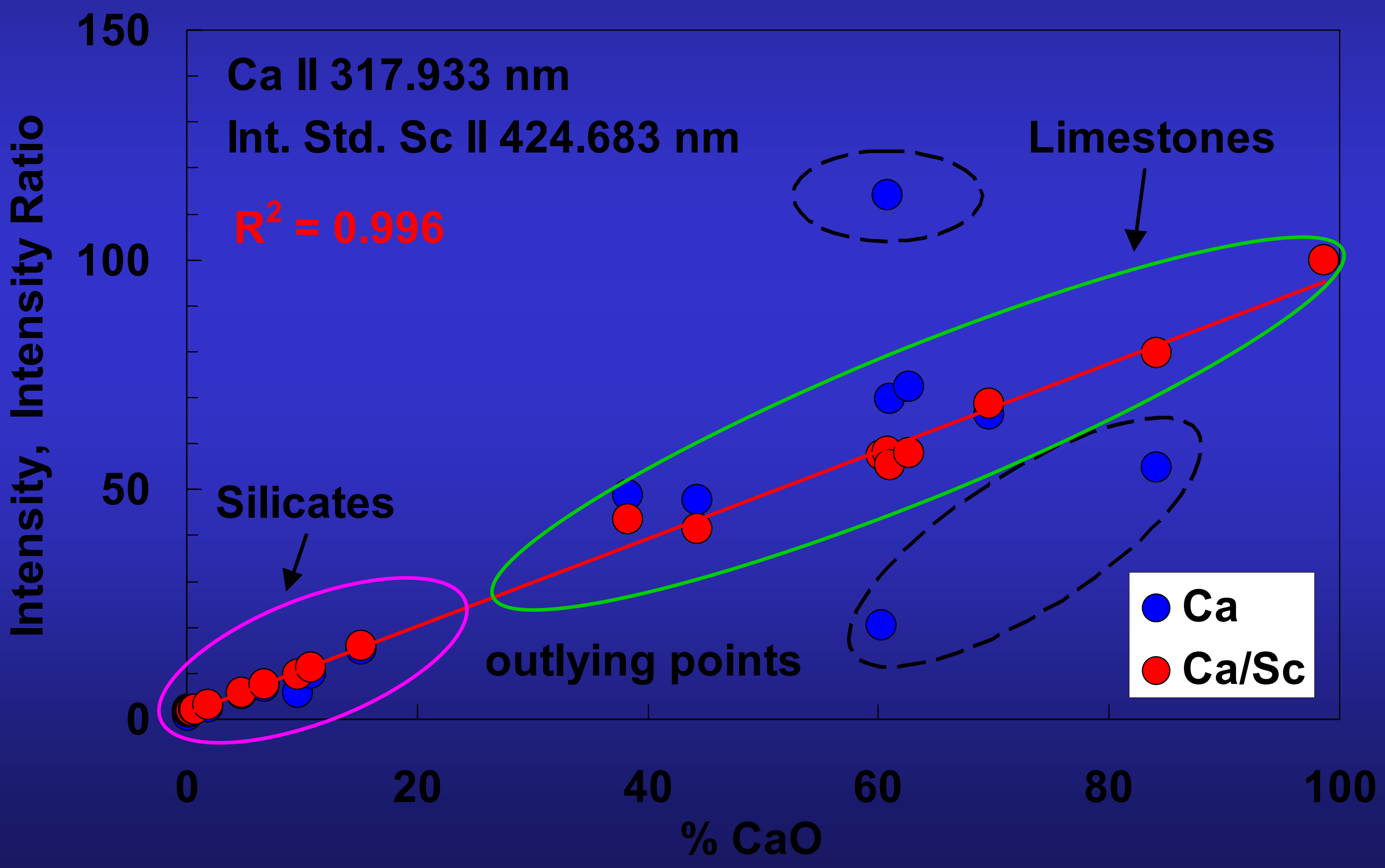
LINA laser 1064 nm, ICP OPTIMA PE Axial, Quantel Brilliant laser 1064 nm, ICP Jobin-Yvon JY Ultrace, lateral, ablation Circle, Point, Sample: steel



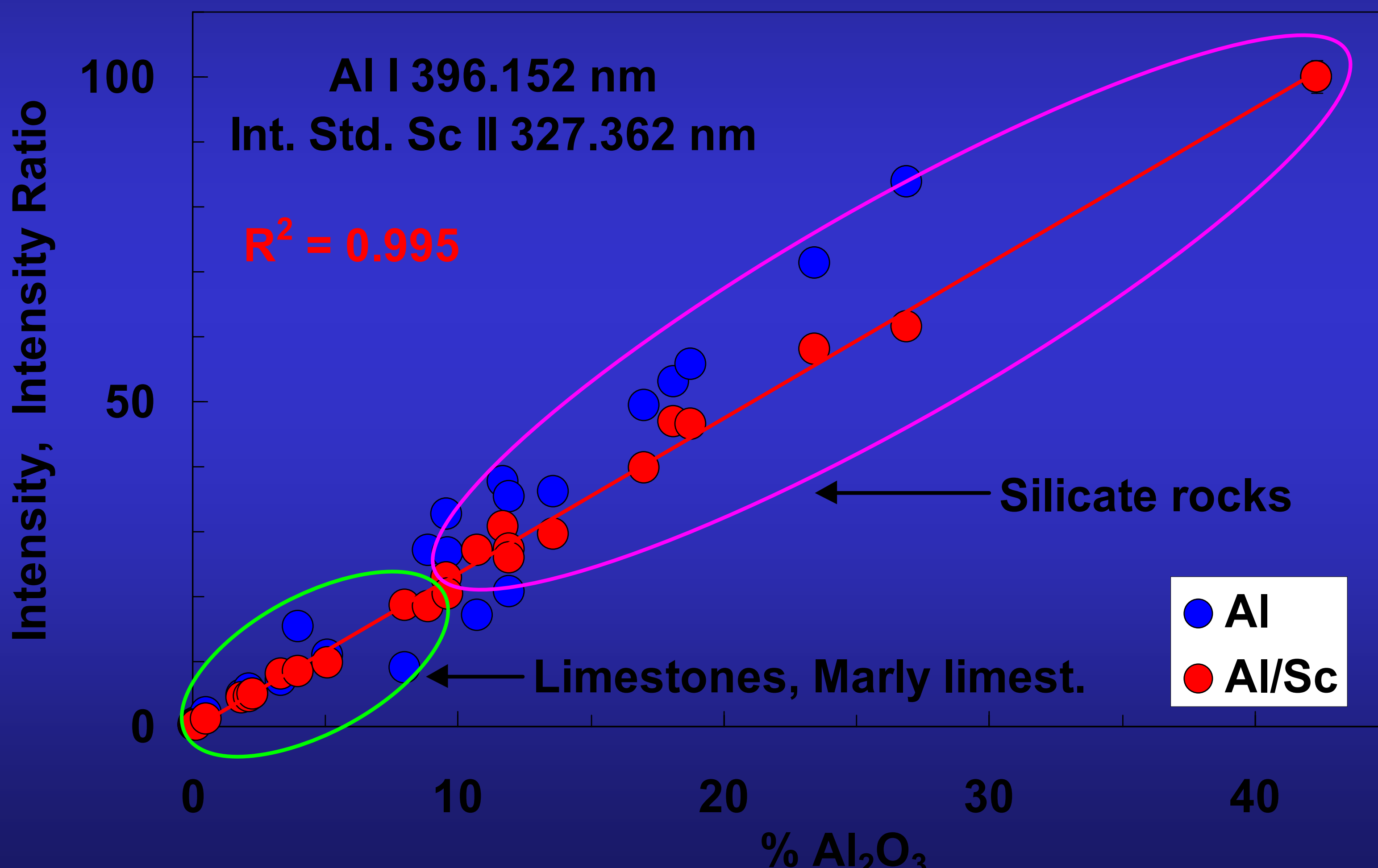
Continuum Nd:YAG, 355 nm, 10 Hz, ICP OPTIMA 3000 Lateral, 10 mJ, focusing 3 mm behind surface, fused disks: sample + $Li_2B_4O_7$, 1:10, ad. Y_2O_3, Sc_2O_3



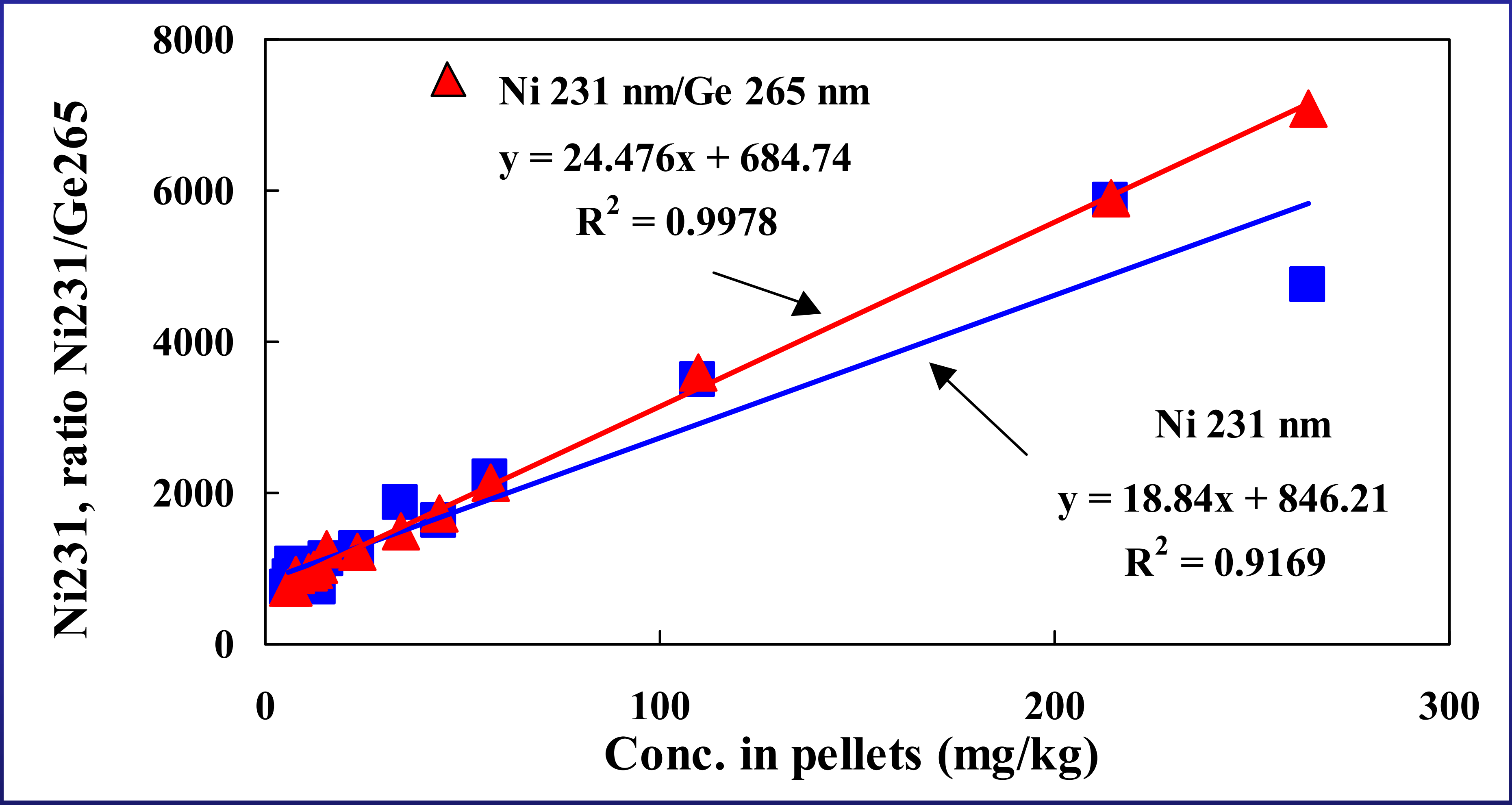
Continuum Nd:YAG, 355 nm, 10 Hz, ICP OPTIMA 3000 Lateral, 10 mJ, focusing 3 mm behind surface, fused disks: sample + $Li_2B_4O_7$, 1:10, ad. Y_2O_3, Sc_2O_3



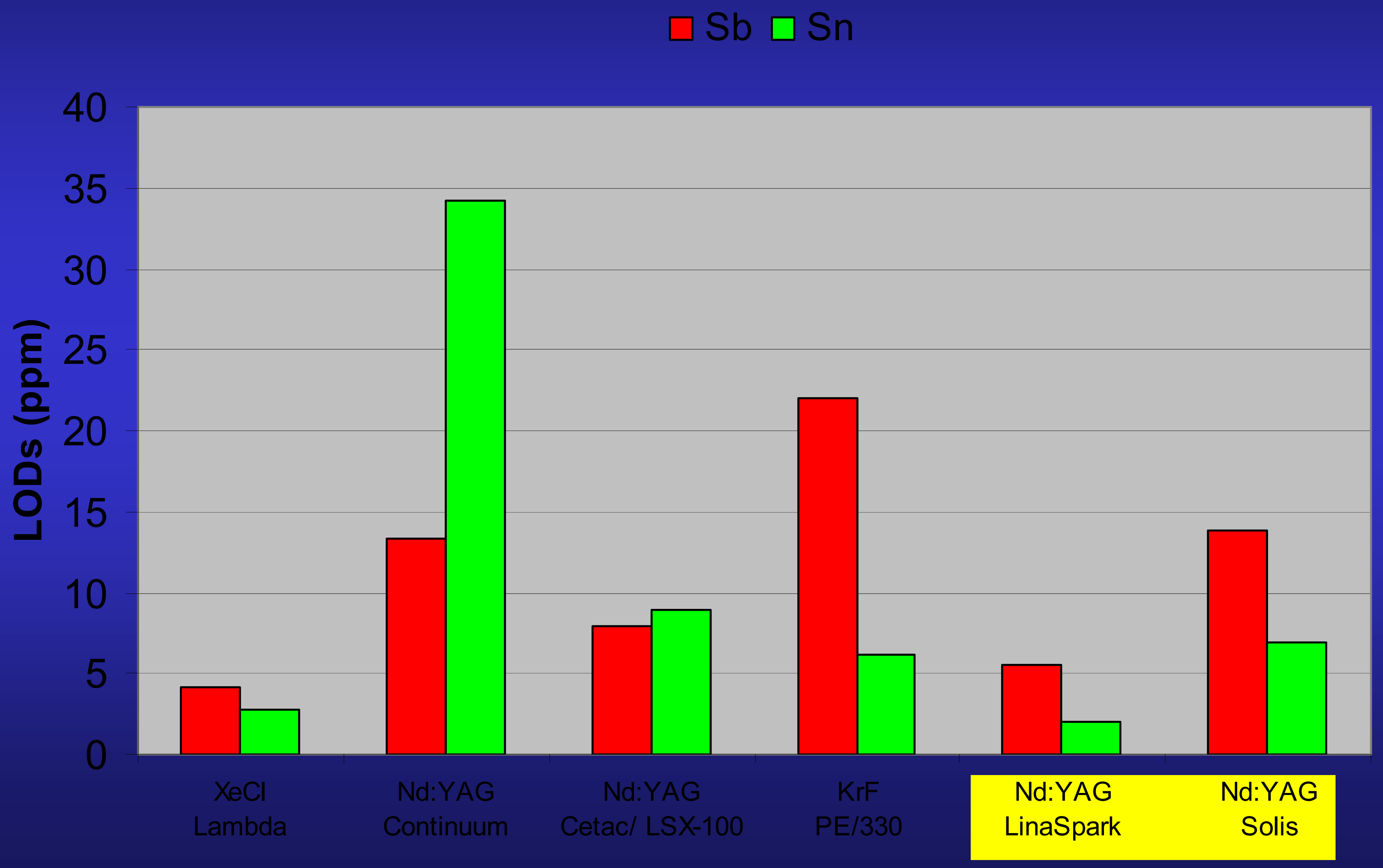
Continuum Nd:YAG, 355 nm, 10 Hz, ICP OPTIMA 3000 Lateral, 10 mJ, focusing 3 mm behind surface, fused disks: sample + $Li_2B_4O_7$, 1:10, ad. Y_2O_3, Sc_2O_3



Calibration graph for nickel in pellets Al/soil 1:1 with and without IS (Ge)



LODs in PVC for Sb and Sn



Limits of detection in brass (NIST 1107)

laser	Cetac/LSX-100	LinaSpark	Solis
system	Nd:YAG	Nd:YAG	Nd:YAG
lambda	266 nm	1064 nm	1064 nm
energy	4.2 mJ	300 mJ	50 mJ
rate	20 Hz	20 Hz	20 Hz
RSD_B (%)	1.24	1.17	1.2
Cu	163	173	95
Ni	247	5.0	4
Pb	79	100	32
Sn	64	8.5	12
Zn	129	229	212

Limits of detection in steel (NIST c1152a)

laser	Cetac/ LSX-100	LinaSpark	Solis
system	Nd:YAG	Nd:YAG	Nd:YAG
lambda	266 nm	1064 nm	1064 nm
energy	4.2 mJ	300 mJ	50 mJ
rate	20 Hz	20 Hz	20 Hz
RSD_B (%)	1.36	0.99	2.8
Co	52	17	39
Cu	26	6.2	18
Mn	29	3.4	11
Mo	49	10	12
Ni	207	24	116
Pb	2.9	3.9	9
Si	86	26	62
V	79	4.1	17

Conclusions on LA-ICP-AES bulk analysis

- LA-ICP-AES-based bulk analysis does not require sophisticated imaging, focusing and displacement devices.
- No memory effects/contamination resulting from the ICP-AES system.
- Precision and LODs in the solids are close or even similar to those obtained with solutions.
- LA systems for bulk analysis are cheaper, but still expensive. However, they save time and money.
- A current limitation is the availability of adequate standards (ceramics, polymers, powders,…).

General Conclusions

- IR-LA-ICP-OES is applicable to averaged depth profiling and main constituent determination in thick coatings
- IR laser enables to distinguish intermetallic phases – positive consequence of usually adverese thermal effects
- UV-LA-ICP-MS is suitable for planar mapping and shallow depth profiling of microstructure
- LIBS is convenient for depth profiling
- Preparation of pellets is the fundamental step of LA-ICP analysis of powdered materials

Acknowledgement

- ✓ Dr. Karel Novotny, Dr. Marketa Hola, Ing. Linda Zaoralkova, Mgr. Ivona Hubova, Mgr. Ales Hrdlicka (MU, Brno)
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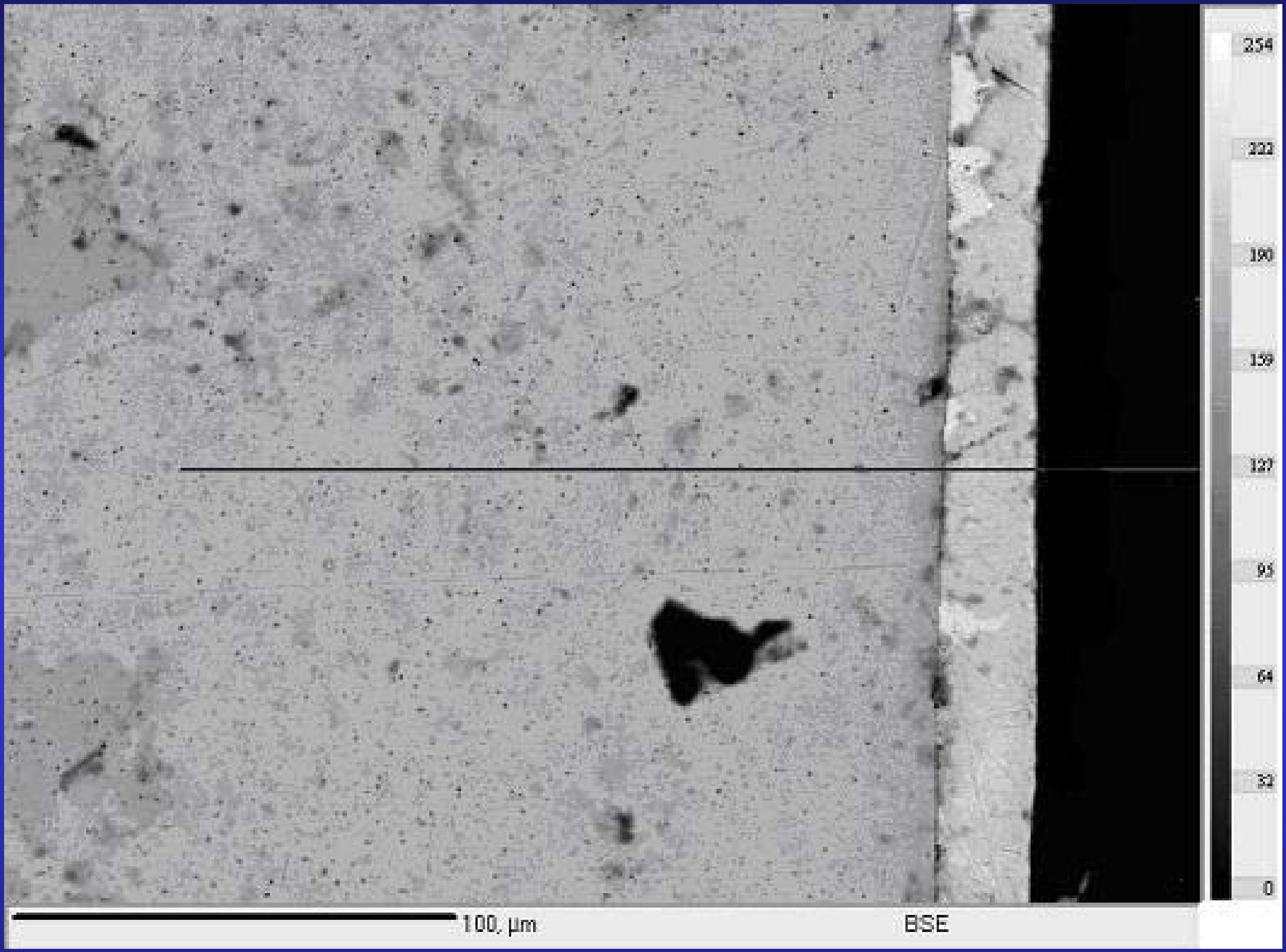
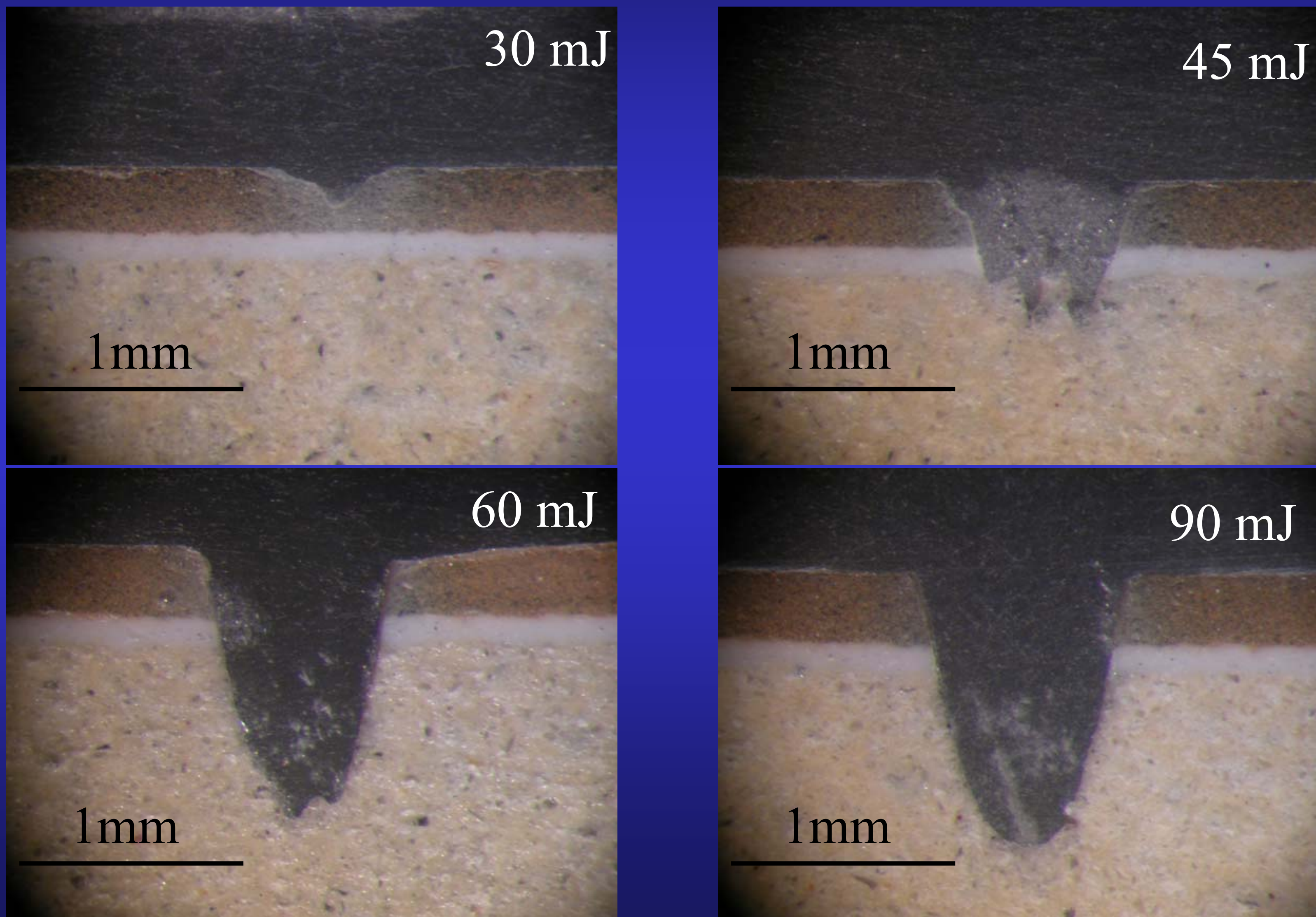
- ✓ the Ministry of Education, Youth and Sports of the Czech Republic, the research projects MSM 21622112/11
- ✓ Programme Erasmus (Swiss)

Thank you for your attention



Hot dipped Zn profile – an image in backscattered electrons (BSE). The line indicates the path of EDX measurement

Profiles of the craters at different energy levels: LINA-Spark, Vista Pro ICP-OES



Laser-assisted analysis of solids

- **Features of laser ablation based techniques**
  - Elimination of decomposition for solution analysis
  - Elimination of water, O, N, S, Cl from acids; resulting species cause spectral interferences in ICP-MS
  - Universal: electric conductors, non(semi)conductors
  - Non-destructive: material removing from the area 10 μm^2 to $1 mm^2$ to the depth cca 0.01-0.1μm/laser pulse
  - 2D-3D „speciation”: preserves information on spatial distribution of elements