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LA-ICP-MS
AS A POWERFUL TOOL FOR
ELEMENTAL IMAGING

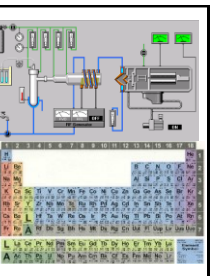
Tomáš Vaculovič

LAS LABORATORY OF ATOMIC SPECTROCHEMISTRY

OUTLINE

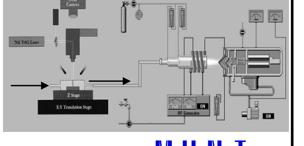
- Principle of laser ablation and ICP-MS
- Imaging
  - corroded layers
  - in geology
  - bio-samples
- Summary and Outlook of imaging

ICP-MS – PRINCIPLE



– Inductively Coupled Plasma of Mass Spectrometry

– argon plasma – source of atoms and ions (16 eV, 10000 K)



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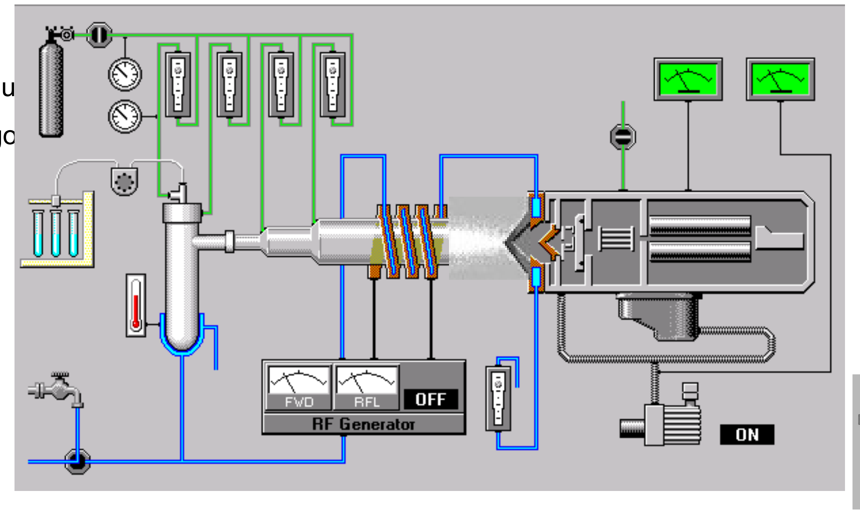
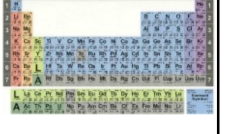
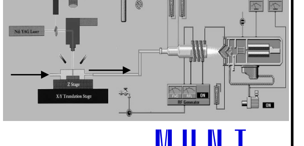
ICP-MS – PRINCIPLE



– Indu

– argo





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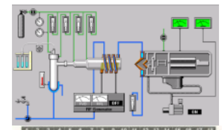
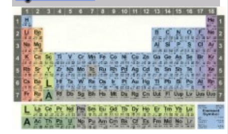
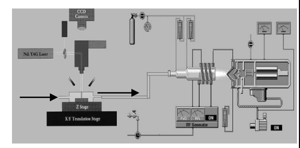
ICP-MS – PRINCIPLE





– Inductively Coupled Plasma of Mass Spectrometry
– argon plasma – source of atoms and ions (16 eV, 10000 K)
– atomization and ionization of the most elements of P.T.
– elemental specific detector (no molecules)



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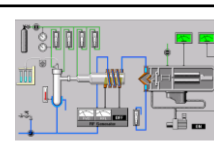
ICP-MS – PRINCIPLE



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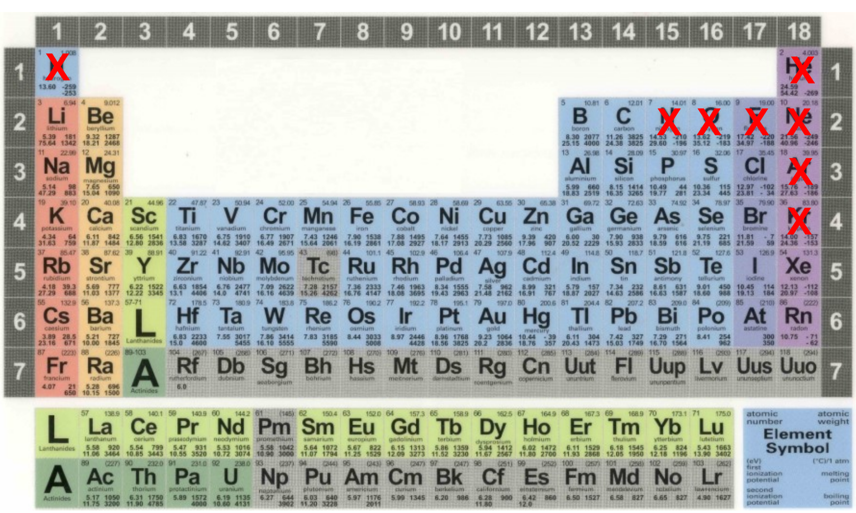

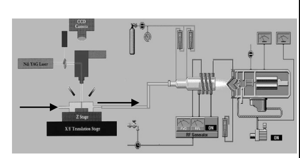

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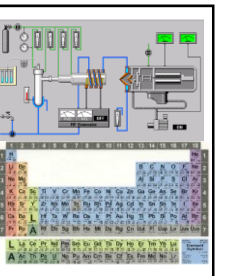
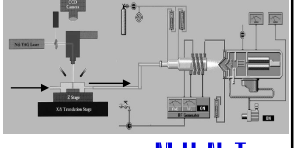
ICP-MS – PRINCIPLE



- Inductively Coupled Plasma of Mass Spectrometry
- argon plasma – source of atoms and ions (16 eV, 10000 K)
- atomization and ionization of the most elements of P.T.
- elemental specific detector (no molecules)
- analysis of solution and solid samples (laser ablation)
- limit of detection – pg/l, ng/g



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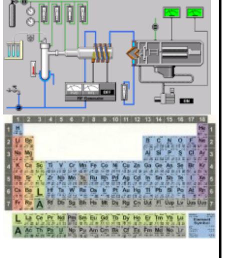
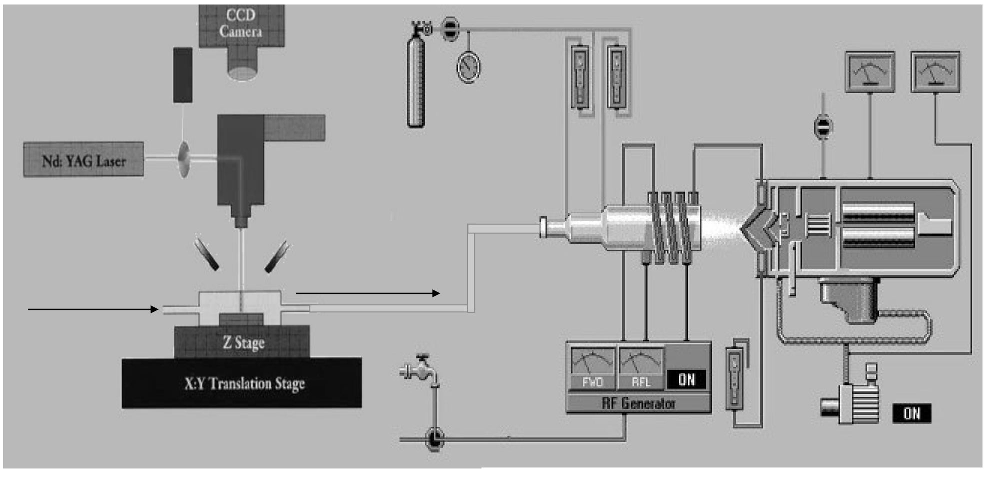
ICP-MS – PRINCIPLE





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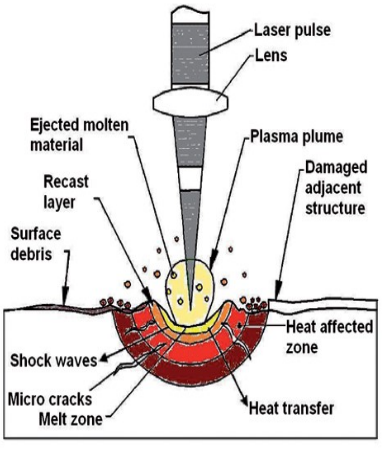
PRINCIPLE OF LASER ABLATION



- Laser ablation
  - explosive interaction of the laser beam and material (> 10^9 W/cm^2)
  - produced dry aerosol (particles and vapours)

composition of dry aerosol and analyzed surface are same – necessary for analytical purpose

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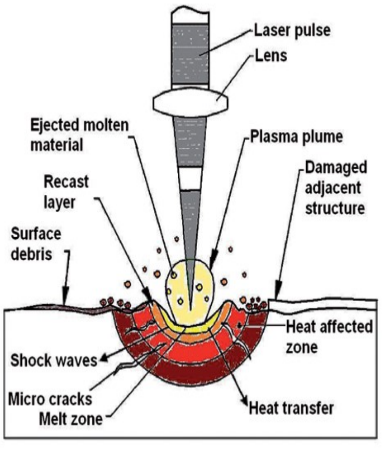
PRINCIPLE OF LASER ABLATION



- Advantages
  - analysis of any type of materials
  - direct analysis of solid samples
  - laser beam diameter 4 – 200 μm (optional lateral resolution)
  - possibility of local microanalysis
  - possibility of lateral distribution of elements (imaging)

- Drawbacks
  - different ablation rate for various materials (IS needed)
  - additional equipment

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PRINCIPLE OF LASER ABLATION

– Different ablation rate

garnet

10 ug/g Sc

quartz

10 ug/g Sc

11

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PRINCIPLE OF LASER ABLATION

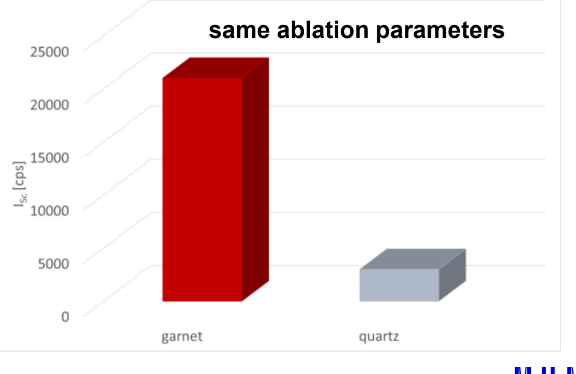
– Different ablation rate

garnet

10 ug/g Sc

quartz

10 ug/g Sc



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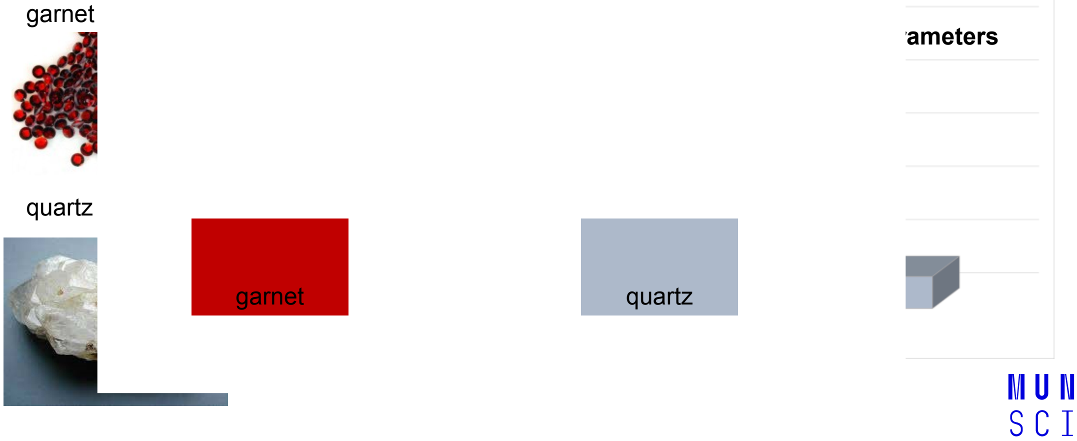
PRINCIPLE OF LASER ABLATION

– Differen



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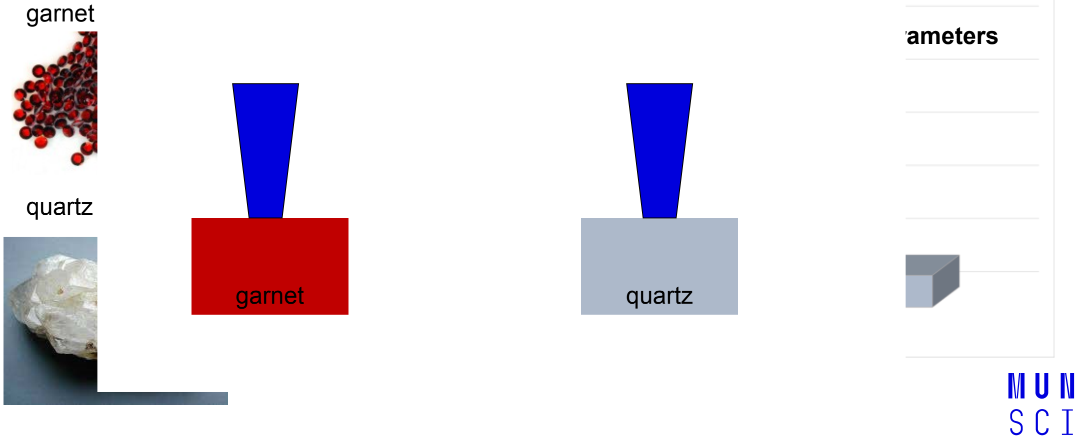
PRINCIPLE OF LASER ABLATION

– Differen



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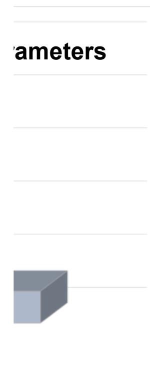
PRINCIPLE OF LASER ABLATION

– Differen

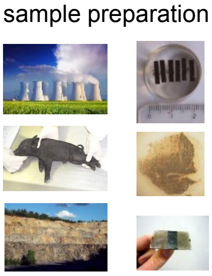
garnet

quartz



LA-ICP-MS IMAGING - SCHEME

sample preparation



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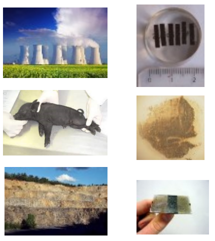
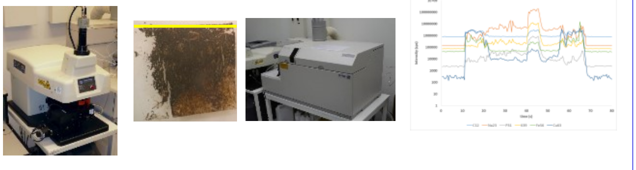
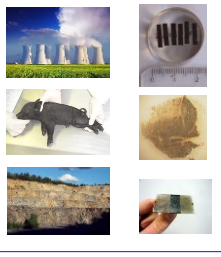


measurement



LA-ICP-MS IMAGING - SCHEME

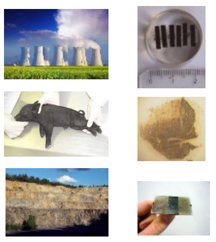
sample preparation



measurement

LA-ICP-MS IMAGING - SCHEME

sample preparation



measurement

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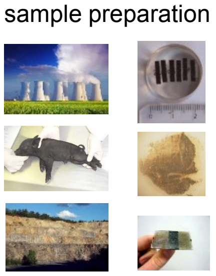
LA-ICP-MS IMAGING - SCHEME

sample preparation



measurement

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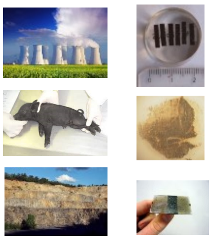
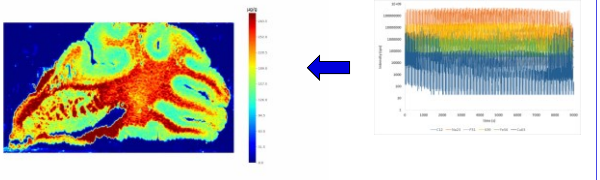
LA-ICP-MS IMAGING - SCHEME

sample preparation



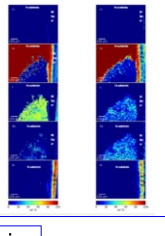
measurement

data processing

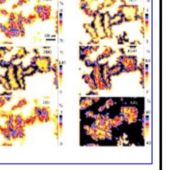


IMAGING IN OUR LAB - OVERVIEW

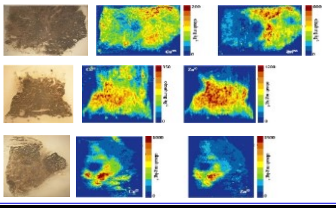
Task 1: Steel sample was exposed to molten LiF-NaF salt treatment. Strong corrosion on sample surface occured. Our task is to obtain content of main constituent of steel and Li and Na in corroded layer.



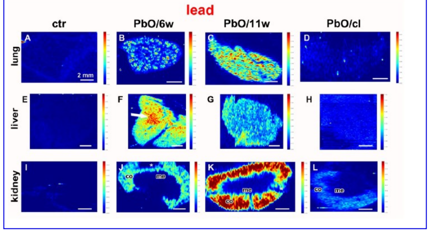
Task 2: My colleague geologist: „I have granitoid sample which contains quartz, mica, feldspar and the other minerals. Would it be possible to obtain elemental map of the granite?“



Task 3: Spontaneous regression is the process by which melanoma disappears. What happens with the elements at spontaneous regression?



Task 4: Nanoparticles are all around us. Do nanoparticles accumulate in the body or are they excreted out?



DISTRIBUTION OF CORROSSION PRODUCTS

- Steel sample was exposed to molten LiF-NaF salt treatment. Strong corrosion on sample surface occured. Our task is to obtain content of main constituent of steel and Li and Na in corroded layer.

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DISTRIBUTION OF CORROSSION PRODUCTS

- Steel sample was exposed to molten LiF-NaF salt treatment. Strong corrosion on sample surface occured. Our task is to obtain content of main constituent of steel and Li and Na in corroded layer.

Why LiF-NaF mixture?

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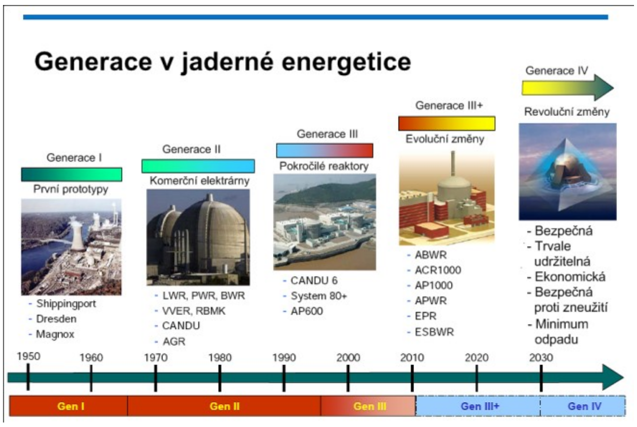

http://ojs.ujf.cas.cz/~wagner/popclan/transmutace/generaceIV.html

GEN IV

six concepts of reactors:

Very High-Temperature gas-cooled Reactor

Gas-cooled Fast Reactor

Sodium-cooled Fast Reactor

Lead-cooled Fast Reactor

Super-critical water-cooled reactor

Molten fluoride salt reactor

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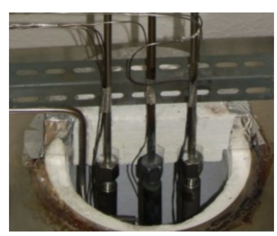
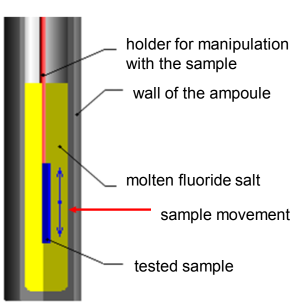
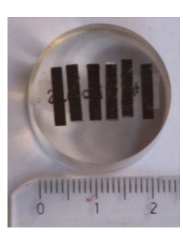
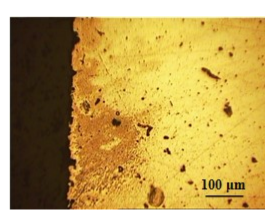
DISTRIBUTION OF CORROSSION PRODUCTS



- sample preparation (in Energovýzkum, Ltd.)
  - tested materials: Ni-based alloys and pure nickel
  - MFS: LiF-NaF, LiF-NaF-ZrF_4
  - exposure: 680°C, 100, 300, and 1000 hours







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DISTRIBUTION OF CORROSSION PRODUCTS

- determination of elements in corroded layer
  - single line scan (crust-corroded layer-intact material; laser beam diameter – 25 µm)
- in 2006 measured in ETH (we did not have ICP-MS)

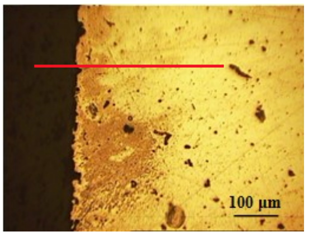
PAPER www.rsc.org/jaas | Journal of Analytical Atomic Spectrometry

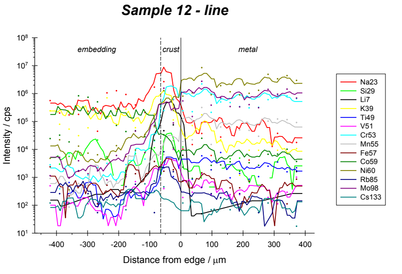
The EPMA, LA-ICP-MS and ICP-OES study of corrosion of structural materials for a nuclear reactor cooling circuit by molten fluoride salt treatment†

T. Vaculovic,[a] P. Sulovsky,[b] J. Machat,[a] V. Otruba,[a] O. Matal,[c] T. Simo,[c] Ch. Latkoczy,[d] D. Günther[d] and V. Kanicky*[a]

Received 24th July 2008, Accepted 9th March 2009
First published as an Advance Article on the web 26th March 2009
DOI: 10.1039/b812766b

Electron probe microanalysis (EPMA), inductively coupled plasma atomic emission spectrometry (ICP-OES), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) were applied to study the interaction of molten LiF-NaF salt mixtures with candidate structural materials (alloys) for a nuclear reactor-transmutor cooling circuit. The corrosion of test ampoules and inserted test specimens made of structural materials was brought about by the action of molten LiF-NaF coolant at 680 °C and its extent and character were examined in dependence on the time of exposure. The material corrosion changes were studied by mapping the sections of ampoule walls and inserted specimen surfaces with EPMA, whereas LA-ICP-MS was employed for linear scanning the salt/ampoule wall boundary. Corrosion-released structural material, dissolved in solidified molten salt, was analyzed by ICP-OES after the salt dissolution. The melt activity was proved to induce a surficial





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DISTRIBUTION OF CORROSSION PRODUCTS

- determination of elements in corroded layer
  - imaging of corroded layer (laser beam diameter – 12 µm)
  - spot by spot

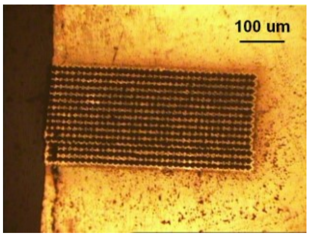
JAAS Dynamic Article Links
Cite this: J. Anal. At. Spectrom., 2012, 27, 1321
www.rsc.org/jaas TECHNICAL NOTE

Elemental mapping of structural materials for a nuclear reactor by means of LA-ICP-MS†

T. Vaculovič,[ab] T. Warchilová,[ab] T. Šimo,[c] O. Matal,[c] V. Otruba,[a] P. Mikuška[d] and V. Kanický*[ab]

Received 6th February 2012, Accepted 23rd April 2012
DOI: 10.1039/c2ja30037k

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to the study of the interaction of molten LiF–NaF salts with candidate structural materials for a nuclear reactor-transmutor cooling circuit. At a working temperature of 680 °C structural materials of heat exchangers are attacked and the melt–alloy interaction provokes microstructural and composition changes of the contact surface. The resulting corrosion-influenced zones were studied by LA-ICP-MS and the maps of elemental distribution were created on the semiquantitative level using the procedure based on the normalization of particular isotopic signals to the sum of signals of all isotopes present in the examined zone. Consequently, LA-ICP-MS signals were measured for structural material constituents (Ni, Cr, Fe, W, Mo, Ti, and Mn) and for cationic constituents of the cooling medium (Li and Na). The hypothetical fluorine signal was calculated as a sum of Li and Na signals. Corrosion products in the exposed cooling medium were determined by ICP-OES after dissolution. Of the three examined candidate structural materials (pure nickel, nickel-based alloy A071EV and nickel-coated iron) pure nickel exhibits the best resistance.



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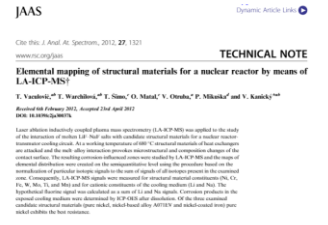
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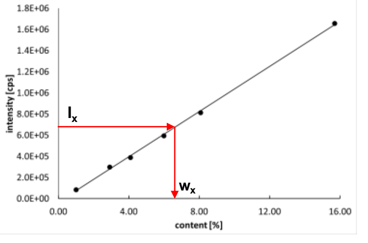
- determination of elements in corroded layer
  - imaging of corroded layer (laser beam diameter – 4 µm)
  - spot by spot
- quantification – external calibration
  - calibration standards – steel standards
  - tested materials – Ni-based alloy



element	reference value [%]	intact layer [%]
Ni	76.3	**76.8**
Cr	7.0	**6.9**
W	4.5	**4.4**
Ti	1.7	**1.8**

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DISTRIBUTION OF CORROSSION PRODUCTS


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- determination of elements in corroded layer
  - imaging of corroded layer (laser beam diameter – 4 µm)
  - spot by spot
- quantification – external calibration
  - calibration standards – steel standards
  - tested materials – Ni-based alloy

element	reference value [%]	intact layer [%]	corroded layer [%]
Ni	76.3	**76.8**	**375**
Cr	7.0	**6.9**	**35**
W	4.5	**4.4**	**21**
Ti	1.7	**1.8**	**10**

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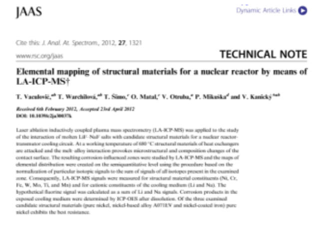
DISTRIBUTION OF CORROSSION PRODUCTS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TECHNICAL NOTE

Elemental mapping of structural materials for a nuclear reactor by means of LA-ICP-MS†

T. Vaculovič,[ab] T. Warchilová,[ab] T. Šimo,[c] O. Matal,[c] V. Otruba,[a] P. Mikuška[d] and V. Kanický[*ab]

Received 6th February 2012, Accepted 23rd April 2012

DOI: 10.1039/c2ja30037k

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to the study of the interaction of molten LiF–NaF salts with candidate structural materials for a nuclear reactor-transmutator cooling circuit. At a working temperature of 680 °C structural materials of heat exchangers are attacked and the melt–alloy interaction provokes microstructural and composition changes of the contact surface. The resulting corrosion-influenced zones were studied by LA-ICP-MS and the maps of elemental distribution were created on the semiquantitative level using the procedure based on the normalization of particular isotopic signals to the sum of signals of all isotopes present in the examined zone. Consequently, LA-ICP-MS signals were measured for structural material constituents (Ni, Cr, Fe, W, Mo, Ti, and Mn) and for cationic constituents of the cooling medium (Li and Na). The hypothetical fluorine signal was calculated as a sum of Li and Na signals. Corrosion products in the exposed cooling medium were determined by ICP-OES after dissolution. Of the three examined candidate structural materials (pure nickel, nickel-based alloy A071EV and nickel-coated iron) pure nickel exhibits the best resistance.

- determination of elements in corroded layer
  - imaging of corroded layer (laser beam diameter – 4 µm)
  - spot by spot
- quantification – external calibration
  - calibration standards – steel standards
  - tested materials – Ni-based alloy

element	reference value [%]	intact layer [%]	corroded layer [%]
Ni	76.3	**76.8**	**375**
Cr	7.0	**6.9**	**35**
W	4.5	**4.4**	**21**
Ti	1.7	**1.8**	**10**

What's wrong?

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- determination of elements in corroded layer
  - imaging of corroded layer (laser beam diameter – 4 µm)
  - spot by spot
- Different ablation rate?

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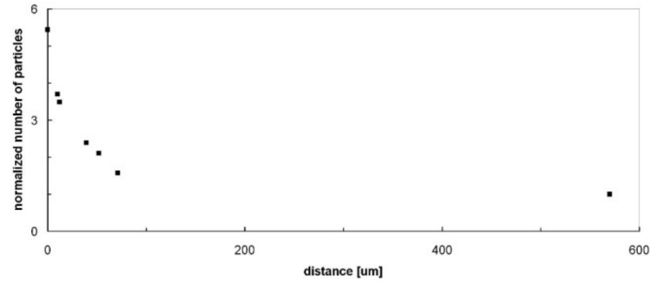
- determination of elements in corroded layer
  - imaging of corroded layer (laser beam diameter – 4 µm)
  - spot by spot
- Different ablation rate?
  - Particle size distribution measurements (Dr. Mikuška, UIACH CAS)



6x higher ablation rate in corroded layer!

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  - spot by spot
- quantification – total sum ion normalization (TSIN)
  - measuring of all elements from the sample

^{7}Li, ^{23}Na, ^{47}Ti, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{60}Ni, ^{182}W

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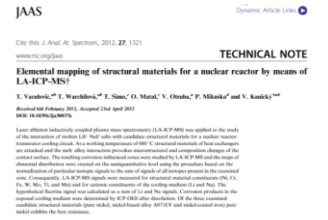
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  - imaging of corroded layer (laser beam diameter – 4 μm)
  - spot by spot
- quantification – total sum ion normalization (TSIN)
  - measuring of all elements from the sample
  - recalculation of measured intensities of isotopes on 100% abundance

$$I(Li) = \frac{I(^{7}Li)}{abundance(^{7}Li)} \qquad I(Na) = \frac{I(^{23}Na)}{abundance(^{23}Na)}$$

$$I(Ni) = \frac{I(^{60}Ni)}{abundance(^{60}Ni)} \qquad \ldots$$

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  - recalculation of measured intensities of isotopes on 100% abundance
  - calculation of content from the sum of intensities

$$w(Li) = \frac{I(Li)}{\sum I(Li)+I(Na)+I(Ni)+\cdots} \cdot 100 \qquad w(Na) = \frac{I(Na)}{\sum I(Li)+I(Na)+I(Ni)+\cdots} \cdot 100$$

$$w(Ni) = \frac{I(Ni)}{\sum I(Li)+I(Na)+I(Ni)+\cdots} \cdot 100$$

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  - calculation of content from the sum of intensities
  - verified by calibration standard

element	reference value [%]	intact layer [%]
Ni	28.5	**28**
Cr	4.3	**4.5**
Fe	62.0	**62.7**
Mn	0.8	**0.7**

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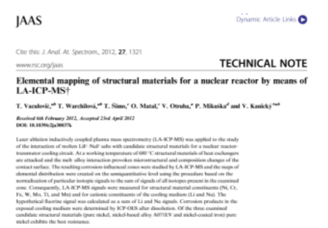
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  - verified by calibration standard
  - tested on Ni-based alloy

element	EPMA value [%]	corroded layer [%]
Ni	74	**73**
Mo	21	**22**
Cr	5.0	**4.4**
Fe	1.3	**1.5**

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TSIN works!

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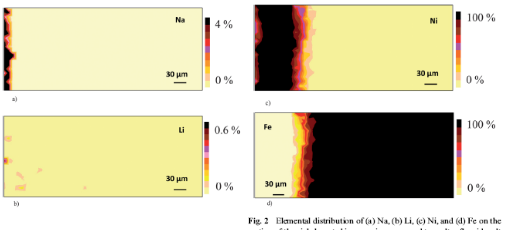

Fig. 2 Elemental distribution of (a) Na, (b) Li, (c) Ni, and (d) Fe on the section of the nickel-coated iron specimen exposed to molten fluoride salt mixture for 1000 h at 680 °C.

Sample	Ni 350 h	Ni 1000 h	A071EV 350 h	A071EV 1000 h	Ni-coating 350 h	Ni-coating 1000 h
Thickness [µm]	**20**	**36**	**144**	**162**	**63**	**81**

the most resistant: pure Ni

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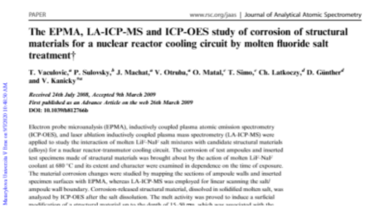

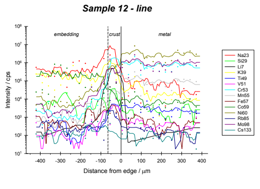

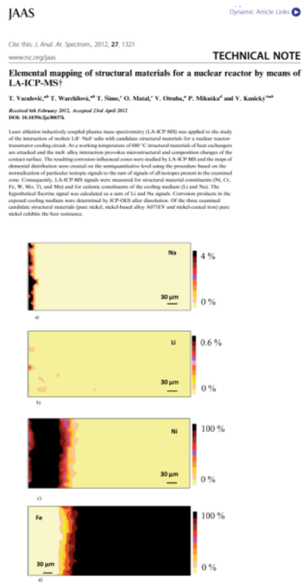

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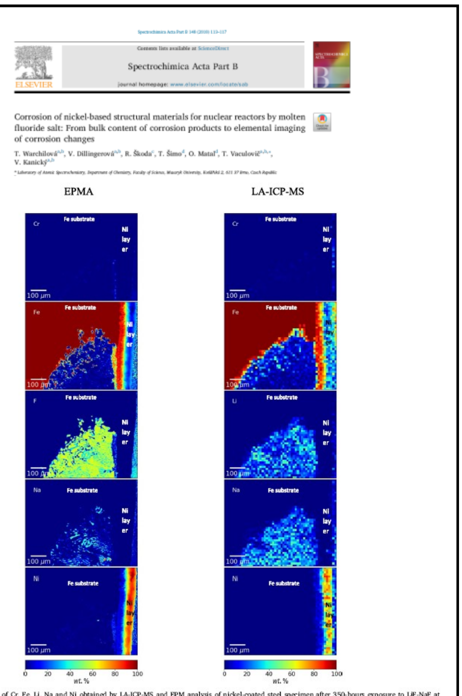

Fig. 2. Elemental maps of Cr, Fe, Li, Na and Ni obtained by LA-ICP-MS and EPM analysis of nickel-coated steel specimen after 350-hours exposure to LiF-NaF at 680 °C.

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- improved lateral distribution from single line scan to elemental maps comparable to EPMA
- corrosion provoked by LiF-NaF mixture is very specific
- utilization for development of alloys for implants
  - determination of elements released from implants into tissue (bones, teeth, muscle)

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IMAGING IN GEOLOGY

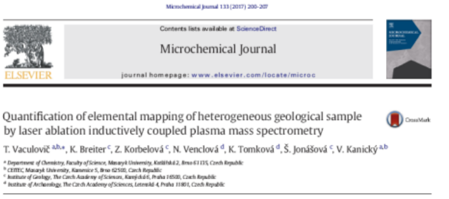
- My colleague geologist: „I have granitoid sample which contains quartz, mica, feldspar and the other minerals. Would it be possible to obtain elemental map of the granite?“

IMAGING IN GEOLOGY

- My colleague geologist: „I have granitoid sample which contains quartz, mica, feldspar and the other minerals. Would it be possible to obtain elemental map of the granite?“

My answer: „Yes, no problem.“

IMAGING IN GEOLOGY


Microchemical Journal 133 (2017) 200–207

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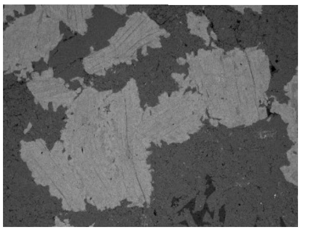
- Li-muskovite (mica) from Argamela mine (Portugal)



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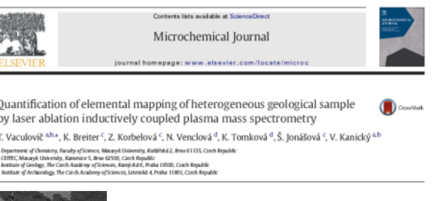
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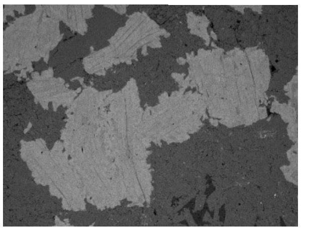
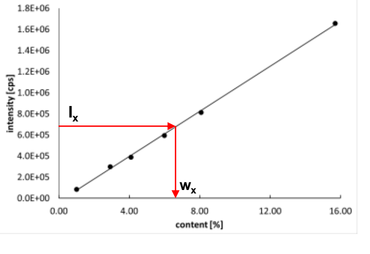
- Li-muskovite (mica) from Argamela mine (Portugal)
- quantification – external calibration with internal standardization

$$w(X)_{norm} = \frac{w(X)_{meas} \times w\ (IS)_{EPMA}}{w\ (IS)_{meas}}$$





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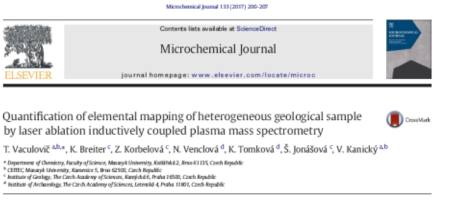
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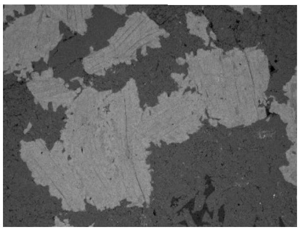
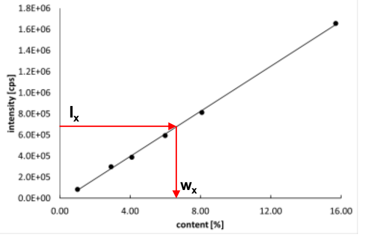


$w(SiO_2)_{EPMA}$ = 48.1 %

$$w(X)_{norm} = \frac{w(X)_{meas} \times w\,(IS)_{EPMA}}{w\,(IS)_{meas}}$$



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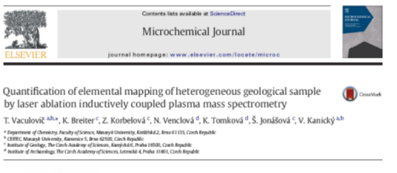
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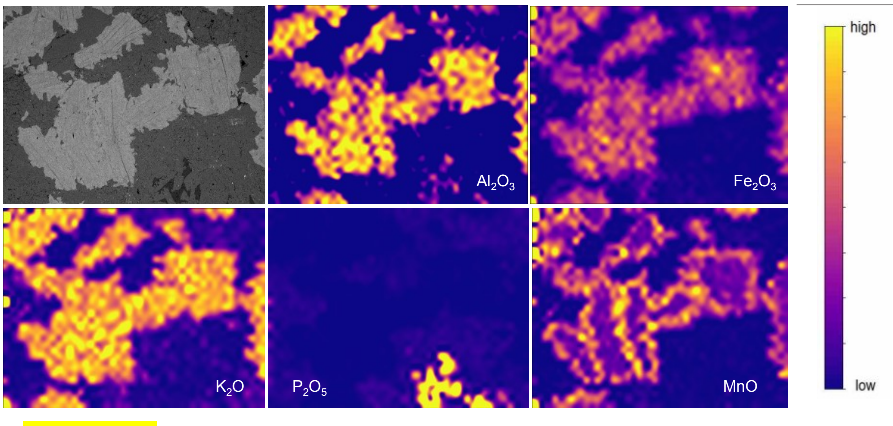

SiO_2
48.1 %

48

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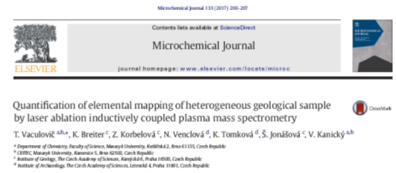
Microchemical Journal 133 (2017) 200–207

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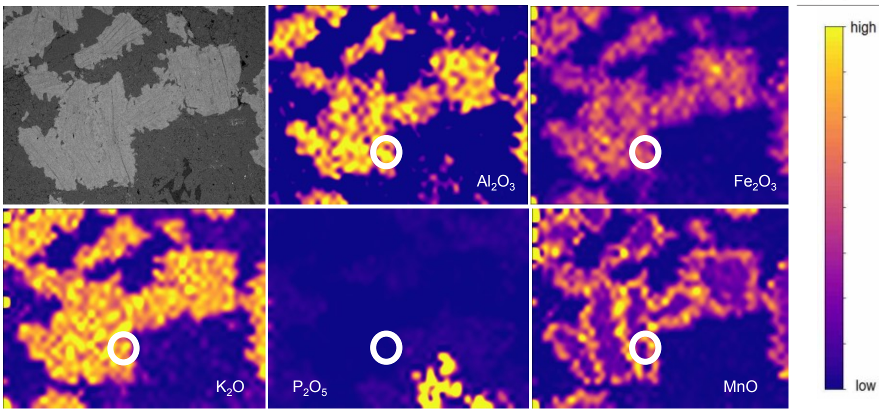

Li_2O: 1.1 %
Al_2O_3: 54.6 %
K_2O: 11.8 %
Na_2O: 0.7 %
P_2O_5: 0.5 %
Fe_2O_3: 4.3 %
SiO_2 : 48.1 %
∑ **122.1 %**

49

SiO_2
48.1 %

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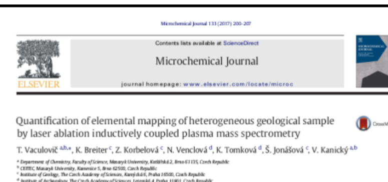

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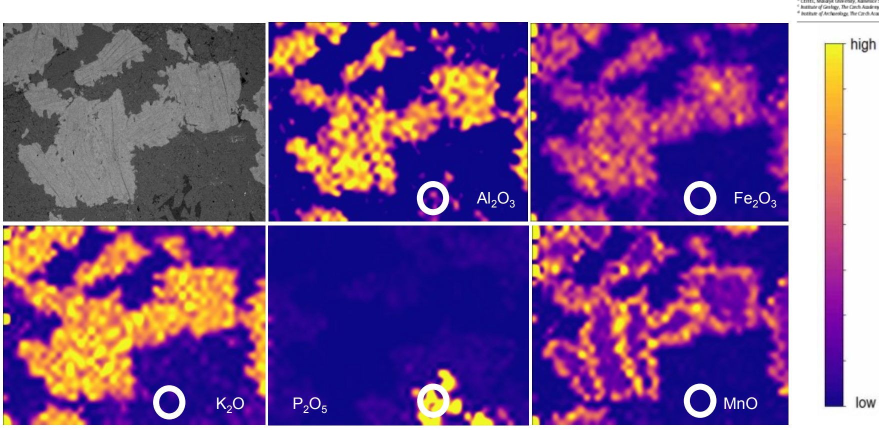

Li_2O: 79.3 %
Al_2O_3: 64.6 %
K_2O: 0.7 %
Na_2O: 8.5 %
P_2O_5: 39.7 %
SiO_2 48.1 %
∑ **240.9 %**

50

SiO_2
48.1 %

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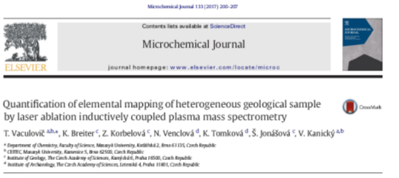
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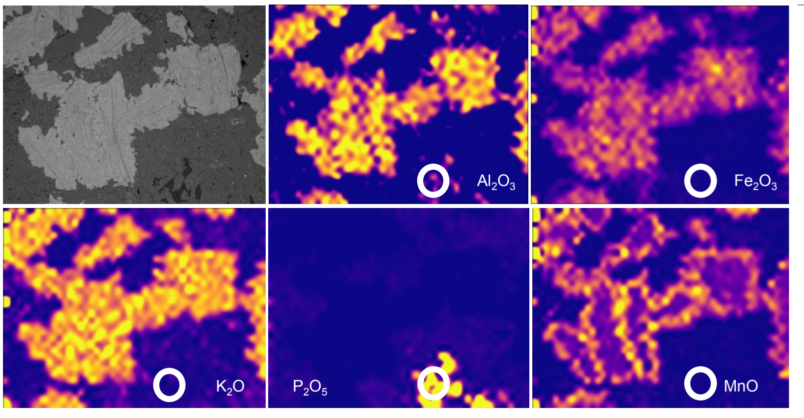

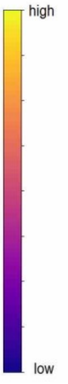

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Al_2O_3:	64.6 %
K_2O:	0.7 %
Na_2O:	8.5 %
P_2O_5:	39.7 %
SiO_2	48.1 %
∑	**240.9 %**

SiO_2
48.1 %

What is wrong?

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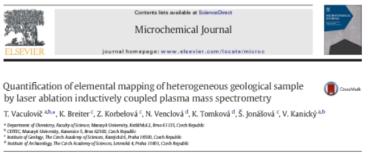
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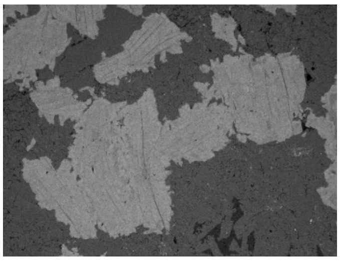
- more detailed view on the sample:

mica core:	45.8 % SiO_2
mica rim:	50.5 % SiO_2
apatite:	< 1 % SiO_2



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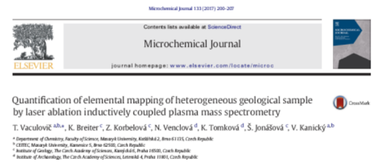

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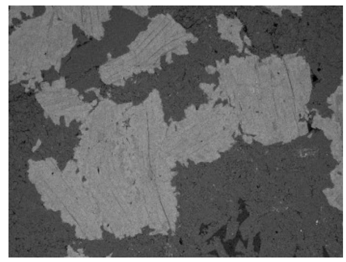

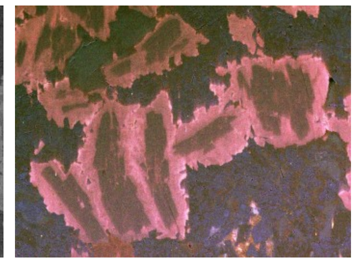

internal standardization is not applicable!

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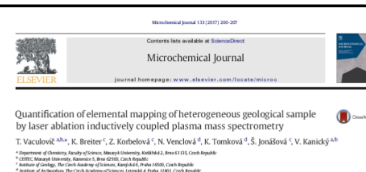
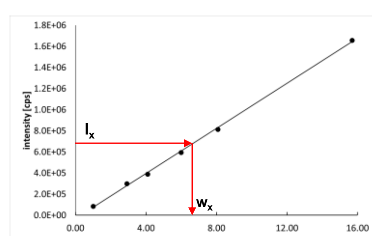


– external calibration with sum oxide normalization (SON) to 100 %
  – content of elements to recalculate to oxide form

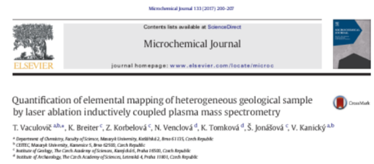
$$w(XO)_{norm} = \frac{w(XO)_{meas} \times 100}{\sum w(XO)_{meas}}$$



– no complementary analysis (e.g. EPMA)

– all main elements of the sample have to be measured

IMAGING IN GEOLOGY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- external calibration with sum oxide normalization (SON)
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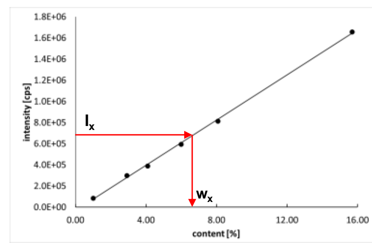

- no complementary analysis (e.g. EPMA)
- all main elements of the sample have to be measured

55

Does it work?

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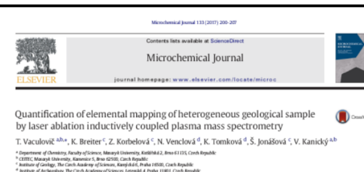
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- analysis of homogenous sample with easy matrix (CRM)
- analysis of real sample (archaeological glass)
- analysis of heterogeneous real sample (mica from Argemela)

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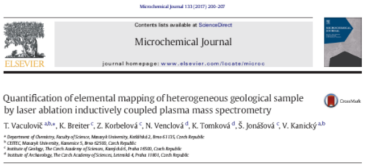
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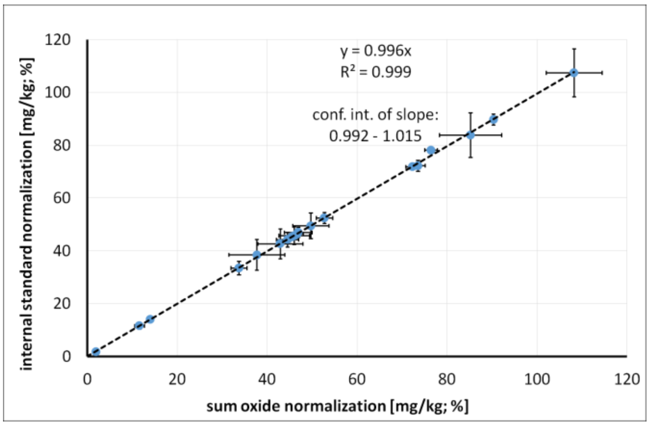
– glass standard NIST 612



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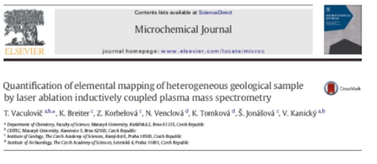

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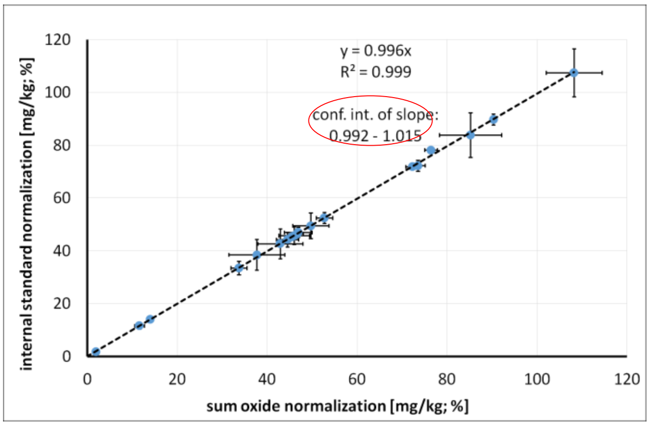

Youden graph:

if: **slope = 1, intercept = 0**

then: **methods are same**

58

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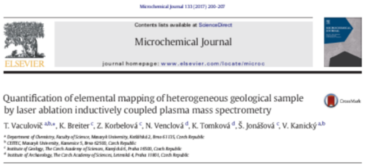
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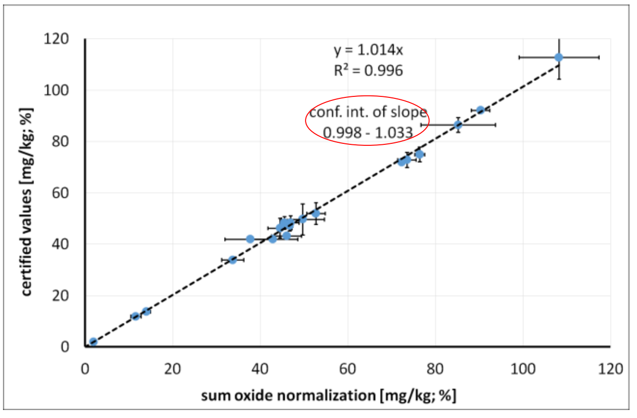

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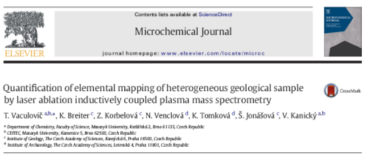
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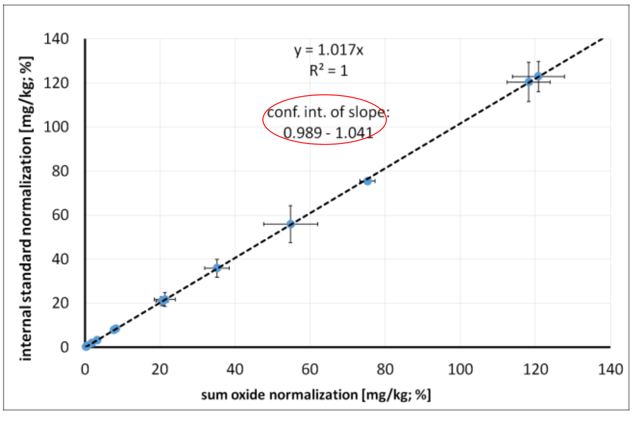
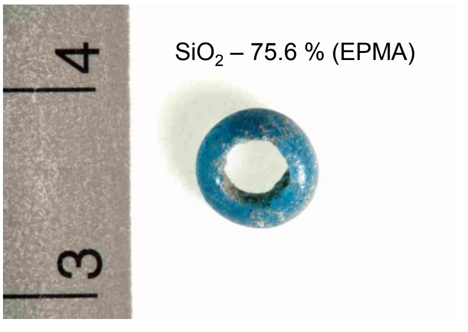
- ancient glass – blue beads; Late Bronz Age (1300 A.C.); Holubice (Czech Rep.);





SiO_2 – 75.6 % (EPMA)

60

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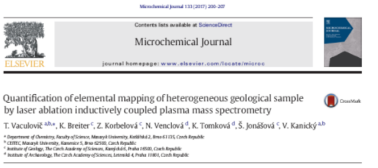

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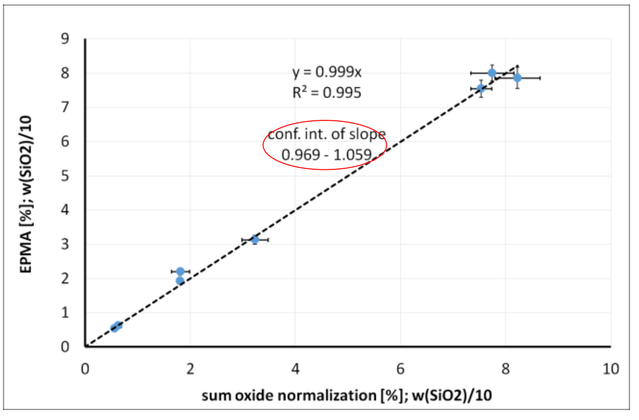

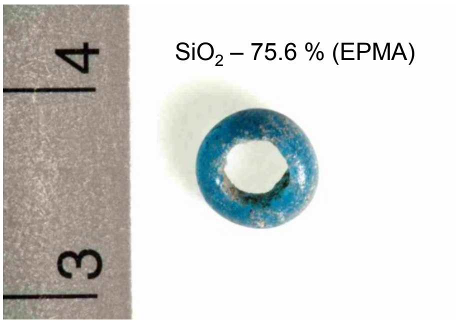

SiO_2 – 75.6 % (EPMA)

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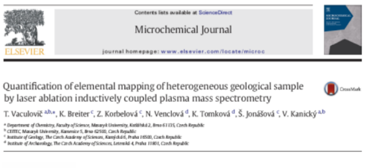

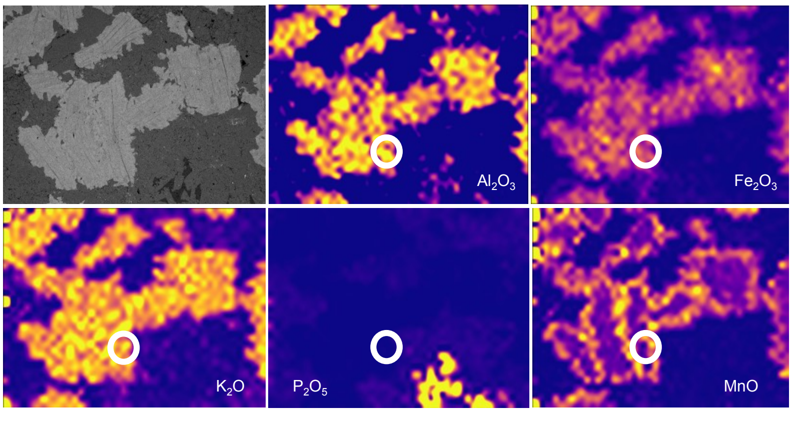

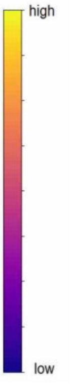

Li_2O:	1.1 %
Al_2O_3:	33.9 %
K_2O:	9.83 %
Na_2O:	0.90 %
Fe_2O_3:	2.51 %
SiO_2 :	45.3 %
F:	4.9 %
...:	1.56 %
∑	**100.0 %**

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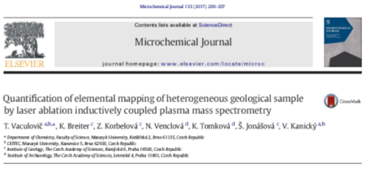

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[c] Institute of Geology, The Czech Academy of Sciences, Rozvojová 269, Praha 16500, Czech Republic
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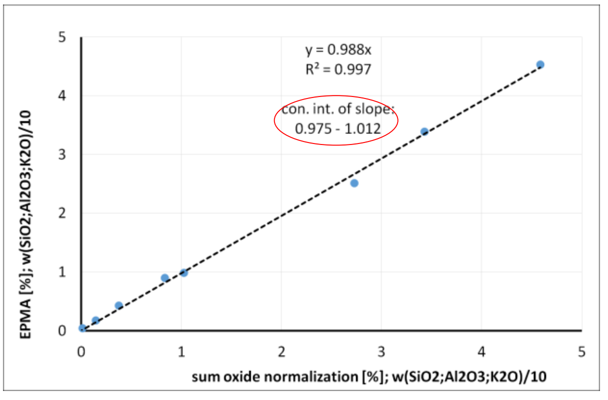
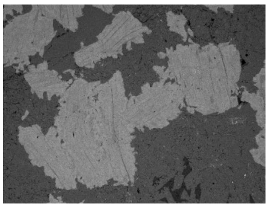
– mica sample froma Argamela





Youden graph:

if: **slope = 1, intercept = 0**

then: **methods are same**

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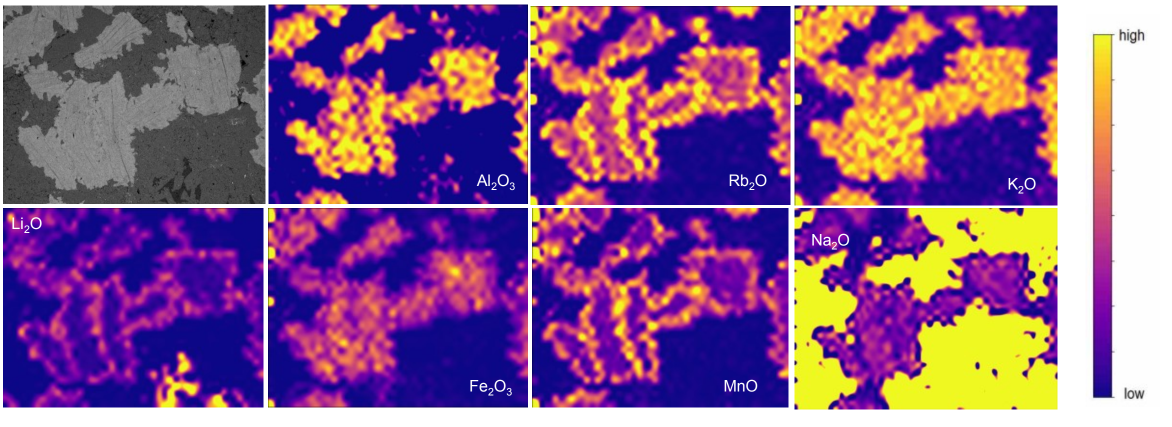

Li_2O: 0 – 4%

Al_2O_3: 20 – 50 %
Fe_2O_3: 0 – 3%

Rb_2O: 0 – 0.8 %
MnO: 0 – 0.5 %

K_2O: 0 – 10 %
Na_2O: 0 – 1 %

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IMAGING IN GEOLOGY

- normalization on total sum oxide is applicable for heterogeneous samples
- improving of explanations „what happen with elements during minerals and rocks forming“

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SPONTANEOUS REGRESSION

- Spontaneous regression is the process by which melanoma disappears. What happens with the elements at spontaneous regression?

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SPONTANEOUS REGRESSION

- Spontaneous regression is the process by which melanoma disappears. What happens with the elements at spontaneous regression?

- spontaneous regression – the process leading from melanoma (tumour tissue) to healthy tissue; (*GMT – growing melanoma tissue; ESR – early spontaneous regression (approx. 12 weeks); LSR – late spontaneous regression (approx. 22 weeks); FT – fibrous tissue (30 weeks)*)

- melanoma tissues from Melanoma-bearing Liběchov Minipig (MeLiM)

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SPONTANEOUS REGRESSION

- sample preparation (in Institute of Animal Physiology and Genetics, CAS)
  - cryosections (thickness of 30 μm)
  - different stages of spontaneous regression
  - placed on glass slide

- laser ablation parameters
  - laser spot diameter – 100 μm
  - scan speed – 200 μm

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SPONTANEOUS REGRESSION

- LA-ICP-MS parameters
  - laser beam spot – 100 μm
  - scan speed – 200 μm/s
  - laser beam fluence – 2 J/cm^2
- Suppression of different ablation rate
  - recommended normalization on signal ^{12}C

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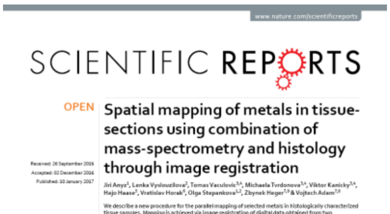
SPONTANEOUS REGRESSION

- LA-ICP-MS parameters
  - laser beam spot – 100 μm
  - scan speed – 200 μm/s
  - laser beam fluence – 2 J/cm^2
- Suppression of different ablation rate
  - recommended normalization on signal ^{12}C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SCIENTIFIC REPORTS

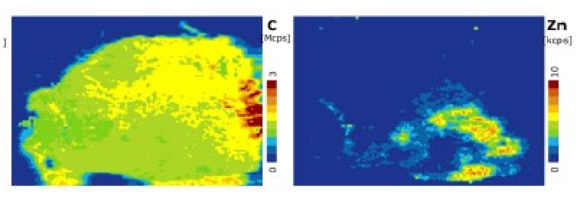
OPEN

Spatial mapping of metals in tissue-sections using combination of mass-spectrometry and histology through image registration

Received: 26 September 2016
Accepted: 02 December 2016
Published: 10 January 2017

Jiri Anyz[1], Lenka Vyslouzilova[2], Tomas Vaculovic[3,4], Michaela Tvrdonova[3,4], Viktor Kanicky[3,4], Hajo Haase[5], Vratislav Horak[6], Olga Stepankova[1,2], Zbynek Heger[7,8] & Vojtech Adam[7,8]

We describe a new procedure for the parallel mapping of selected metals in histologically characterized tissue samples. Mapping is achieved via image registration of digital data obtained from two



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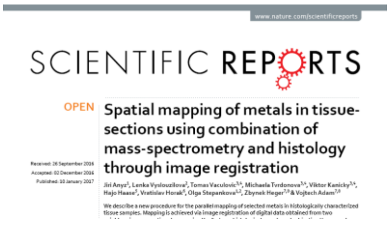
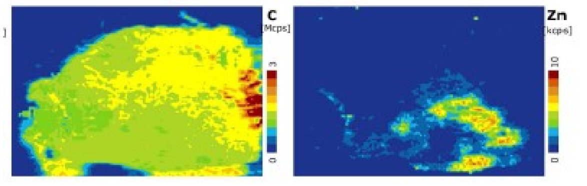
SPONTANEOUS REGRESSION



- LA-ICP-MS parameters
  - laser beam spot – 100 µm
  - scan speed – 200 µm/s
  - laser beam fluence – 2 J/cm²
- Suppression of different ablation rate
  - recomended normalization on signal ^{12}C
  - C is not homogeneous in sample



How to compensate the different ablation rate?

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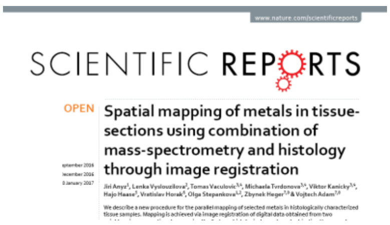
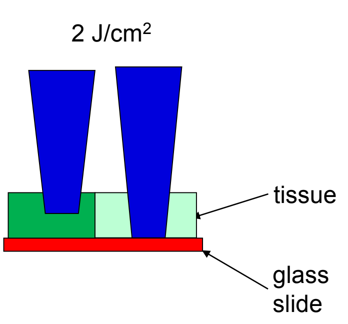
SPONTANEOUS REGRESSION





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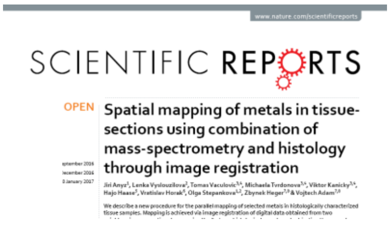
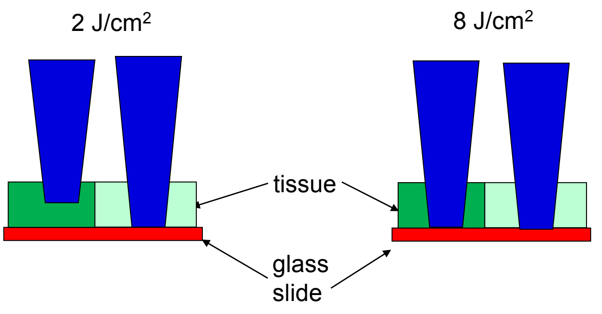
SPONTANEOUS REGRESSION





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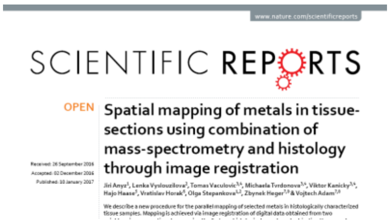
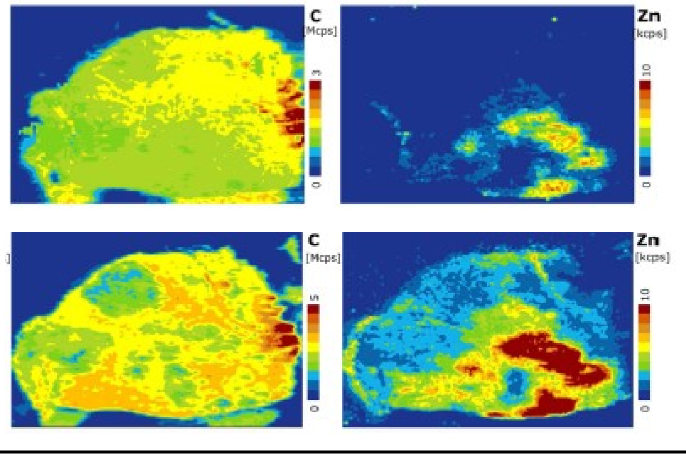


- Higher laser beam fluence
  - 2 J/cm^2
  - 8 J/cm^2



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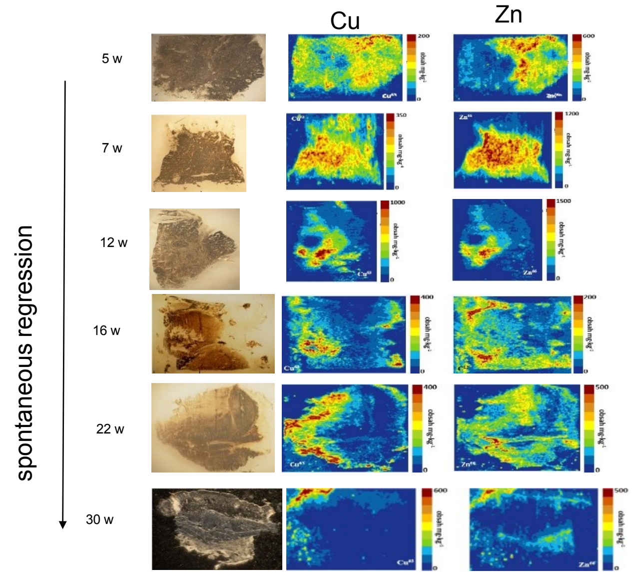

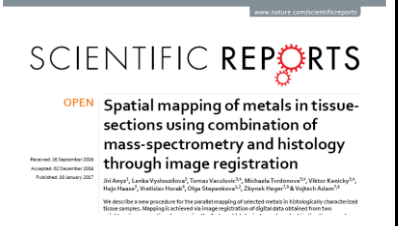
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SCIENTIFIC REPORTS

OPEN

Received: 26 September 2016
Accepted: 02 December 2016
Published: 10 January 2017

Spatial mapping of metals in tissue-sections using combination of mass-spectrometry and histology through image registration

Jiri Anyz[1], Lenka Vyslouzilova[2], Tomas Vaculovic[3,4], Michaela Tvrdonova[3,4], Viktor Kanicky[3,4], Hajo Haase[5], Vratislav Horak[6], Olga Stepankova[1,2], Zbynek Heger[7,8] & Vojtech Adam[7,8]

We describe a new procedure for the parallel mapping of selected metals in histologically characterized tissue samples. Mapping is achieved via image registration of digital data obtained from two

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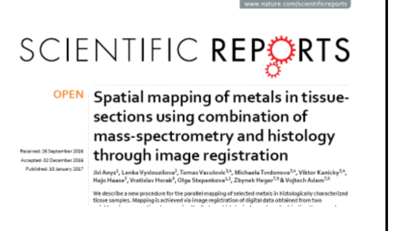

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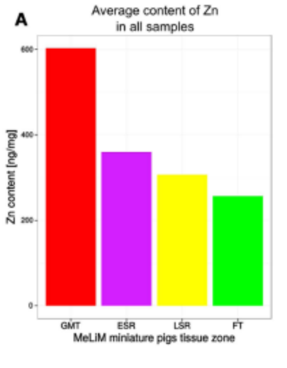
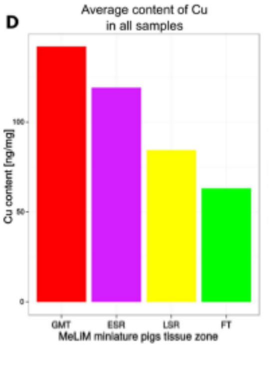
- the distribution and content of Cu and Zn changes significantly





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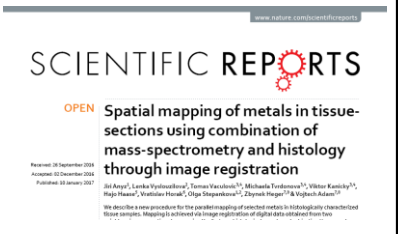
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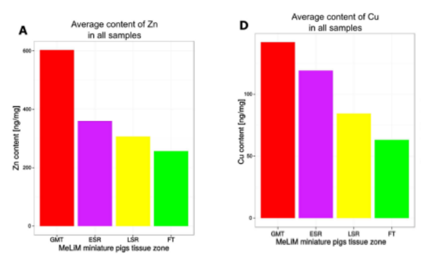
Spatial mapping of metals in tissue-sections using combination of mass-spectrometry and histology through image registration

- the distribution and content of Cu and Zn changes significantly

Can we determine specific protein?



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SPONTANEOUS REGRESSION

- ICP-MS – elemental specific detector
- proteins – **C, O, H, N, S, P,** Fe, Cu, Zn, Co …
- O, H, N – non-determinable by ICP
- S, P, C – part of each protein

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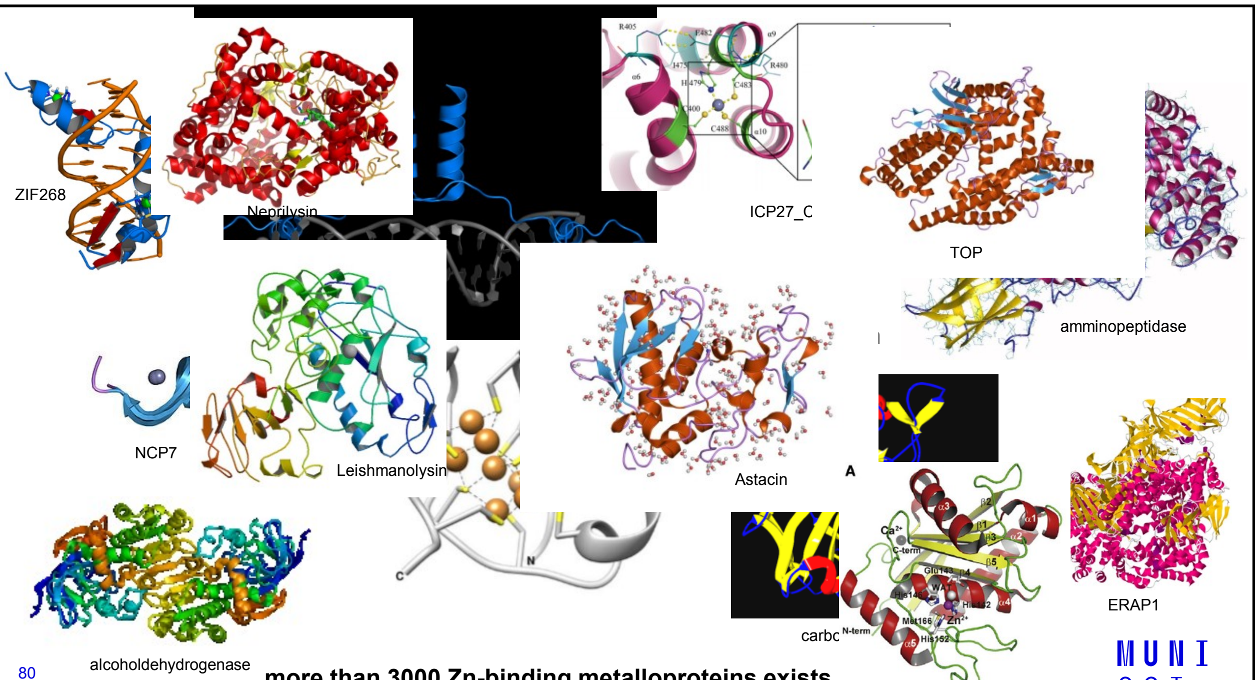

more than 3000 Zn-binding metalloproteins exists

80

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Is there some possibility how to determine specific proteins?

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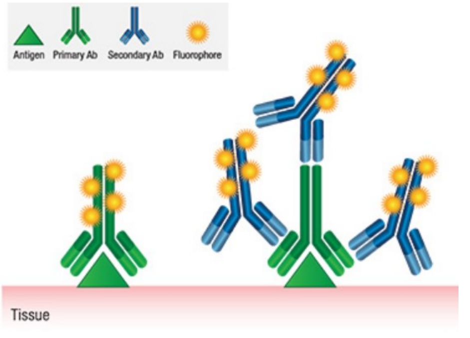
ICP-MS AND PROTEINS

- **immunochemistry**



https://www.cellsignal.com/contents/resources-applications/flourescent-multiplex-immunohistochemistry/fluoresence-mihc

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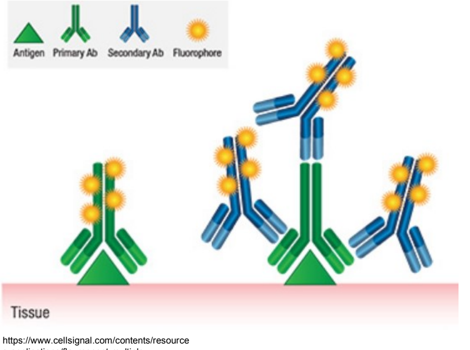
ICP-MS AND PROTEINS

- **immunochemistry**



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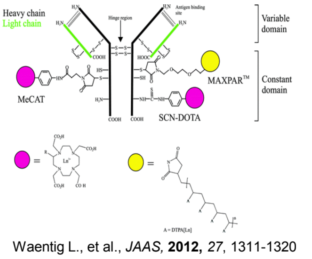
- **REE and chelates**

MeCAT – 1 REE on 1 chelate

SCN-DOTA – 4 REE on 1 chelate



Waentig L., et al., *JAAS*, **2012,** *27*, 1311-1320

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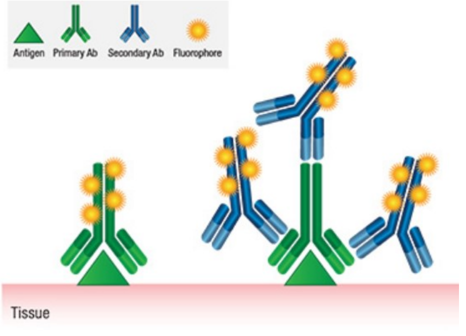
ICP-MS AND PROTEINS

- immunochemistry



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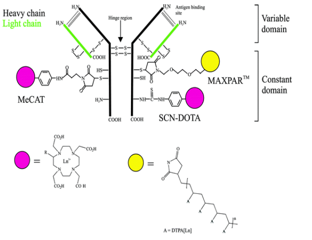

Waentig L., et al., *JAAS*, **2012,** *27*, 1311-1320

Could we amplify the signal?

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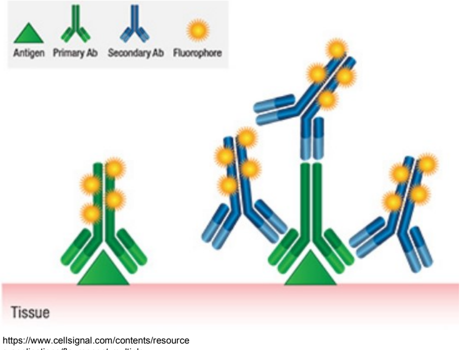
ICP-MS AND PROTEINS

- immunochemistry



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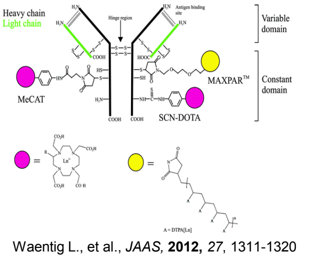
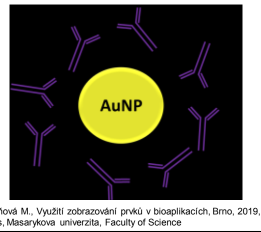


Waentig L., et al., *JAAS*, **2012,** *27*, 1311-1320

- **nanoparticles**



Tvrdoňová M., Využití zobrazování prvků v bioaplikacích, Brno, 2019, Ph.D. Thesis, Masarykova univerzita, Faculty of Science

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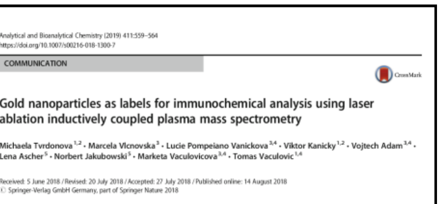


Analytical and Bioanalytical Chemistry (2019) 411:559–564
https://doi.org/10.1007/s00216-018-1300-7

COMMUNICATION

Gold nanoparticles as labels for immunochemical analysis using laser ablation inductively coupled plasma mass spectrometry

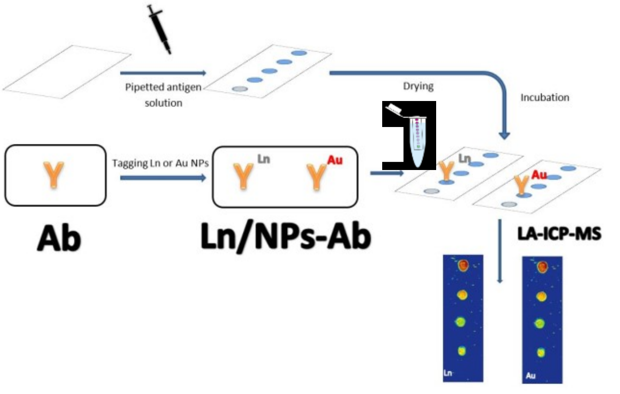
Michaela Tvrdonova[1,2] · Marcela Vlcnovska[3] · Lucie Pompeiano Vanickova[3,4] · Viktor Kanicky[1,2] · Vojtech Adam[3,4] · Lena Ascher[5] · Norbert Jakubowski[5] · Marketa Vaculovicova[3,4] · Tomas Vaculovic[1,4]

Received: 5 June 2018 / Revised: 20 July 2018 / Accepted: 27 July 2018 / Published online: 14 August 2018

- **scheme of the labelling of Ab**

- Au NPs – 10 and 60 nm
- MeCAT – with Ho

- model analyte: protein IgG



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ICP-MS AND PROTEINS

- **determination of IgG**
  - antiIgG-AuNPs vs. antiIgG-MeCAT(Ho)

	MeCAT	10 nm Au NPs	60 nm Au NPs
sensitivity	2×10^3	6×10^5	4×10^7
LOD IgG [pg]	**260**	**51**	**11**

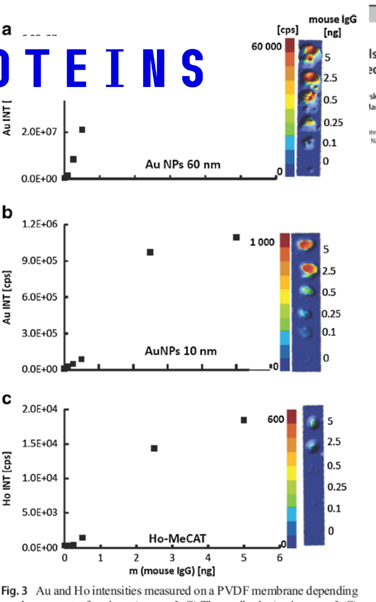

Fig. 3 Au and Ho intensities measured on a PVDF membrane depending on the amount of antigen (mouse IgG).The antibody (anti-mouse IgG) have been labelled by **a** AuNPs—60 nm, **b** AuNPs—10 nm, and **c** Ho-MeCAT; a total amount of 6.66 ng AB has been applied for all three experiments

sensitivity of NPs is better than MeCAT by factor 20000

LOD „only“ by 20

=> non-specific sorption of Au NPs

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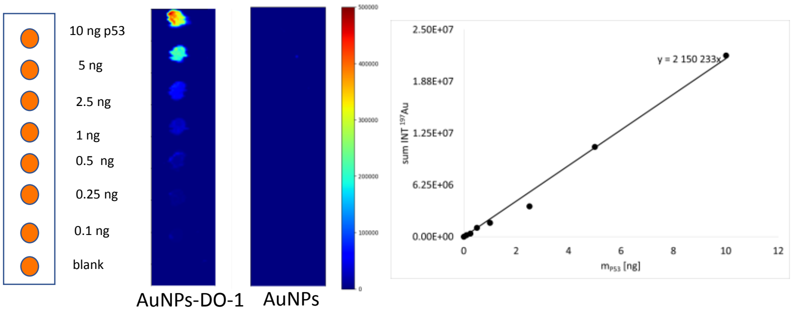
ICP-MS AND PROTEINS

- **determination of p53** – supressor of tumors („sensor“ of DNA damage); antibody DO-1
  - DO1-Au NPs, negative control Au NPs
  - standard of p53



Vlčnovská et al., Proof-of-Concept of Simultaneous Elemental and Molecular Mass Spectrometric Imaging – metal/p53 visualization, submitted in Analytical Chemistry

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ICP-MS AND PROTEINS

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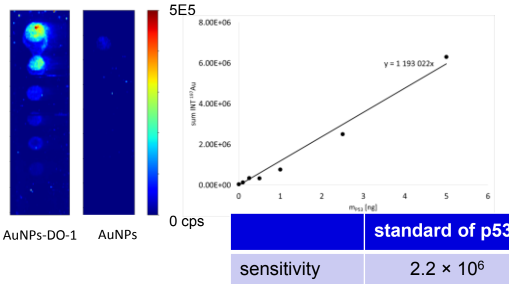
  - protein ladder spiked with p53



	standard of p53	spiked protein ladder
sensitivity [cps g μg^{-1}]	2.2 × 10^6	1.2 × 10^6
LOD p53 [pg]	**2**	**13**

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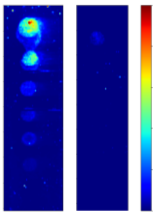

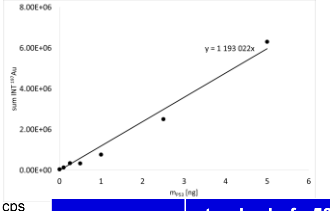

high specificity of the labelled DO-1

	standard of p53	spiked protein ladder
sensitivity [cps g μg^{-1}]	2.2 × 10^6	1.2 × 10^6
LOD p53 [pg]	**2**	**13**

90

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ICP-MS AND PROTEINS

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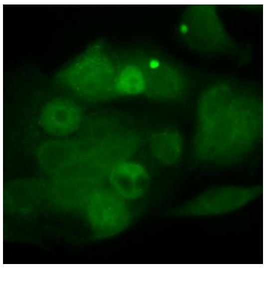
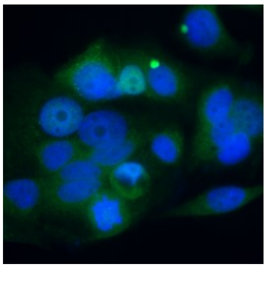
– DO1-Au NPs, negative control Au NPs

– MCF-7 cells (breast cancer)
– MCF-7 cells treated with cis Pt
(doc. Masařík, LF MU)





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ICP-MS AND PROTEINS

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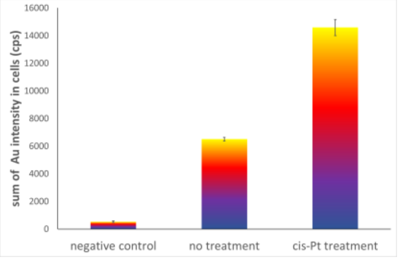

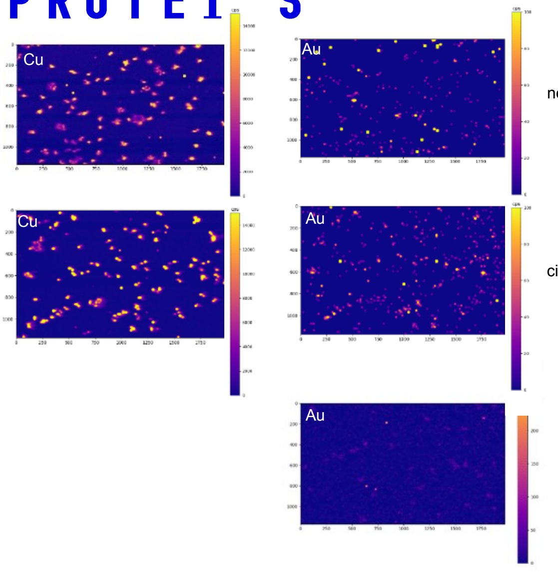

no treatment

cis-Pt treatment

negative control
(Au NPs)

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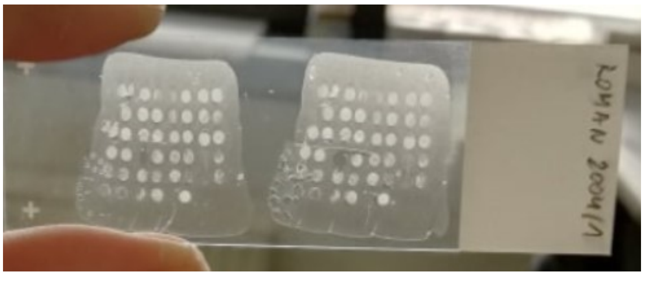
ICP-MS AND PROTEINS

– **determination of p53** – supressor of tumors („sensor“ of DNA damage); antibody DO-1

– DO1-Au NPs, negative control Au NPs

– 30 breast tumor samples
(doc. Hrstka, Masaryk Memorial Cancer Institute)



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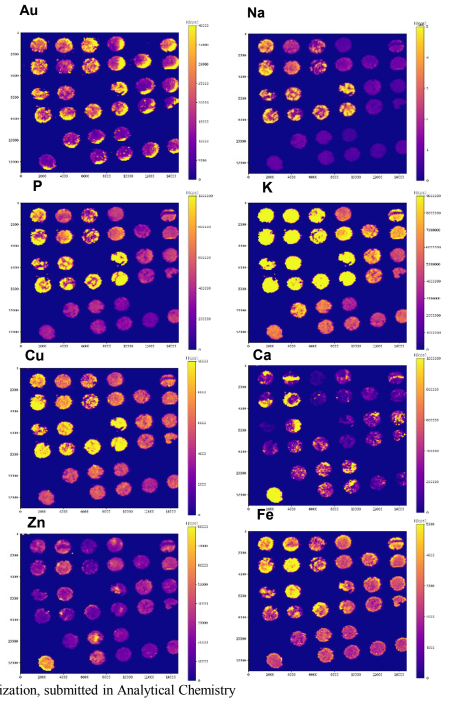

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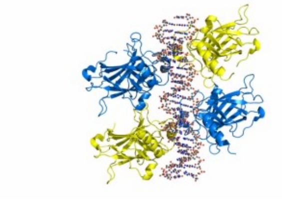

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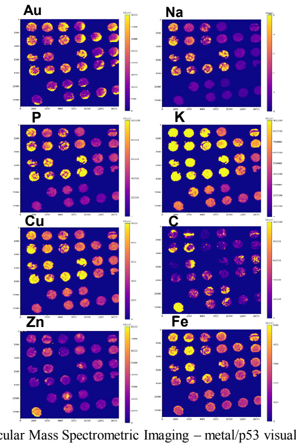

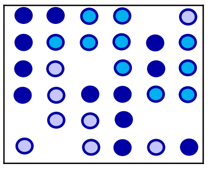

IHC staining
dark blue (3) – high intensities
lighter blue (2) – middle intensities
light blue (1) – low intensities

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ICP-MS AND PROTEINS

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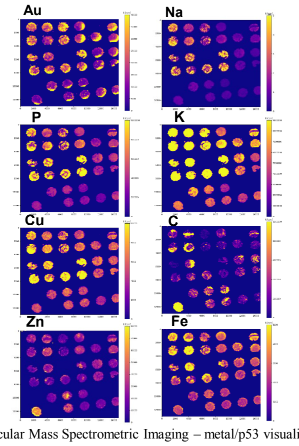

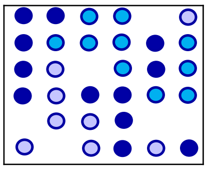

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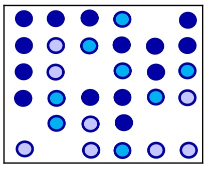

Au intensities *10^7 [cps]
dark blue > 1.5*10^7 cps
lighter blue 1.4 – 1.1*10^7 cps
light blue < 1.0*10^7 cps

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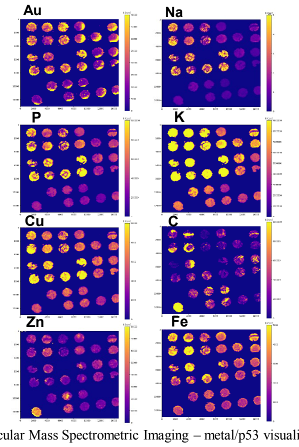

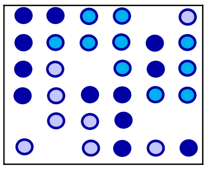

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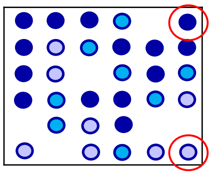

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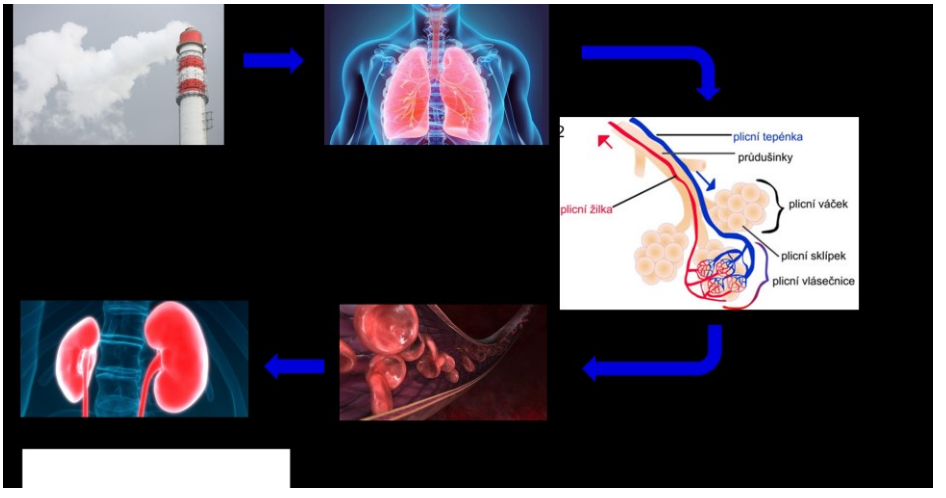
Vlčnovská et al., Proof-of-Concept of Simultaneous Elemental and Molecular Mass Spectrometric Imaging – metal/p53 visualization, submitted in Analytical Chemistry

NANOPARTICLES IN ORGANISM



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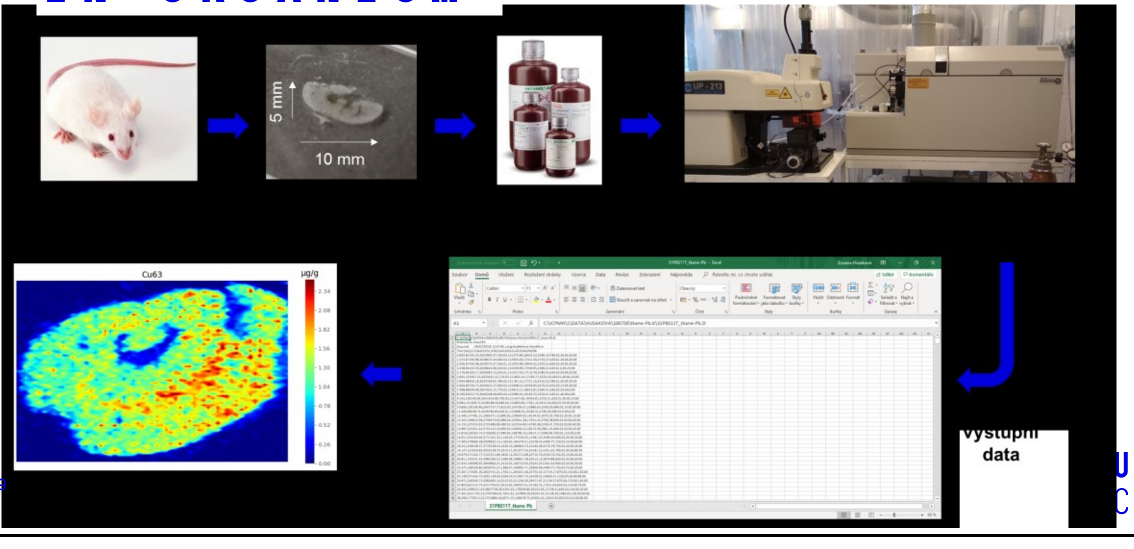
NANOPARTICLES IN ORGANISM



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NANOPARTICLES IN ORGANISM


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ARTICLE

Variability in the Clearance of Lead Oxide Nanoparticles Is Associated with Alteration of Specific Membrane Transporters

Jana Dumková,[#] Tereza Smutná,[#] Lucie Vrlíková, Hana Kotasová, Bohumil Dočekal, Lukáš Čapka, Michaela Tvrdoňová, Veronika Jakešová, Vendula Pelková, Kamil Křůmal, Pavel Coufalík, Pavel Mikuška, Zbyněk Večeřa, Tomáš Vaculovič, Zuzana Husáková, Viktor Kanický, Aleš Hampl, and Marcela Buchtová*

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5 groups of mice

- inhalation of PbO NPs (20-30 nm) for **2 weeks**
- inhalation of PbO NPs (20-30 nm) for **6 weeks**
- inhalation of PbO NPs (20-30 nm) for **11 weeks**
- **clearance** –inhalation of clean air for 5 weeks after inhalation PbO NPs (11 weeks)
- **control group**

3 different organs

- lung
- liver
- kidney

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NANOPARTICLES IN ORGANISM


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ARTICLE

Variability in the Clearance of Lead Oxide Nanoparticles Is Associated with Alteration of Specific Membrane Transporters

Jana Dumková,[#] Tereza Smutná,[#] Lucie Vrlíková, Hana Kotasová, Bohumil Dočekal, Lukáš Čapka, Michaela Tvrdoňová, Veronika Jakešová, Vendula Pelková, Kamil Křůmal, Pavel Coufalík, Pavel Mikuška, Zbyněk Večeřa, Tomáš Vaculovič, Zuzana Husáková, Viktor Kanický, Aleš Hampl, and Marcela Buchtová*

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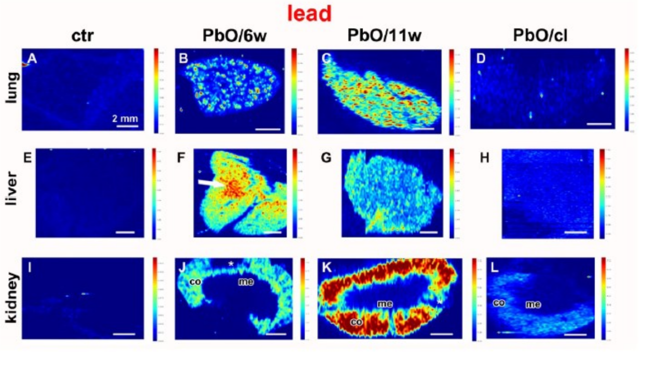

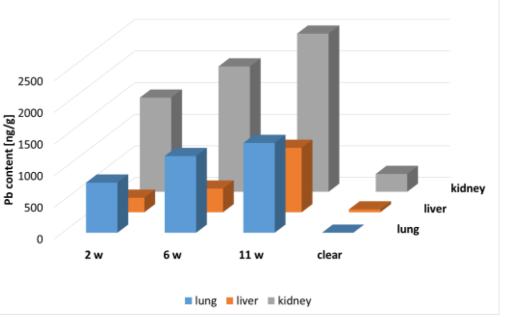

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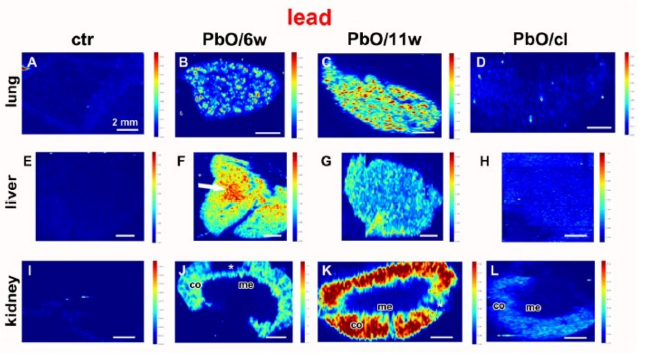

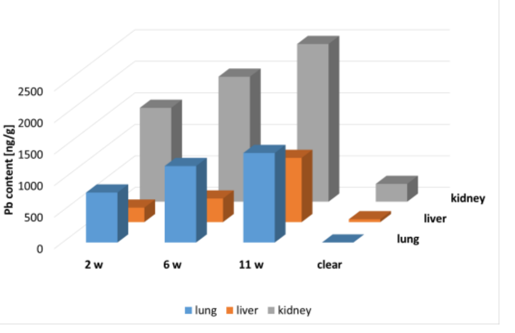

Pb in dissolved form or as NPs?

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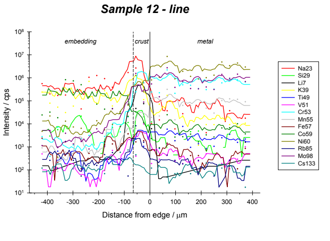
SUMMARY

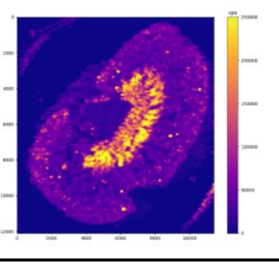
- LA-ICP-MS – applicable for any type of material
- supression of different ablation rate – crucial step for correct results
- elemental specific detector + imunochemistry = determination of specific proteins

- improving of distribution from single line scan of elements to imaging of specific proteins

2006



2020



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OUTLOOK

- **elemental microscope** - improving of lateral resolution and shortening time analysis
  - 1 Mpx images of all elements with resolution 10 µm during 2 hours

- **molecular microscope** – utilization of biorecognition tools
  - labelling of antibodies – multianalyte detection (a lot of labels – e.g. REE, Au, Ag, QDs,...)
  - imaging of elements and proteins in one analysis
  - utilization in clinical analysis

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GA14-13600S
Otevřené procesy v granitoidech z pohledu zonality minerálů a horninových textur

CEITEC 2020 LQ1601

GA13-18154S
Elemental mapping of plant and animal accumulators of heavy metals; where are they accumulated?

GA20-02203S
Analýza tkáňové odpovědi na inhalaci nanočástic kovů a mechanismus jejich čištění

GA101/08/1100
Studium interakcí chladicích médií za vysokých teplot s konstrukčními materiály tepelných výměníků metodami plazmové spektrometrie

ME10012
Laserová ablace se spektrometrií v indukčně vázaném plazmatu a spektroskopie laserem buzeného mikroplazmatu v archeologii a antropologii

GA101/08/1100
Studium interakcí chladicích médií za vysokých teplot s konstrukčními materiály tepelných výměníků metodami plazmové spektrometrie

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