

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

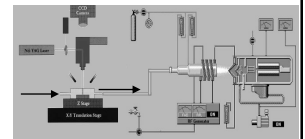
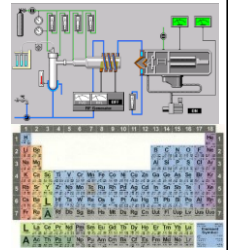
Tomáš Vaculovič

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)

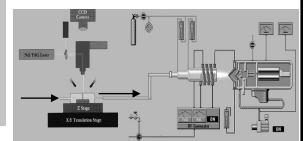
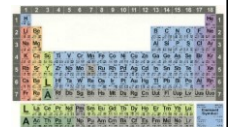
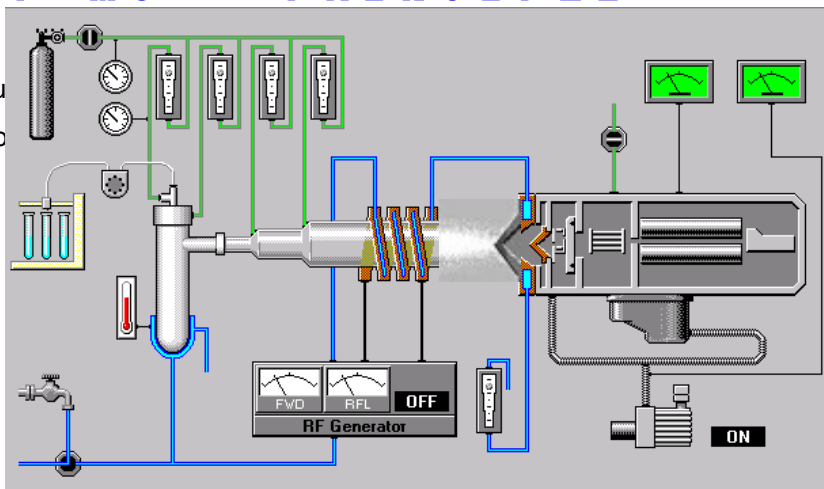


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# ICP-MS - PRINCIPLE

- Indu
- argo

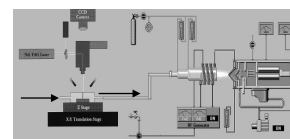
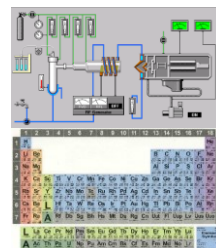


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# ICP-MS - PRINCIPLE

- 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)



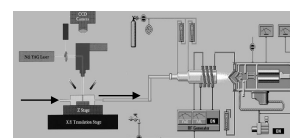
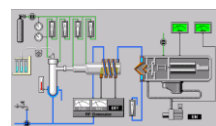
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# ICP-MS - PRINCIPLE

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- a  
- a  
- e

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	<b>X</b> H 1.00794 -258																	<b>X</b> He 4.002602 -269
2	Li 6.941 -251	Be 9.012182 -252											B 10.811 -257	C 12.0107 -258	<b>X</b> N 14.003074 -259	<b>X</b> O 15.999 -260	<b>X</b> F 18.9984032 -261	<b>X</b> Ne 20.1797 -262
3	Na 22.98976928 -263	Mg 24.304694 -264											Al 26.9815386 -265	Si 28.0855836 -266	P 30.973761998 -267	S 32.06 -268	Cl 35.453 -269	<b>X</b> Ar 39.948 -270
4	K 39.0983 -271	Ca 40.078 -272	Sc 44.9559376 -273	Ti 47.88 -274	V 50.9415 -275	Cr 51.9961 -276	Mn 54.938044 -277	Fe 55.845 -278	Co 58.933194 -279	Ni 58.6934 -280	Cu 63.546 -281	Zn 65.38 -282	Ga 69.723 -283	Ge 72.630 -284	As 74.9216 -285	Se 78.96 -286	Br 79.904 -287	<b>X</b> Kr 83.80 -288
5	Rb 85.4678 -289	Sr 87.62 -290	Y 88.905842 -291	Zr 91.224 -292	Nb 92.90638 -293	Mo 95.94 -294	Tc 98.90625 -295	Ru 101.07 -296	Rh 102.90550 -297	Pd 106.42 -298	Ag 107.8682 -299	Cd 112.411 -300	In 114.818 -301	Sn 118.710 -302	Sb 121.757 -303	Te 127.603 -304	I 126.905447 -305	Xe 131.29 -306
6	Cs 132.90545196 -307	Ba 137.327 -308	L 138.9047 -309	Hf 178.49 -310	Ta 180.94788 -311	W 183.84 -312	Re 186.207 -313	Os 190.23 -314	Ir 192.222 -315	Pt 195.084 -316	Au 196.966569 -317	Hg 200.59 -318	Tl 204.38 -319	Pb 207.2 -320	Bi 208.9804 -321	Po 209 -322	At 210 -323	Rn 222 -324
7	Fr 223 -325	Ra 226 -326	A 227 -327	Rf 261 -328	Db 262 -329	Sg 263 -330	Bh 264 -331	Hs 265 -332	Mt 266 -333	Ds 267 -334	Rg 268 -335	Cn 269 -336	Uut 270 -337	Uuq 271 -338	Uup 272 -339	Lv 273 -340	Uus 274 -341	Uuo 275 -342

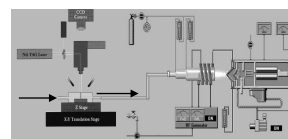
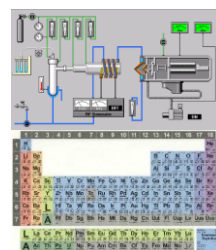


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# ICP-MS - PRINCIPLE

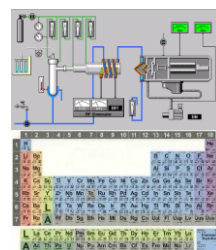
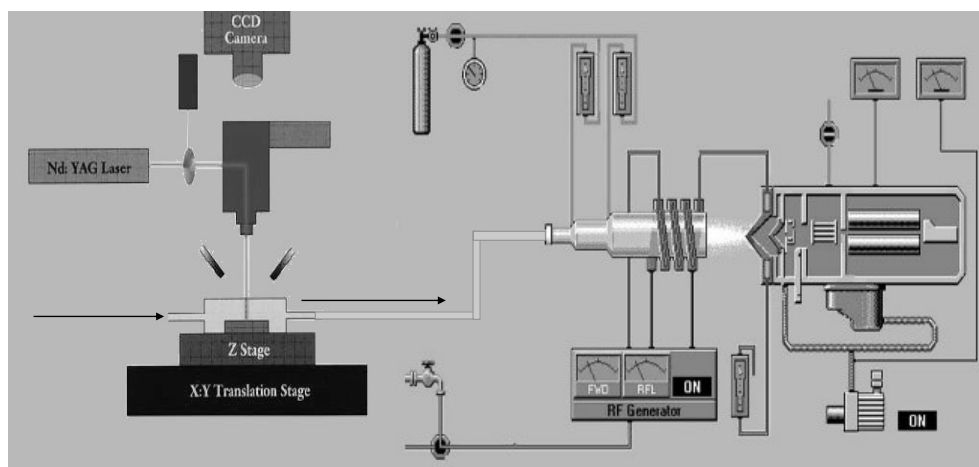
- Inductively Coupled Plasma of Mass Spectrometry
- argon plasma – source of atoms and ions (16 eV, 10000 K)
- atomization and ionization of the most elements of P.T.
- elemental specific detector (no molecules)
- analysis of solution and solid samples (laser ablation)
- limit of detection – pg/l, ng/g



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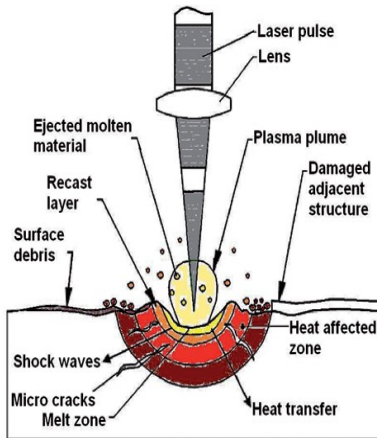
# ICP-MS - PRINCIPLE



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# PRINCIPLE OF LASER ABLATION



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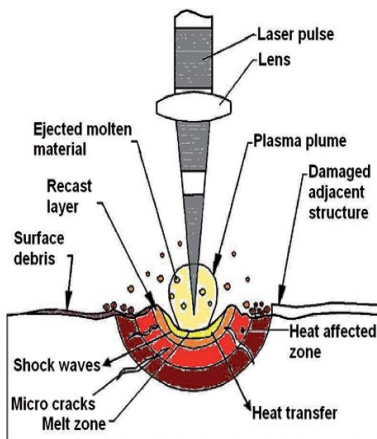
## – Laser ablation

- explosive interaction of the laser beam and material ( $> 10^9 \text{ W/cm}^2$ )
- 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



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## – Advantages

- analysis of any type of materials
- direct analysis of solid samples
- laser beam diameter 4 – 200  $\mu\text{m}$  (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

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# PRINCIPLE OF LASER ABLATION

– Different ablation rate

garnet

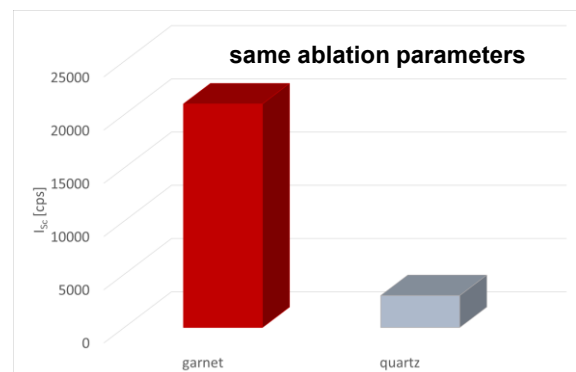


10 ug/g Sc

quartz



10 ug/g Sc

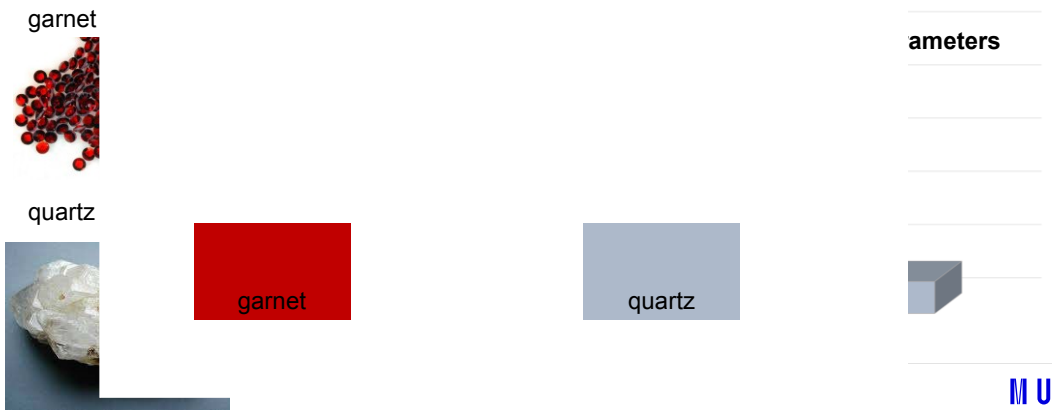


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# PRINCIPLE OF LASER ABLATION

– Differen

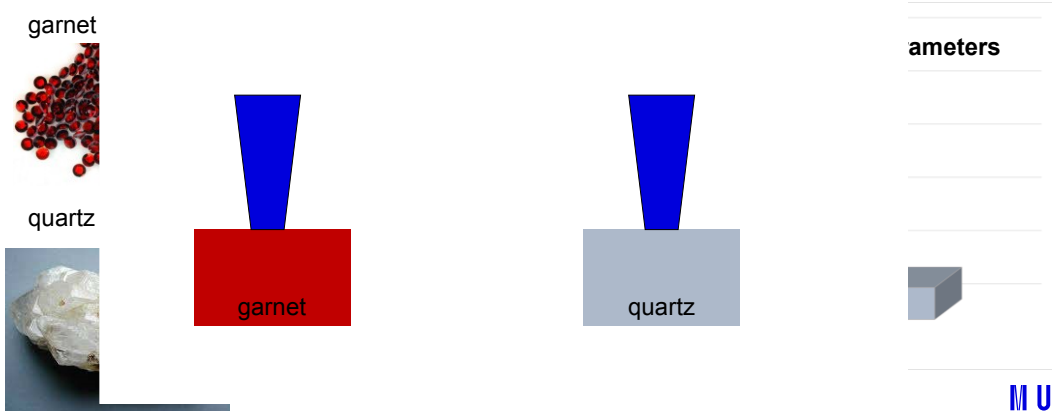


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# PRINCIPLE OF LASER ABLATION

– Differen

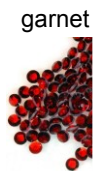


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# PRINCIPLE OF LASER ABLATION

– Differen

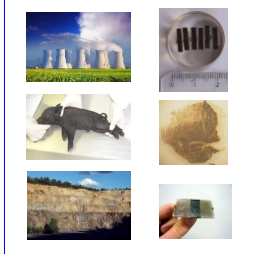


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# LA-ICP-MS IMAGING - SCHEME

sample preparation



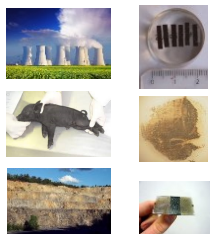
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# LA-ICP-MS IMAGING - SCHEME

sample preparation



measurement

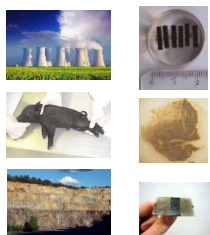


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# LA-ICP-MS IMAGING - SCHEME

sample preparation



measurement

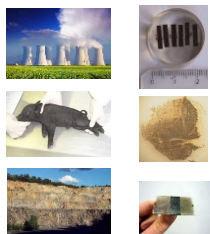


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# LA-ICP-MS IMAGING - SCHEME

sample preparation



measurement

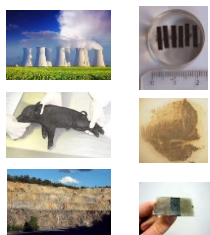


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# LA-ICP-MS IMAGING - SCHEME

sample preparation



measurement

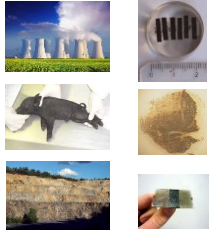


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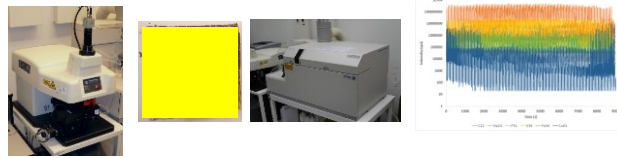
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# LA-ICP-MS IMAGING - SCHEME

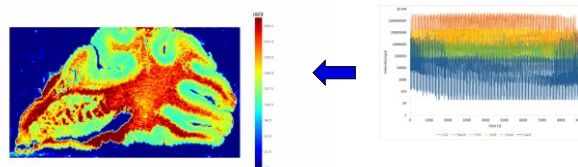
sample preparation



measurement



data processing

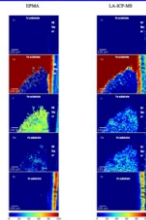


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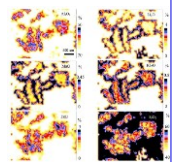
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# IMAGING IN OUR LAB - OVERVIEW

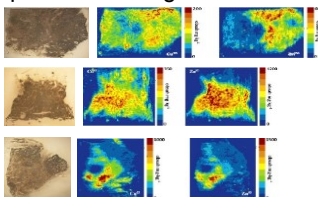
**Task 1:** Steel sample was exposed to molten LiF-NaF salt treatment. Strong corrosion on sample surface occurred. Our task is to obtain content of main constituent of steel and Li and Na in corroded layer.



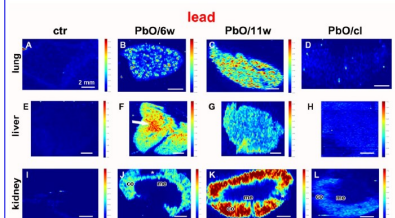
**Task 2:** My colleague geologist: „I have granitoid sample which contains quartz, mica, feldspar and the other minerals. Would it be possible to obtain elemental map of the granite?“



**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?



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## DISTRIBUTION OF CORROSION PRODUCTS

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

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## DISTRIBUTION OF CORROSION PRODUCTS

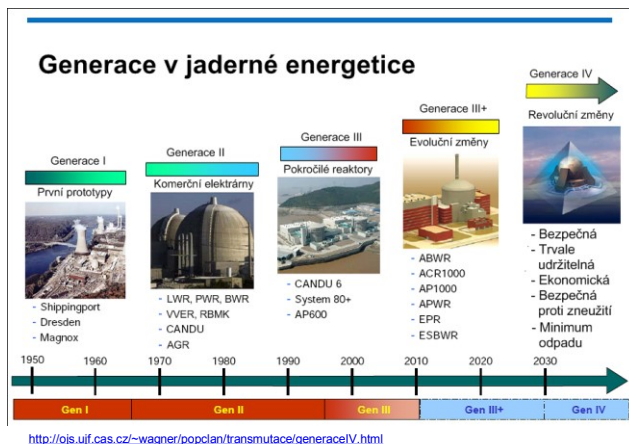
- Steel sample was exposed to molten LiF-NaF salt treatment. Strong corrosion on sample surface occurred. Our task is to obtain content of main constituent of steel and Li and Na in corroded layer.

**Why LiF-NaF mixture?**

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# DISTRIBUTION OF CORROSION PRODUCTS



## 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

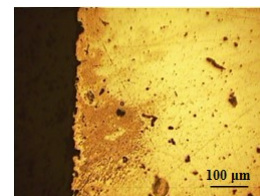
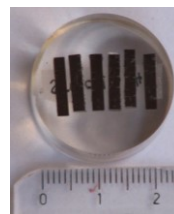
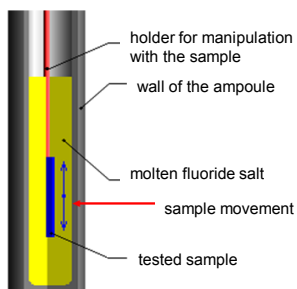
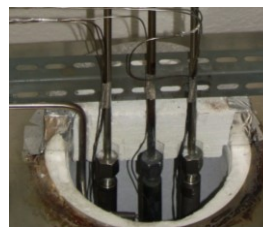
**Molten fluoride salt reactor**

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# DISTRIBUTION OF CORROSION PRODUCTS

- sample preparation (in Energovýzkum, Ltd.)
  - tested materials: Ni-based alloys and pure nickel
  - MFS: LiF-NaF, LiF-NaF-ZrF<sub>4</sub>
  - exposure: 680°C, 100, 300, and 1000 hours



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# DISTRIBUTION OF CORROSION 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)

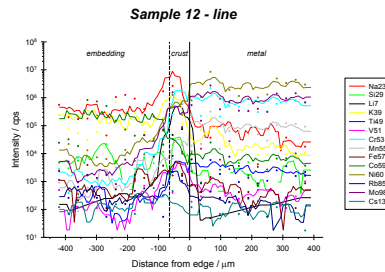
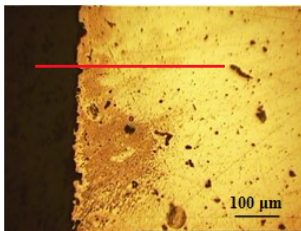
PEPER [www.rsc.org/jaas](http://www.rsc.org/jaas) | Journal of Analytical Atomic Spectrometry

## 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. Vaynskiy,<sup>a</sup> P. Sidorov,<sup>a</sup> J. Machat,<sup>a</sup> V. Otruba,<sup>a</sup> O. Matat,<sup>a</sup> T. Simo,<sup>a</sup> Ch. Larkoczy,<sup>a</sup> D. Günther<sup>a</sup> and V. Kaniuk<sup>a</sup>\*

Received 26th July 2008, accepted 9th March 2009  
First published as an Advance Article on the web 26th March 2009  
DOI: 10.1039/b812566a

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 intermediate cooling circuit. The corrosion of test specimens and structural test specimens made of structural materials was brought about by the action of molten LiF-NaF coolant at 600 °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 eroded walls and eroded specimen surfaces with EPMA, whereas LA-ICP-MS was employed for linear scanning the salt/samples wall boundary. Corrosion released structural material, dissolved in distilled molten salt, was analyzed by ICP-OES after the salt dissolution. The salt activity was proved to induce a surficial modification of a structural material on to the depth of 10 µm, which was associated with the



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# DISTRIBUTION OF CORROSION PRODUCTS

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

JAAS

Dynamic Article Link

Chen *et al.*, *J. Anal. At. Spectrom.*, 2012, **27**, 1321  
[www.rsc.org/jaas](http://www.rsc.org/jaas)

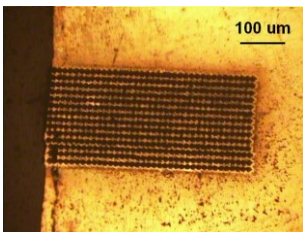
TECHNICAL NOTE

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

T. Vaynskiy,<sup>a</sup> T. Vaynskiy,<sup>a</sup> T. Simo,<sup>a</sup> O. Matat,<sup>a</sup> V. Otruba,<sup>a</sup> P. Mhaska<sup>a</sup> and V. Kaniuk<sup>a</sup>\*

Received 10th February 2012, accepted 2nd April 2012  
DOI: 10.1039/c2ja00075a

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to the study of the interaction of molten LiF-NaF salt with candidate structural materials for a nuclear reactor intermediate cooling circuit. As a working temperature of 600 °C, structural materials of these mixtures are tested and the salt after interaction provides microstructural and composition change of the structural material. The mapping process of structural materials was studied by LA-ICP-MS with the aim of elemental distribution within material on the composition level using the approach based on the determination of elemental ratios against the mass of ligand of the laser plasma by the eroded area. Consequently, LA-ICP-MS signals were measured for structural material corrosion (Na, Ca, Fe, Ni, Mo, Cr, and Mn) and for various components of the cooling medium (Li and Na). The hypothetical fluorine signal was calculated as a sum of Li and the signal. Corrosion products in the eroded cooling medium were determined by ICP-OES after dilution. For the first time, elemental mapping of structural materials (spot by spot) could be used after ATR-FTIR and microanalysis to precisely define the test outcomes.



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# DISTRIBUTION OF CORROSION PRODUCTS

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Chin. Phys. J. Anal. At. Spectrom., 2012, 27, 1321

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TECHNICAL NOTE

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

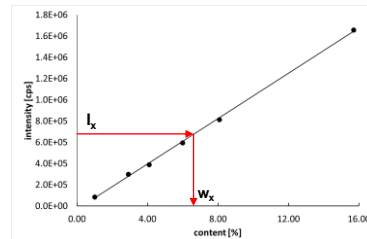
T. Yanahiro<sup>1,2</sup>, T. Watanabe<sup>1,2</sup>, T. Sano<sup>1</sup>, O. Matsui<sup>1</sup>, Y. Otsuka<sup>1</sup>, P. Mikucki<sup>3</sup> and V. Kuncik<sup>3,4</sup>

Received 10 February 2012; accepted 23 April 2012

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to the study of the distribution of nickel (Ni), Ni<sup>2+</sup> ions with variable structural materials for a nuclear reactor corrosion product. The working temperature (400 °C) structural materials of these materials are studied and the each after irradiation process microstructural and composition changes of the corrosion product. The mapping process of the corrosion product was studied by LA-ICP-MS with the use of elemental distribution maps created on the comparative level using the procedure based on the correlation of elemental mapping spectra to the level of signal of the process by the corrosion product. Consequently, LA-ICP-MS spectra were measured for structural material composition (Ni, Cr, W, Mo, Ti, and Nb) and the representative composition of the working product (Cr and Ni). The hypothetical kinetic signal was calculated as a sum of Cr and Ni and the signal comparison between the original working product was distributed by ICP-MS after distribution. Of the three corrosion products, structural material composition (steel, nickel based alloy, AlTiV) was enhanced every part which contains the best corrosion.

- 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	<b>76.8</b>
Cr	7.0	<b>6.9</b>
W	4.5	<b>4.4</b>
Ti	1.7	<b>1.8</b>



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# DISTRIBUTION OF CORROSION PRODUCTS

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Chin. Phys. J. Anal. At. Spectrom., 2012, 27, 1321

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TECHNICAL NOTE

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

T. Yanahiro<sup>1,2</sup>, T. Watanabe<sup>1,2</sup>, T. Sano<sup>1</sup>, O. Matsui<sup>1</sup>, Y. Otsuka<sup>1</sup>, P. Mikucki<sup>3</sup> and V. Kuncik<sup>3,4</sup>

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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	<b>76.8</b>	<b>375</b>
Cr	7.0	<b>6.9</b>	<b>35</b>
W	4.5	<b>4.4</b>	<b>21</b>
Ti	1.7	<b>1.8</b>	<b>10</b>

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# DISTRIBUTION OF CORROSION PRODUCTS

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Choi *et al.* *J. Anal. At. Spectrom.* 2012, **27**, 1321

[www.rsc.org/jaas](http://www.rsc.org/jaas)

TECHNICAL NOTE

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

T. Yasuhiko,<sup>a</sup> T. Watanabe,<sup>a</sup> T. Sano,<sup>a</sup> O. Matsui,<sup>a</sup> Y. Omoto,<sup>a</sup> P. Mikasa<sup>a</sup> and Y. Kaneko<sup>a\*</sup>

*Received 16 February 2012, accepted 23rd April 2012*

DOI: 10.1039/c2ja10075a

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to the study of the distribution of various LA-ICP-MS suitable with suitable structural materials for a nuclear reactor. The working temperature of 4000 °C structural materials of these materials are intended and the each after irradiation process microstructural and composition changes of the reactor surface. The mapping process of structural materials was studied by LA-ICP-MS with the map of elemental distribution were created on the computerized level using the procedure based on the correlation of elemental mapping signal to the map of depth of laser process by the structural materials. Consequently, LA-ICP-MS signals were measured for structural material components (Ni, Cr, W, Mo, Ti, and Nb) and the spatial concentration of the working medium (Li and Na). The hypothetical atomic signal was calculated as a sum of Li and the spatial concentration products in the exposed working medium were distributed by ICP-MS after ablation. Of the three structural materials, structural materials (steel, nickel, and Inconel) were analyzed every year. Table 1 shows the best results.

- 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	<b>76.8</b>	<b>375</b>
Cr	7.0	<b>6.9</b>	<b>35</b>
W	4.5	<b>4.4</b>	<b>21</b>
Ti	1.7	<b>1.8</b>	<b>10</b>

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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<sup>a</sup> National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

<sup>b</sup> Institute of Physics, Prague, Czech Republic

† E-mail: vaynskiy@nist.gov

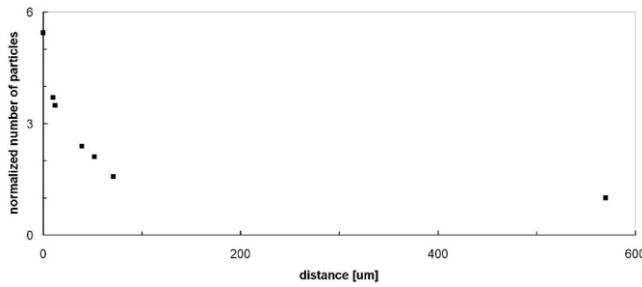
Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to the study of the distribution of various 19 LAE ions with variable structural materials for a nuclear reactor corrosion product. The working temperature of 4000 °C structural materials of these materials are studied and the work after interaction provides microstructural and composition changes of the surface. The mapping process is followed using LA-ICP-MS and the results of elemental distribution were obtained on the composition level using the procedure based on the normalization of particle size to the total amount of particles in the analyzed area. Consequently, LA-ICP-MS signals were measured for structural material composition (Ni, Cr, Fe, Mn, Ti, and Nb) and for various compositions of the working medium (Li and Na). The hypothetical fusion signal was calculated as a sum of Li and the specific Corrosion products in the expected working medium were identified by ICP-MS after ablation. Of the three compared available structural materials (steel, Inconel and Hastelloy) the latter was determined to be the most suitable for the best results.

## – 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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<sup>b</sup> Institute of Physics, Prague, Czech Republic

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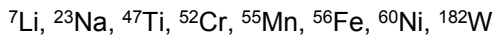
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## – determination of elements in corroded layer

- imaging of corroded layer (laser beam diameter – 4 μm)
- spot by spot

## – quantification – total sum ion normalization (TSIN)

- measuring of all elements from the sample



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T. Vaynskiy,<sup>a</sup> T. Warkhlova,<sup>a</sup> F. Sims,<sup>a</sup> O. Malin,<sup>a</sup> V. Oshin,<sup>a</sup> P. Mikhaik<sup>a</sup> and V. Kuzkiy<sup>a\*</sup>

*Received 16 February 2012, accepted 23rd April 2012*

DOI: 10.1039/c2ja00075a

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to the study of the distribution of various LiF, NaF, and CsF salts with variable structural materials for a nuclear reactor. The working temperature of 400 °C structural materials of these substances are studied and the work after irradiation process microstructural and composition changes of the reactor surface. The mapping process of the reactor was studied by LA-ICP-MS with the help of elemental distribution maps created on the computerized level using the program based on the calculation of particle size range spectra by the method of digital image processing by the computerized data. Consequently, LA-ICP-MS signals were measured for structural materials (Ni, Cu, Fe, W, Mo, Ti, and Nb) and the relative contribution of the working medium (Li and Na). The hypothetical kinetic signal was calculated as a sum of Li and the signal. Comparison between the expected working medium was described by ICP-MS after distribution of the three structural materials structural materials (pure metal, metal based alloy, AlTiTiV) and reduced to the pure metal within the first column.

- determination of elements in corroded layer
  - 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

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

$$I(Ni) = \frac{I(^{60}Ni)}{\text{abundance}(^{60}Ni)} \quad \dots$$

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- determination of elements in corroded layer
  - 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
  - calculation of content from the sum of intensities

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

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

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Received 16 February 2012, accepted 23rd April 2012

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to the study of the distribution of various 15–18 elements with variable structural materials for a nuclear reactor. The working temperature of 4000 °C structural materials of these materials are studied and the effect of temperature on microstructural and composition changes of the reactor surface. The mapping process is discussed and was studied by LA-ICP-MS with the help of elemental distribution were studied on the comparative level using the procedure based on the normalization of particular sample against the mass of signal of reference element (Ni, Cr, Fe, Mo, W, U, and Nb) and the relative contribution of the working medium (U and Nb). The hypothesis of the reactor material was calculated as a sum of U and the signal of the reactor material. The elemental mapping was studied by LA-ICP-MS after distribution of the three corrosion products: structural materials (steel, nickel, nickel based alloy, AlTiTiV) and reduced metal (steel) which contains the best corrosion.

- determination of elements in corroded layer
  - 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
  - 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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  - measuring of all elements from the sample
  - recalculation of measured intensities of isotopes on 100% abundance
  - calculation of content from the sum of intensities
  - 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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Received 18 February 2012, accepted 23rd April 2012

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to the study of the distribution of various LP-AGE rods with various structural materials for a nuclear reactor. The working temperature of 400 °C structural materials of the rods were annealed and the rods after irradiation process microstructural and composition changes of the reactor surface. The resulting corrosion products were analyzed by LA-ICP-MS and the map of elemental distribution were created on the comparative level using the procedure based on the normalization of particular sample against the sum of signal of all elements from the measured area. Consequently, LA-ICP-MS signals were measured for structural materials (Ni, Cr, Fe, Mo, W, U, and Pu) and the average composition of the coating products (Li and Na). The distribution of various elements was calculated on a scale of 1 and the signal of various products in the exposed coating surface were distributed by ICP-MS after detection. Of the three corrosion products, structural materials (pure nickel, nickel based alloy AOTiV) and reduced amount pure nickel exhibit the best resistance.

- determination of elements in corroded layer
  - 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
  - calculation of content from the sum of intensities
  - verified by calibration standard
  - tested on Ni-based alloy

TSIN works!

element	EPMA value [%]	corroded layer [%]
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Mo	21	22
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Fe	1.3	1.5

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- determination of elements in corroded layer

- imaging of corroded layer (laser beam diameter – 4 µm)
- spot by spot

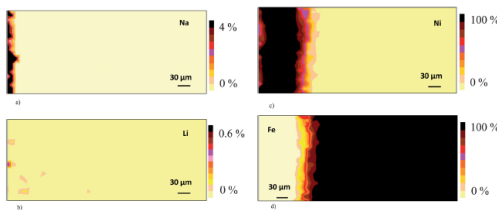


Fig. 2 Elemental distribution of (a) Na, (b) Li, (c) Ni, and (d) Fe on the section of the nickel-coated specimen exposed to molten fluoride salt mixture for 1000 h at 600 °C.

the most resistant: pure Ni

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

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Corrosion of nickel-based structural materials for nuclear reactors by molten fluoride salt: From bulk content of corrosion products to elemental imaging of corrosion changes

T. Vacholík<sup>a,\*</sup>, V. Dillingová<sup>a,b</sup>, B. Štádl<sup>a</sup>, T. Šimů<sup>a</sup>, O. Matul<sup>a</sup>, T. Vacholík<sup>a,b,c</sup>, Y. Kankyo<sup>d</sup>

<sup>a</sup>University of West Bohemia, Department of Chemistry, Faculty of Science, Univerzitní ulice, 301 00 Pilsen, Czech Republic

Cite this J. Anal. At. Spectrom., 2012, 27, 1321

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T. Vacholík<sup>a,\*</sup>, V. Dillingová<sup>a,b</sup>, Y. Šimů<sup>a</sup>, O. Matul<sup>a</sup>, T. Šimů<sup>a</sup>, P. Mikšanek<sup>a</sup> and Y. Kankyo<sup>d</sup>

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to the study of the distribution of nickel, LiF, NaF and various corrosion products on a nuclear reactor component. The resulting corrosion products were analyzed by LA-ICP-MS and the maps of elemental distribution were created as an independent tool using the principle based on the neutralization of particles (except negative ions) in the case of all elements present in the examined area. Consequently, LA-ICP-MS signals were measured for individual elements (Ni, Cu, Fe, W, Mo, U, and Mn) and for various combinations of the cooling medium (Li and Na). The elemental distribution signal was calculated as a sum of Li and Na signals. Corrosion products in the exposed coating material were determined by ICP-OES after dissolution. Of the three examined corrosion products, nickel-based alloy (NiCrFe) and nickel-based iron-pump nickel (NiFe) were the most common.

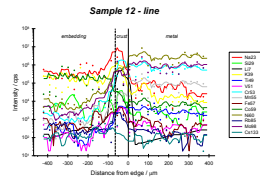
†www.rsc.org/jaas | Journal of Analytical Atomic Spectrometry

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<sup>†</sup>

T. Vacholík<sup>a</sup>, P. Sádovský<sup>a</sup>, J. Macháček<sup>a</sup>, V. Otáhal<sup>a</sup>, O. Matul<sup>a</sup>, T. Šimů<sup>a</sup>, Ch. Lathauze<sup>b</sup>, D. Günther<sup>c</sup> and Y. Kankyo<sup>d</sup>

Received 29th July 2008, Accepted 16th March 2009  
First published on the internet 26th March 2009  
DOI: 10.1039/B815007A

Elemental analysis by means of inductively coupled plasma atomic emission spectrometry (ICP-AES) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) were applied to study the distribution of nickel, LiF, NaF and various corrosion products on a nuclear reactor component. The corrosion of test specimens and treated test specimens made of structural materials was brought about by the action of molten LiF–NaF coolant at 600 °C and its content and character were examined in dependence on the time of exposure. The material corrosion changes were studied by mapping the surface of samples with and without specimen surface with EPMA, whereas LA-ICP-MS was employed for faster scanning the salt-impregnated wall boundary. Corrosion-related structural materials, dissolved in distilled water, were analyzed by ICP-OES after the salt dissolution. The salt activity was proved to induce a significant modification of a corrosion product on the surface of the NiCrFe, which was measured with the



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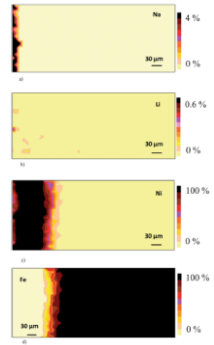


Fig. 2 Elemental distribution of (a) Na, (b) Li, (c) Ni, and (d) Fe on the surface of the nickel-coated iron specimen exposed to molten fluoride salt mixture for 1000 h at 600 °C.

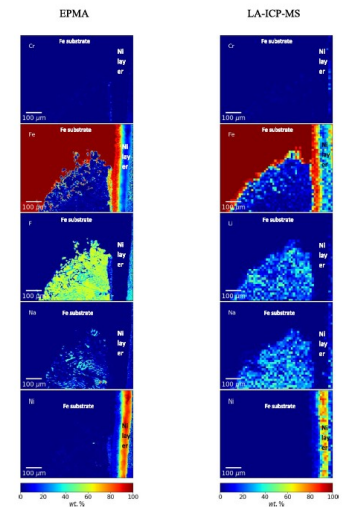


Fig. 3 Elemental maps of Cu, Fe, Li, Na and Ni obtained by LA-ICP-MS and EPMA analysis of nickel-coated steel specimen after 350-hour exposure to LiF–NaF at 600 °C.

# DISTRIBUTION OF CORROSION PRODUCTS

- 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?“

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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?“

My answer: „Yes, no problem.“

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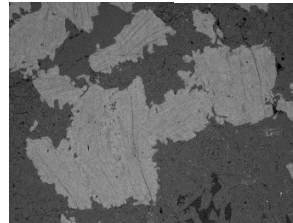
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# IMAGING IN GEOLOGY

Quantification of elemental mapping of heterogeneous geological sample by laser ablation inductively coupled plasma mass spectrometry  
 T. Vaculová<sup>a,b,\*</sup>, K. Breiter<sup>c</sup>, Z. Korbelová<sup>d</sup>, N. Venčová<sup>d</sup>, K. Tomková<sup>d</sup>, Š. Jonášová<sup>e</sup>, V. Kanický<sup>a,b</sup>

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<sup>b</sup> CEITEC Microanal. Laboratory, 60200 Brno, Czech Republic  
<sup>c</sup> Institute of Geology, The Czech Academy of Sciences, 460 01, Písek, Czech Republic  
<sup>d</sup> Institute of Analytical Chemistry, The Czech Academy of Sciences, 250 68, Písek, Czech Republic  
<sup>e</sup> Institute of Archaeology, The Czech Academy of Sciences, 118 01, Prague, Czech Republic

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

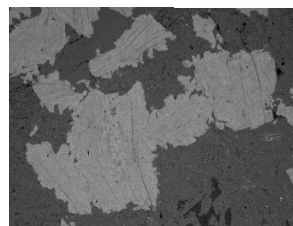


# IMAGING IN GEOLOGY

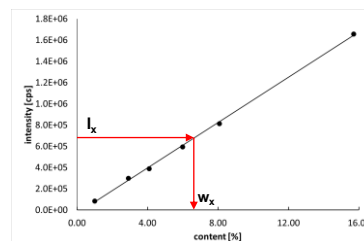
Quantification of elemental mapping of heterogeneous geological sample by laser ablation inductively coupled plasma mass spectrometry  
 T. Vaculová<sup>a,b,\*</sup>, K. Breiter<sup>c</sup>, Z. Korbelová<sup>d</sup>, N. Venčová<sup>d</sup>, K. Tomková<sup>d</sup>, Š. Jonášová<sup>e</sup>, V. Kanický<sup>a,b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Masaryk University, 60200 Brno, Czech Republic  
<sup>b</sup> CEITEC Microanal. Laboratory, 60200 Brno, Czech Republic  
<sup>c</sup> Institute of Geology, The Czech Academy of Sciences, 460 01, Písek, Czech Republic  
<sup>d</sup> Institute of Analytical Chemistry, The Czech Academy of Sciences, 250 68, Písek, Czech Republic  
<sup>e</sup> Institute of Archaeology, The Czech Academy of Sciences, 118 01, Prague, Czech Republic

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



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

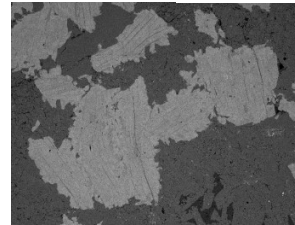


# IMAGING IN GEOLOGY

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 T. Vaculovc<sup>a,b,\*</sup>, K. Breiter<sup>c</sup>, Z. Korbelovc<sup>d</sup>, N. Venkovc<sup>d</sup>, K. Tomkovc<sup>d</sup>, S. Jonsovc<sup>d</sup>, V. Kanicky<sup>a,b</sup>

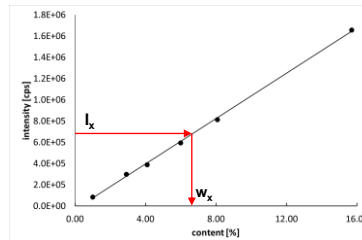
<sup>a</sup> Department of Chemistry, Faculty of Science, Masaryk University, 60200 Brno, Czech Republic  
<sup>b</sup> CEITEC, Central Laboratory, Masaryk University, 60200 Brno, Czech Republic  
<sup>c</sup> Institute of Geology, The Czech Academy of Sciences, 460 01 Luc, Czech Republic  
<sup>d</sup> Institute of Petrology and Geochemistry, The Czech Academy of Sciences, 60200 Brno, Czech Republic

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



$w(\text{SiO}_2)_{\text{EPMA}} = 48.1 \%$

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



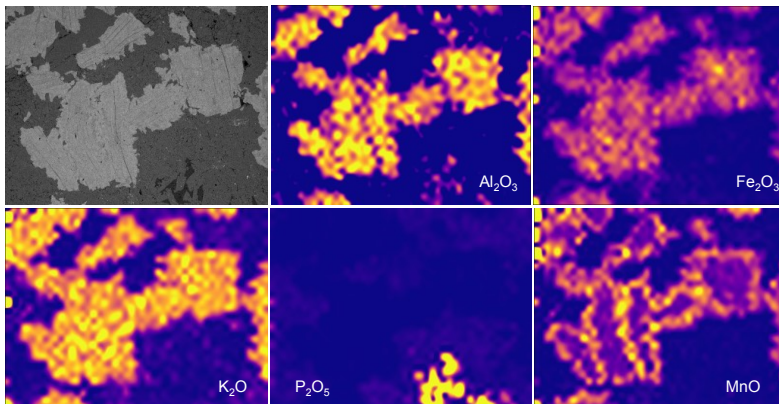
47

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# IMAGING IN GEOLOGY

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 T. Vaculovc<sup>a,b,\*</sup>, K. Breiter<sup>c</sup>, Z. Korbelovc<sup>d</sup>, N. Venkovc<sup>d</sup>, K. Tomkovc<sup>d</sup>, S. Jonsovc<sup>d</sup>, V. Kanicky<sup>a,b</sup>

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<sup>c</sup> Institute of Geology, The Czech Academy of Sciences, 460 01 Luc, Czech Republic  
<sup>d</sup> Institute of Petrology and Geochemistry, The Czech Academy of Sciences, 60200 Brno, Czech Republic



**SiO<sub>2</sub>**  
48.1 %

48

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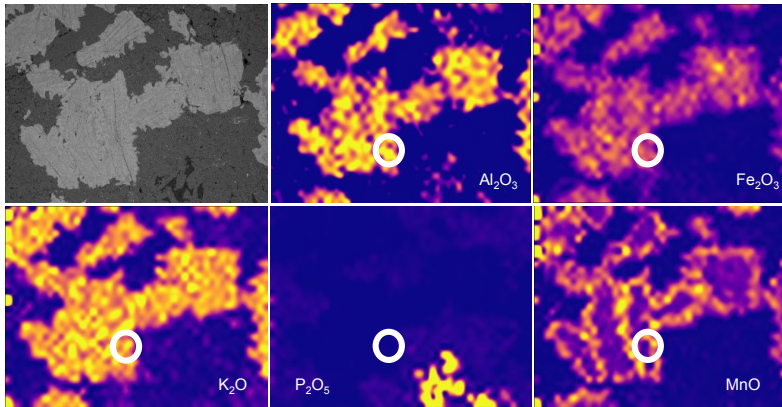


# IMAGING IN GEOLOGY

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T. Vaculová<sup>a,b,c</sup>, K. Breiter<sup>c</sup>, Z. Korbelová<sup>c</sup>, N. Venclová<sup>d</sup>, R. Tomková<sup>d</sup>, S. Jonšová<sup>e</sup>, V. Kanický<sup>a,b</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science, Masaryk University, Brno 602 00, Czech Republic  
<sup>b</sup>CEITEC Central Laboratory, Brno 602 00, Czech Republic  
<sup>c</sup>Institute of Geology, The Czech Academy of Sciences, Brno 602 00, Czech Republic  
<sup>d</sup>Institute of Petrology, The Czech Academy of Sciences, Brno 602 00, Czech Republic  
<sup>e</sup>Institute of Archaeology, The Czech Academy of Sciences, Brno 602 00, Czech Republic



Li <sub>2</sub> O:	1.1 %
Al <sub>2</sub> O <sub>3</sub> :	54.6 %
K <sub>2</sub> O:	11.8 %
Na <sub>2</sub> O:	0.7 %
P <sub>2</sub> O <sub>5</sub> :	0.5 %
Fe <sub>2</sub> O <sub>3</sub> :	4.3 %
SiO <sub>2</sub> :	48.1 %
Σ	122.1 %

49

SiO<sub>2</sub>  
48.1 %

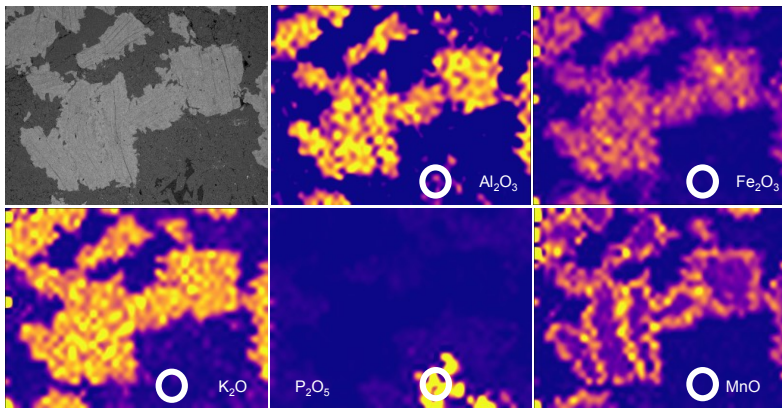
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# IMAGING IN GEOLOGY

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T. Vaculová<sup>a,b,c</sup>, K. Breiter<sup>c</sup>, Z. Korbelová<sup>c</sup>, N. Venclová<sup>d</sup>, R. Tomková<sup>d</sup>, S. Jonšová<sup>e</sup>, V. Kanický<sup>a,b</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science, Masaryk University, Brno 602 00, Czech Republic  
<sup>b</sup>CEITEC Central Laboratory, Brno 602 00, Czech Republic  
<sup>c</sup>Institute of Geology, The Czech Academy of Sciences, Brno 602 00, Czech Republic  
<sup>d</sup>Institute of Petrology, The Czech Academy of Sciences, Brno 602 00, Czech Republic  
<sup>e</sup>Institute of Archaeology, The Czech Academy of Sciences, Brno 602 00, Czech Republic



Li <sub>2</sub> O:	79.3 %
Al <sub>2</sub> O <sub>3</sub> :	64.6 %
K <sub>2</sub> O:	0.7 %
Na <sub>2</sub> O:	8.5 %
P <sub>2</sub> O <sub>5</sub> :	39.7 %
SiO <sub>2</sub> :	48.1 %
Σ	240.9 %

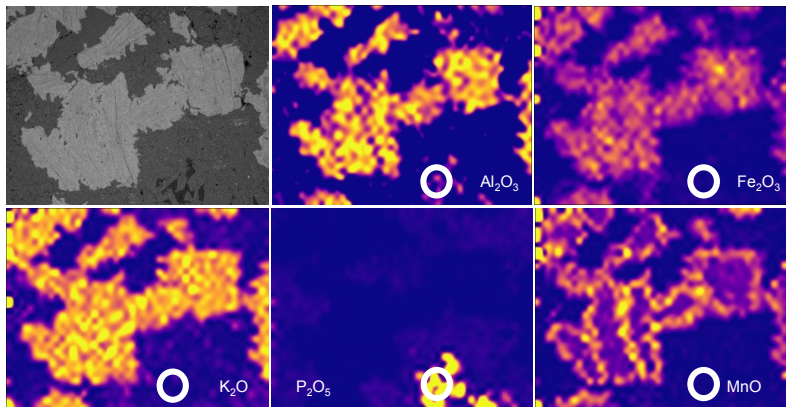
50

SiO<sub>2</sub>  
48.1 %

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# IMAGING IN GEOLOGY

Quantification of elemental mapping of heterogeneous geological sample by laser ablation inductively coupled plasma mass spectrometry  
 T. Vaculová<sup>a,b,c</sup>, K. Breiter<sup>c</sup>, Z. Korbelová<sup>c</sup>, N. Venclová<sup>d</sup>, K. Tomková<sup>e</sup>, S. Jonášová<sup>f</sup>, V. Kanický<sup>a,b</sup>



Li <sub>2</sub> O:	79.3 %
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Na <sub>2</sub> O:	8.5 %
P <sub>2</sub> O <sub>5</sub> :	39.7 %
SiO <sub>2</sub>	48.1 %
Σ	240.9 %

SiO<sub>2</sub>  
48.1 %

51

What is wrong?

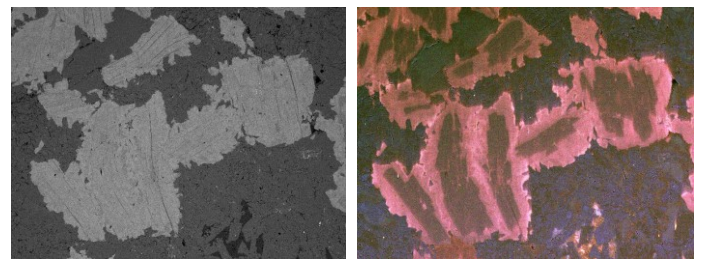
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– more detailed view on the sample:

- mica core: 45.8 % SiO<sub>2</sub>
- mica rim: 50.5 % SiO<sub>2</sub>
- apatite: < 1 % SiO<sub>2</sub>



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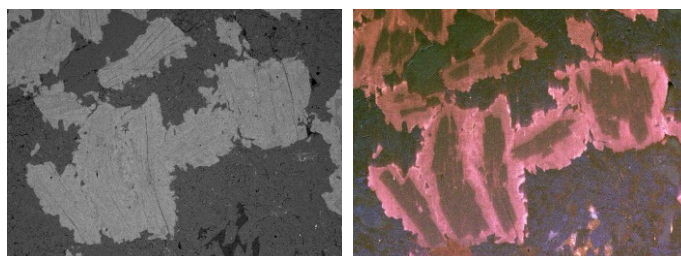
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<sup>a</sup> Department of Geology, Faculty of Science, Masaryk University, 60200 Brno, Czech Republic  
<sup>b</sup> IRI, Institute of Geology, Academy of Sciences of the Czech Republic, 478 01, Písek, Czech Republic  
<sup>c</sup> Institute of Geology, Masaryk University of Brno, 60200, Czech Republic  
<sup>d</sup> Institute of Geology, Masaryk University of Brno, 60200, Czech Republic  
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- more detailed view on the sample:

mica core:	45.8 % SiO <sub>2</sub>
mica rim:	50.5 % SiO <sub>2</sub>
apatite:	< 1 % SiO <sub>2</sub>



internal standardization is not applicable!

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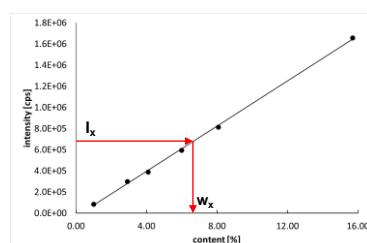
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<sup>i</sup> Institute of Geology, Masaryk University of Brno, 60200, Czech Republic

- 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



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# IMAGING IN GEOLOGY

Microchemical Journal 110 (2017) 200–207  
 Contents lists available at ScienceDirect  
 Microchemical Journal  
 journal homepage: www.elsevier.com/locate/microj

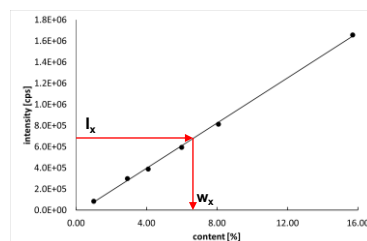
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<sup>a</sup> Department of Chemistry, Faculty of Science, Masaryk University, 60200 Brno, Czech Republic  
<sup>b</sup> IRIE, Masaryk University, 60200 Brno, Czech Republic  
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- external calibration with sum oxide normalization (SON)
  - content of elements to recalculate to oxide form

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



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Does it work?

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# IMAGING IN GEOLOGY

Microchemical Journal 110 (2017) 200–207  
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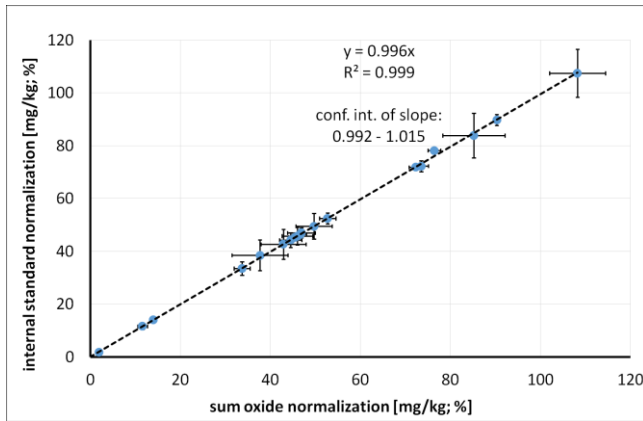
- analysis of homogenous sample with easy matrix (CRM)
- analysis of real sample (archaeological glass)
- analysis of heterogeneous real sample (mica from Argemela)

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# IMAGING IN GEOLOGY

– glass standard NIST 612

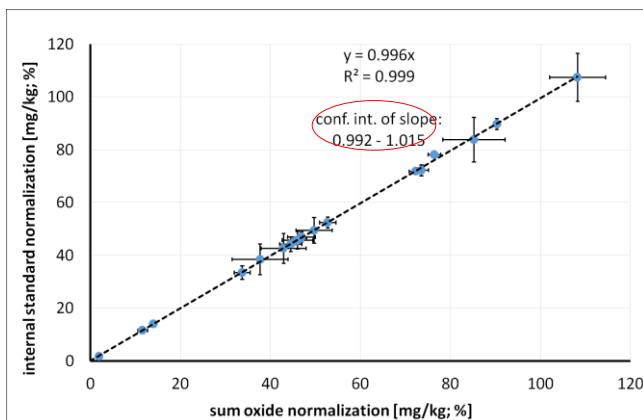


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# IMAGING IN GEOLOGY

– glass standard NIST 612



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Youden graph:

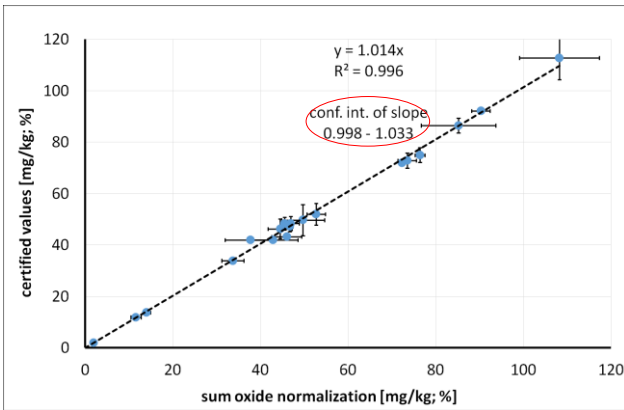
if: **slope = 1, intercept = 0**

then: **methods are same**

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# IMAGING IN GEOLOGY

– glass standard NIST 612

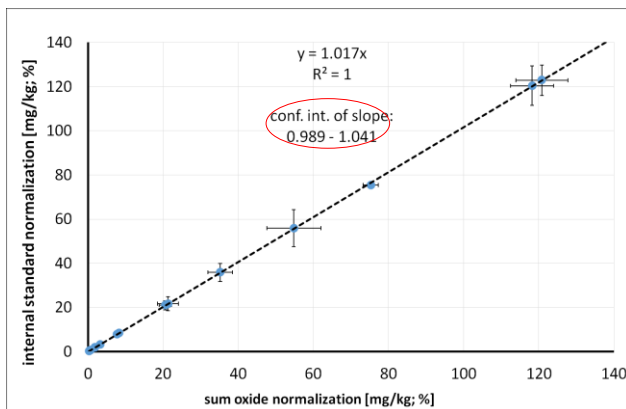


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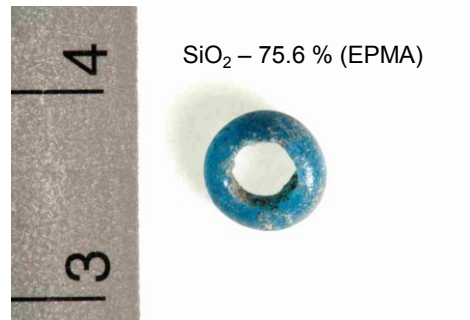
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# IMAGING IN GEOLOGY

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



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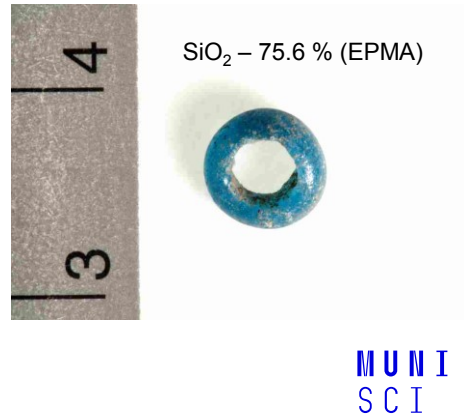
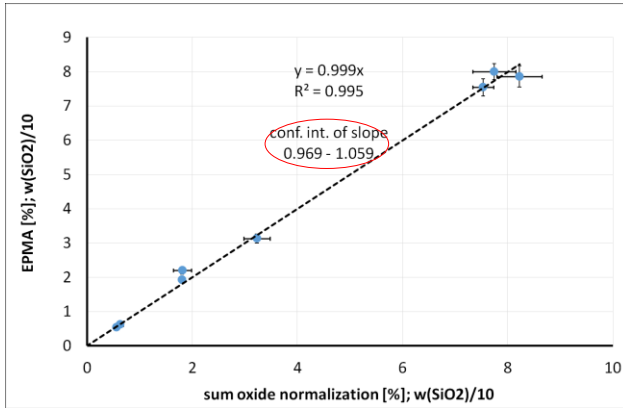


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<sup>a</sup>Department of Chemistry, Faculty of Science, Masaryk University, 60200 Brno, Czech Republic  
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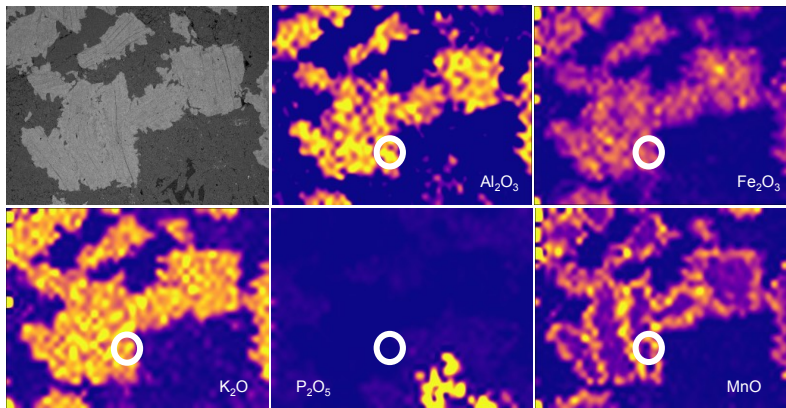
– ancient glass – blue beads; Late Bronze Age (1300 A.C.); Holubice (Czech Rep.);



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# IMAGING IN GEOLOGY

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<sup>b</sup>CEITEC, Central Laboratory, Brno University of Technology, 60200 Brno, Czech Republic  
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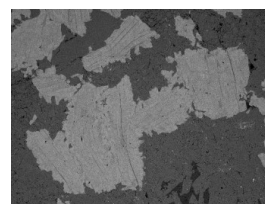
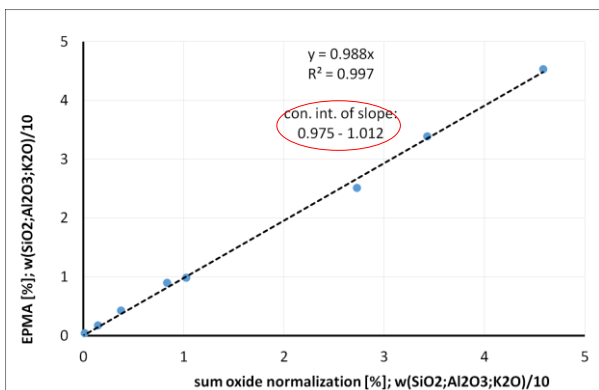
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# IMAGING IN GEOLOGY

Quantification of elemental mapping of heterogeneous geological sample by laser ablation inductively coupled plasma mass spectrometry  
 T. Vachoušek<sup>a,b</sup>, K. Breiter<sup>c</sup>, Z. Korbelová<sup>d</sup>, N. Venclová<sup>e</sup>, J. K. Tomšková<sup>f</sup>, S. Jurešková<sup>g</sup>, V. Kanišky<sup>h,i</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Masaryk University Brno, 60200 Brno, Czech Republic  
<sup>b</sup> IAGLR, Institute of Geology, Brno, 60200, Czech Republic  
<sup>c</sup> Institute of Geology, Masaryk University of Brno, 60200, Czech Republic  
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– mica sample from Argamela



Youden graph:

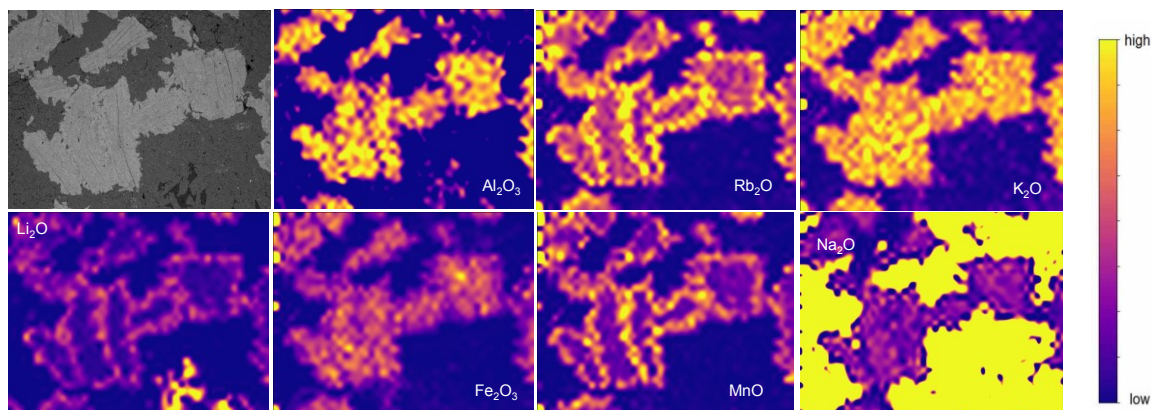
if: **slope = 1, intercept = 0**

then: **methods are same**

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# IMAGING IN GEOLOGY



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Li<sub>2</sub>O: 0 – 4%

Al<sub>2</sub>O<sub>3</sub>: 20 – 50 %

Fe<sub>2</sub>O<sub>3</sub>: 0 – 3%

Rb<sub>2</sub>O: 0 – 0.8 %

MnO: 0 – 0.5 %

K<sub>2</sub>O: 0 – 10 %

Na<sub>2</sub>O: 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  $\mu\text{m}$ )
  - different stages of spontaneous regression
  - placed on glass slide
- laser ablation parameters
  - laser spot diameter – 100  $\mu\text{m}$
  - scan speed – 200  $\mu\text{m}$



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# SPONTANEOUS REGRESSION

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

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# SPONTANEOUS REGRESSION

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

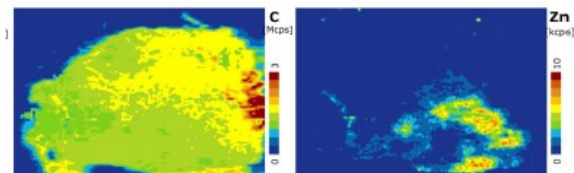
## SCIENTIFIC REPORTS

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

Received: 28 November 2018  
Accepted: 02 December 2018  
Published: 20 January 2019

Jiri Annyš<sup>1</sup>, Lenka Vydrovcová<sup>2</sup>, Tomas Yacubovics<sup>3,4</sup>, Michala Trnkova<sup>5,6</sup>, Viktor Kuncik<sup>5,6</sup>, Radek Hana<sup>7</sup>, Vladimir Horak<sup>8</sup>, Olga Stepanova<sup>9,10</sup>, Zdenek Heger<sup>11</sup> & Radek Adam<sup>12</sup>

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



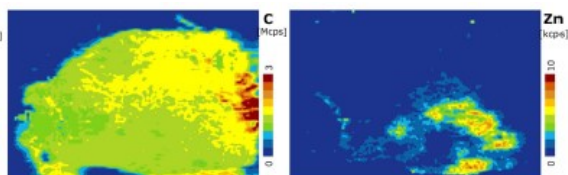
71

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# SPONTANEOUS REGRESSION

- LA-ICP-MS parameters
  - laser beam spot – 100  $\mu\text{m}$
  - scan speed – 200  $\mu\text{m/s}$
  - laser beam fluence – 2  $\text{J/cm}^2$
- Suppression of different ablation rate
  - recommended normalization on signal  $^{12}\text{C}$
  - C is not homogeneous in sample

How to compensate the different ablation rate?



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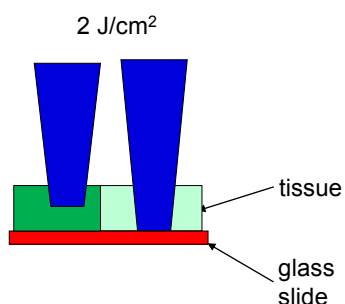
Jiří Anýž<sup>1</sup>, Lenka Vydrovcová<sup>1</sup>, Tamas Yacubovicz<sup>1,2</sup>, Michaela Trifunovic<sup>1,3</sup>, Viktor Kuncik<sup>1,4</sup>, Rigo Hauer<sup>1</sup>, Veronika Horak<sup>1</sup>, Olga Stepanova<sup>1,2</sup>, Zuzana Heger<sup>1,4</sup> & Rigo Haderik<sup>1,4</sup>

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# SPONTANEOUS REGRESSION



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# SPONTANEOUS REGRESSION

www.nature.com/scientificreports

## SCIENTIFIC REPORTS

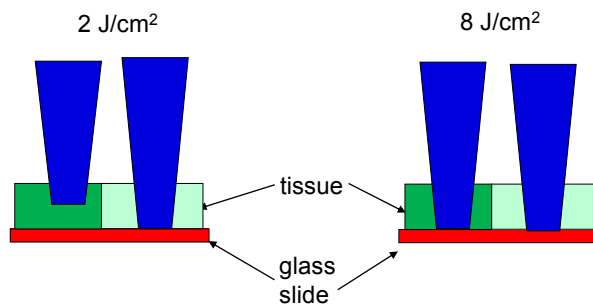
**OPEN** Spatial mapping of metals in tissue-sections using combination of mass-spectrometry and histology through image registration

Received: 28 November 2018  
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 Published: 20 January 2019

Jit Aray<sup>1</sup>, Lenka Vydrovcova<sup>1\*</sup>, Tomas Yacubovics<sup>1,2</sup>, Michaela Terentova<sup>1,3</sup>, Viktor Kuncik<sup>1,4</sup>, Rigo Hauer<sup>1</sup>, Veronika Horak<sup>1</sup>, Olga Stepanova<sup>1,2</sup>, Zdenek Heger<sup>1,4</sup> & Rigoch Adam<sup>1,5</sup>

\*Correspondence: lenka.vydrovcova@univie.ac.at

Full list of author information is available at the end of the article



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# SPONTANEOUS REGRESSION

www.nature.com/scientificreports

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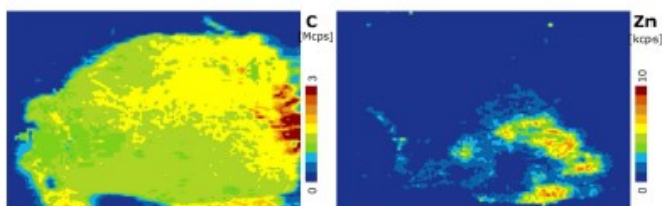
Jit Aray<sup>1</sup>, Lenka Vydrovcova<sup>1\*</sup>, Tomas Yacubovics<sup>1,2</sup>, Michaela Terentova<sup>1,3</sup>, Viktor Kuncik<sup>1,4</sup>, Rigo Hauer<sup>1</sup>, Veronika Horak<sup>1</sup>, Olga Stepanova<sup>1,2</sup>, Zdenek Heger<sup>1,4</sup> & Rigoch Adam<sup>1,5</sup>

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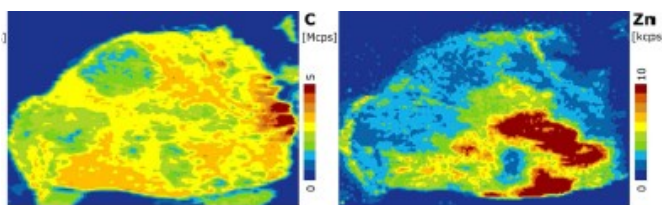
Full list of author information is available at the end of the article

– Higher laser beam fluence

– 2 J/cm<sup>2</sup>



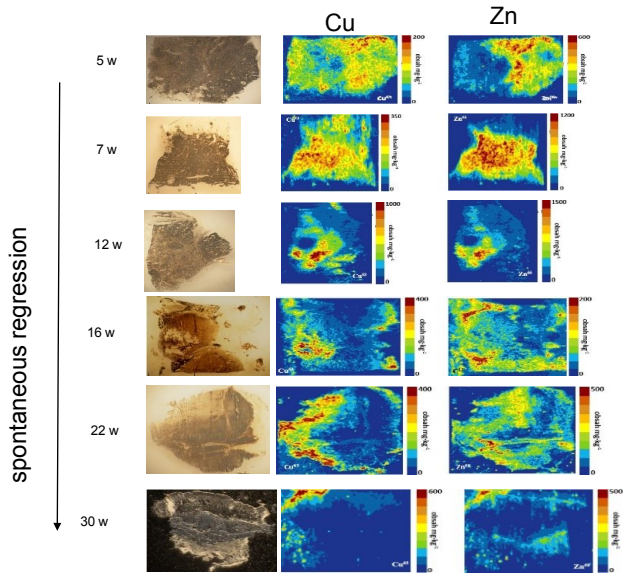
– 8 J/cm<sup>2</sup>



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# SPONTANEOUS REGRESSION



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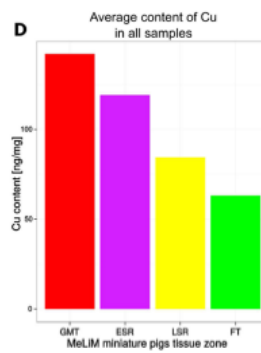
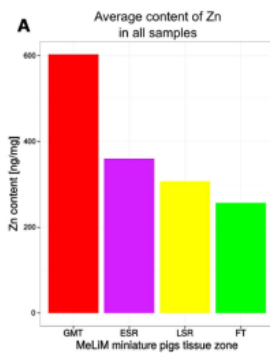
Jit Aray<sup>1</sup>, Lenka Vydrovcikova<sup>1</sup>, Tomas Yacubovics<sup>1,2</sup>, Michaela Trifunova<sup>1,3</sup>, Viktor Kuncik<sup>1,4</sup>, Rigo Hauer<sup>1</sup>, Vladimira Horak<sup>1</sup>, Olga Stepankova<sup>1,2</sup>, Zdenek Heger<sup>1,4</sup> & Rigoch Adamc<sup>1,5</sup>

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# SPONTANEOUS REGRESSION

– the distribution and content of Cu and Zn changes significantly



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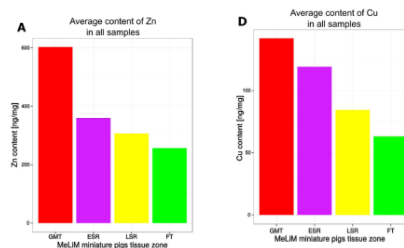
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# SPONTANEOUS REGRESSION

- the distribution and content of Cu and Zn changes significantly

Can we determine specific protein?



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Jiří Aroný<sup>1</sup>, Lenka Kyřanová<sup>1</sup>, Tereza Tachoutová<sup>1,2</sup>, Michaela Trnčáková<sup>1,2</sup>, Viktor Kuncický<sup>1,3</sup>, Petr Hájek<sup>1,2</sup>, Veronika Horová<sup>1</sup>, Olga Stepanková<sup>1,2</sup>, Zdeněk Proházka<sup>1,2</sup> & Jiří Janáček<sup>1,2</sup>

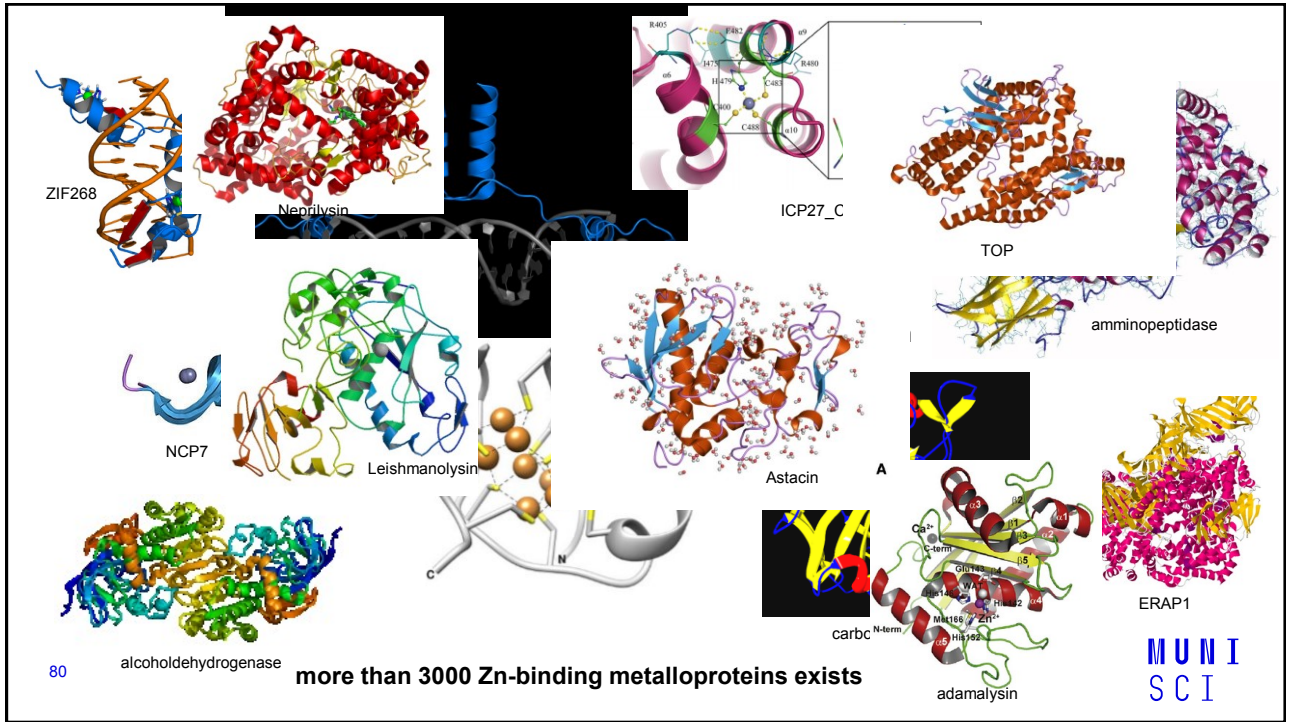
We describe a new procedure for the parallel mapping of selected metals in histologically characterized tissue samples. Mapping is achieved via image registration of digital data obtained from two

# 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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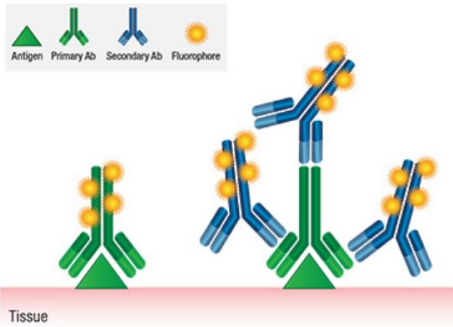


Is there some possibility how to determine specific proteins?



# ICP-MS AND PROTEINS

## ➤ immunochemistry



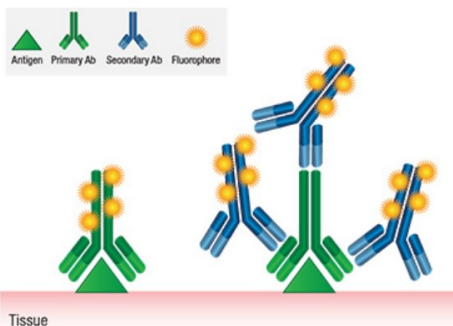
<https://www.cellsignal.com/contents/resource/s-applications/fluorescent-multiplex-immunohistochemistry/fluorescence-mihc>

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# ICP-MS AND PROTEINS

## ➤ immunochemistry



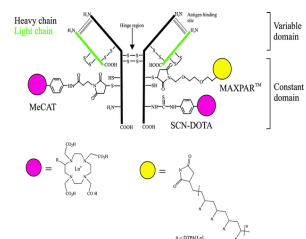
<https://www.cellsignal.com/contents/resource/s-applications/fluorescent-multiplex-immunohistochemistry/fluorescence-mihc>

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## ➤ REE and chelates

MeCAT – 1 REE on 1 chelate

SCN-DOTA – 4 REE on 1 chelate

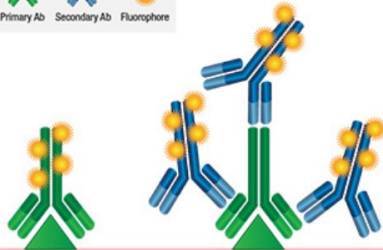


Waentig L., et al., *JAAS*, **2012**, *27*, 1311-1320

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# ICP-MS AND PROTEINS

## immunochemistry



Tissue

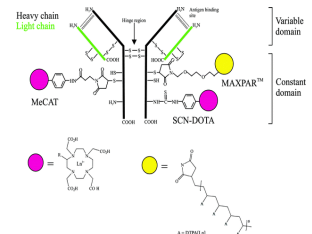
<https://www.cellsignal.com/contents/resource-s-applications/fluorescent-multiplex-immunohistochemistry/fluorescence-mihc>

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## REE and chelates

MeCAT – 1 REE on 1 chelate

SCN-DOTA – 4 REE on 1 chelate



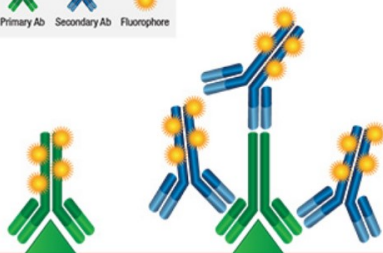
Waentig L., et al., *JAAS*, **2012**, *27*, 1311-1320

Could we amplify the signal?

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# ICP-MS AND PROTEINS

## immunochemistry



Tissue

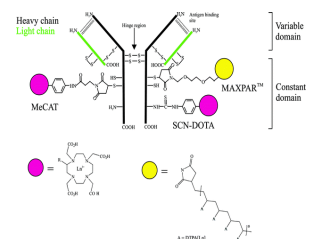
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## REE and chelates

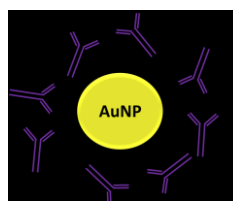
MeCAT – 1 REE on 1 chelate

SCN-DOTA – 4 REE on 1 chelate



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

## nanoparticles



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

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# ICP-MS AND PROTEINS

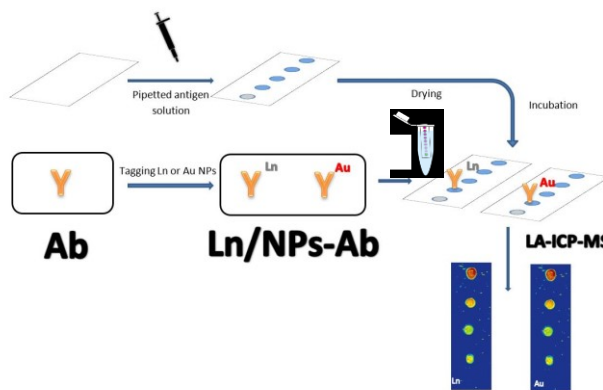
Gold nanoparticles as labels for immunochemical analysis using laser ablation inductively coupled plasma mass spectrometry

Michaela Třifonová<sup>1,2</sup>, Marcela Vřtovská<sup>2</sup>, Lucie Pompelano Vanicková<sup>1,4</sup>, Viktor Kanický<sup>1,3</sup>, Vojtěch Adam<sup>1,4</sup>, Lena Ašcher<sup>1</sup>, Norbert Jakubowski<sup>1</sup>, Marketa Vaculovicová<sup>1,4</sup>, Tomas Vaculovic<sup>1,4</sup>

Received: 5 June 2018 / Revised: 20 July 2018 / Accepted: 27 July 2018 / Published online: 14 August 2018  
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## – scheme of the labelling of Ab

- Au NPs – 10 and 60 nm
- MeCAT – with Ho
- model analyte: protein IgG



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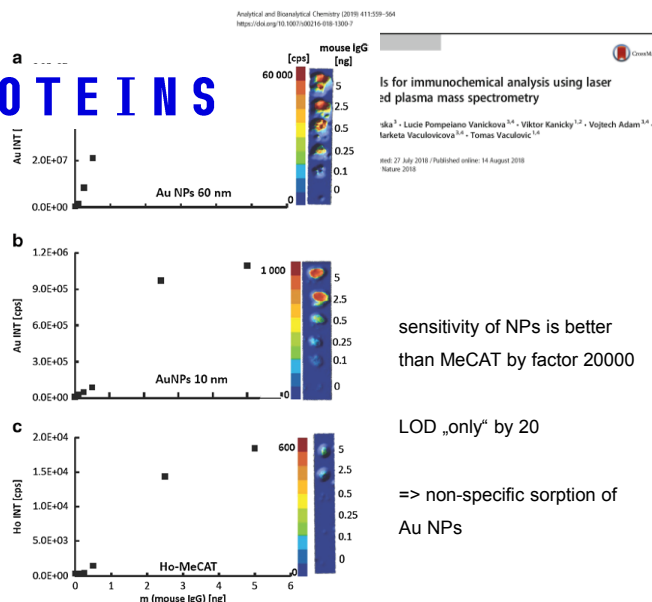
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# ICP-MS AND PROTEINS

## – determination of IgG

- antiIgG-AuNPs vs. antiIgG-MeCAT(Ho)

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



sensitivity of NPs is better than MeCAT by factor 20000

LOD „only“ by 20

=> non-specific sorption of Au NPs

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

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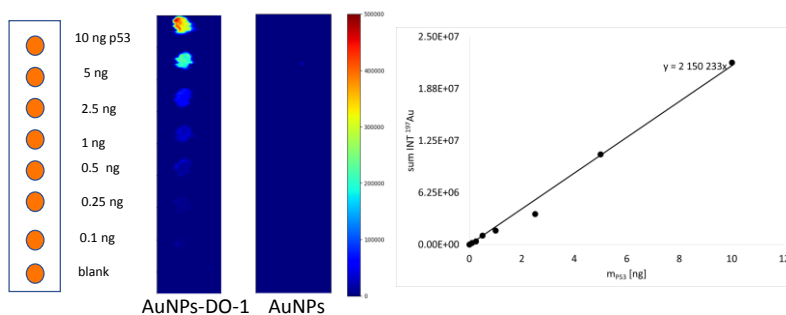
# ICP-MS AND PROTEINS



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

– DO1-Au NPs, negative control Au NPs

– standard of p53



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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

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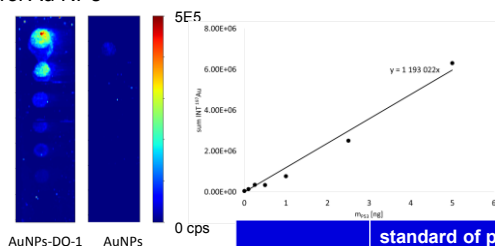
# ICP-MS AND PROTEINS



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

– DO1-Au NPs, negative control Au NPs

– protein ladder  
spiked with p53



	standard of p53	spiked protein ladder
sensitivity [cps g <sup>-1</sup> ]	$2.2 \times 10^6$	$1.2 \times 10^6$
LOD p53 [pg]	<b>2</b>	<b>13</b>

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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

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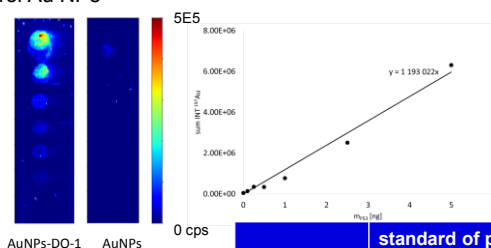
# ICP-MS AND PROTEINS



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

– DO1-Au NPs, negative control Au NPs

– protein ladder spiked with p53



high specificity of the labelled DO-1

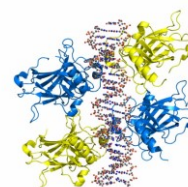
	standard of p53	spiked protein ladder
sensitivity [cps g µg <sup>-1</sup> ]	2.2 × 10 <sup>6</sup>	1.2 × 10 <sup>6</sup>
LOD p53 [pg]	2	13

90

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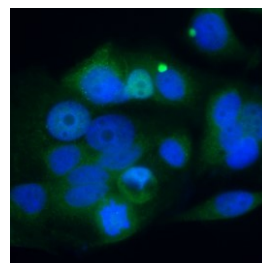
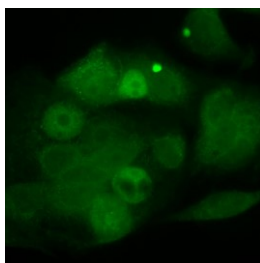
# ICP-MS AND PROTEINS



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

– DO1-Au NPs, negative control Au NPs

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



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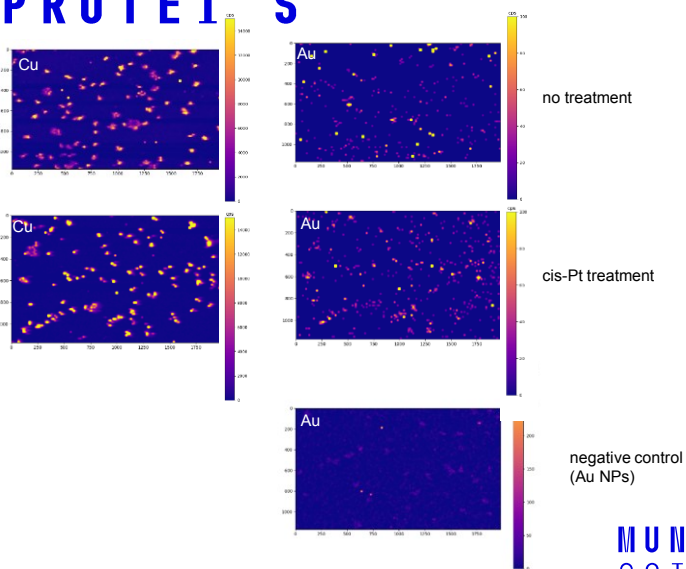
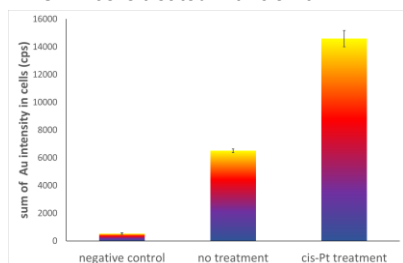
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# ICP-MS AND PROTEINS

## – determination of p53

- DO1-Au NPs, negative control Au NPs
- MCF-7 cells (breast cancer)
- MCF-7 cells treated with cis Pt



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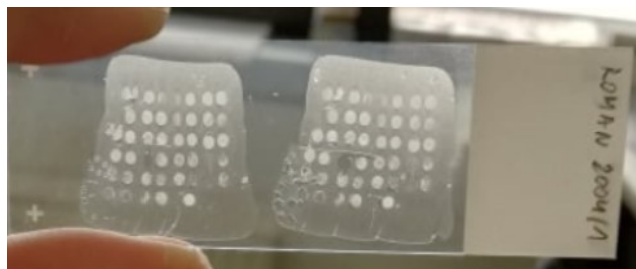
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# ICP-MS AND PROTEINS



## – determination of p53 – suppressor 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)



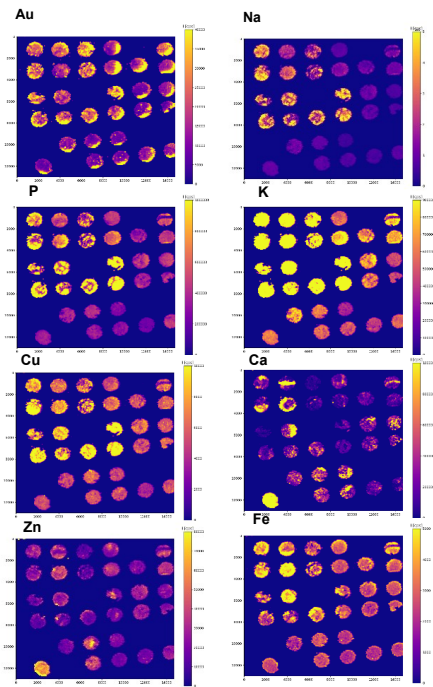
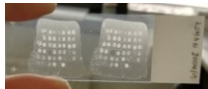
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Vičnovská et al., Proof-of-Concept of Simultaneous Elemental and Molecular Mass Spectrometric Imaging – metal/p53 visualization, submitted in Analytical Chemistry

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# ICP-MS AND PROTEIN

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- DO1-Au NPs, negative control Au NPs
- 30 breast cancer samples



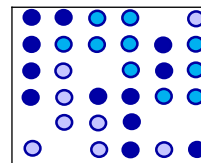
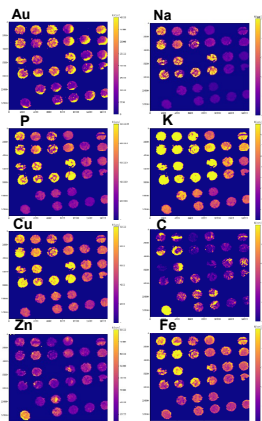
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# ICP-MS AND PROTEINS



- **determination of p53** – suppressor of tumors („sensor“ of DNA damage); antibody DO-1
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- 30 breast cancer samples



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

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

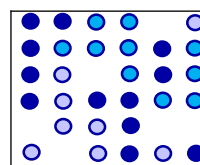
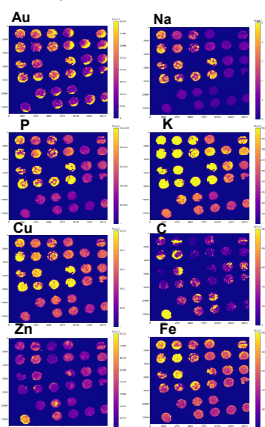
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# ICP-MS AND PROTEINS

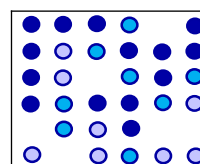


– **determination of p53** – suppressor of tumors („sensor“ of DNA damage); antibody DO-1

- DO1-Au NPs, negative control Au NPs
- 30 breast cancer samples



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



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

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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

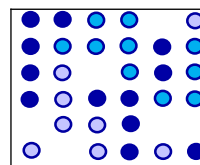
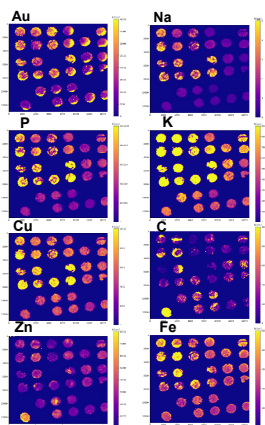
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# ICP-MS AND PROTEINS

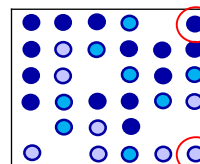


– **determination of p53** – suppressor of tumors („sensor“ of DNA damage); antibody DO-1

- DO1-Au NPs, negative control Au NPs
- 30 breast cancer samples



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



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

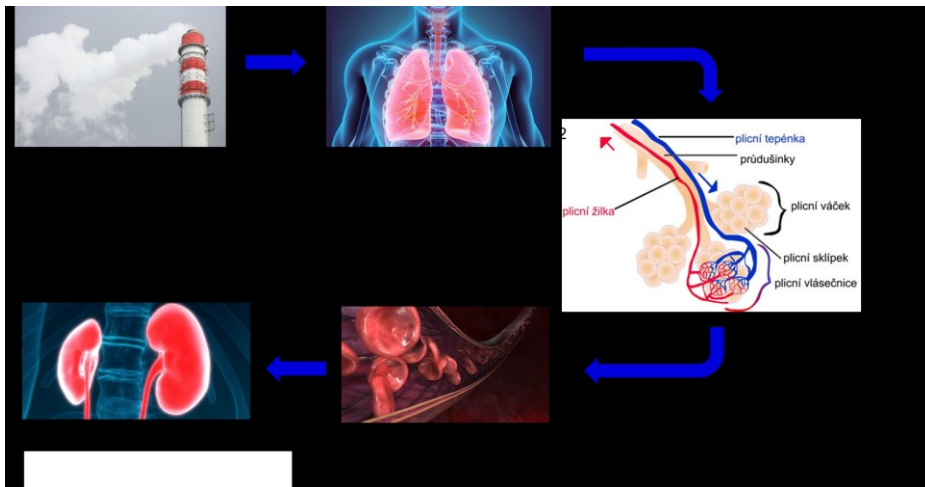
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Vlčnovská et al., Proof-of-Concept of Simultaneous Elemental and Molecular Mass Spectrometric Imaging – metal/p53 visualization, submitted in Analytical Chemistry

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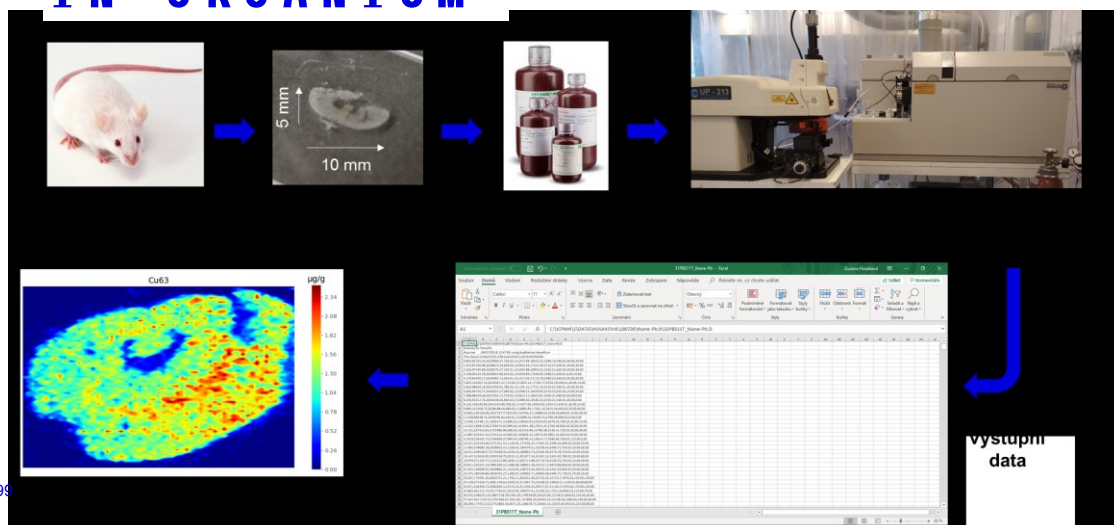
# NANOPARTICLES IN ORGANISM



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# NANOPARTICLES IN ORGANISM



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# NANOPARTICLES IN ORGANISM

## 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**

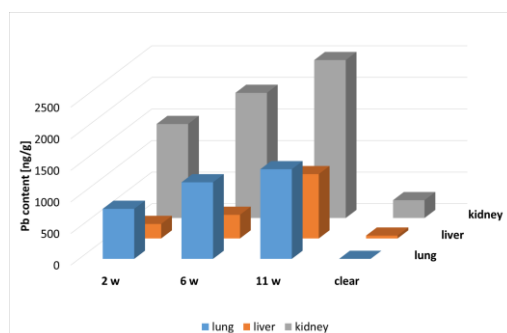
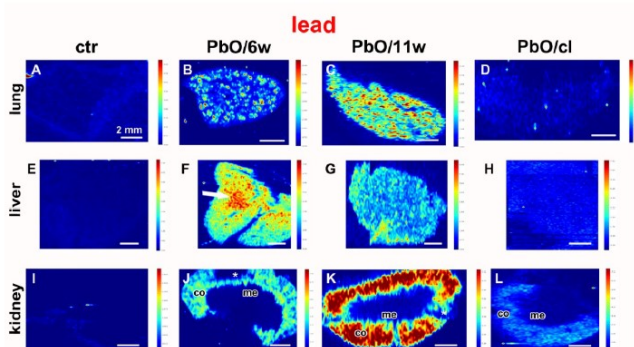
## 3 different organs

- lung
- liver
- kidney

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# NANOPARTICLES IN ORGANISM



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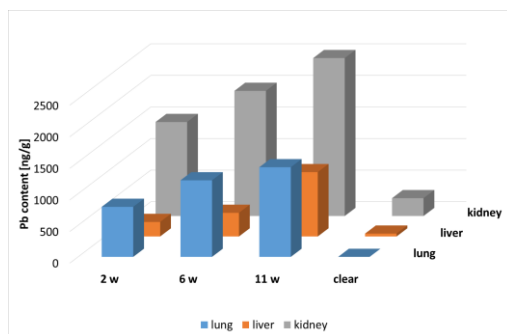
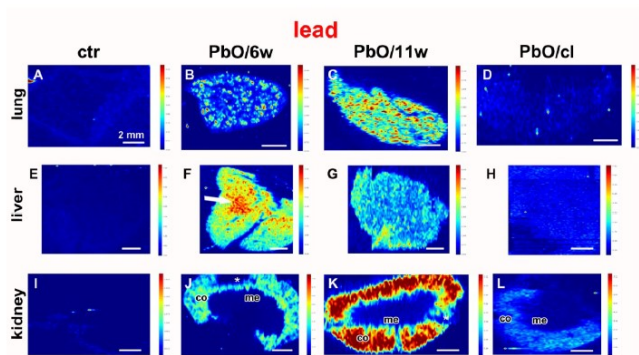
# NANOPARTICLES IN ORGANISM

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

Jana Durnková,<sup>†</sup> Tereza Smutná,<sup>†</sup> Lucie Vráhová, Hana Kotasová, Bohumil Dočkal, Lukáš Čapka, Michaela Tvrdoňová, Veronika Jalašová, Vendula Peřková, Kamel Křimáček, Pavel Coufalík, Pavel Mikuška, Zbyněk Velečta, Tomáš Vaculovík, Zuzana Husáková, Viktor Kanický, Aleš Hampel, and Marcela Buchtová\*

Cite This: ACS Nano 2020, 14, 1096–1120

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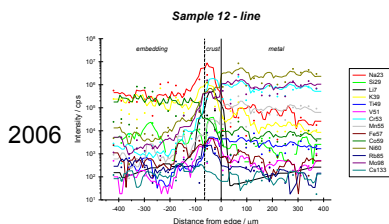
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Pb in dissolved form or as NPs?

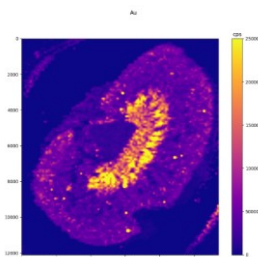
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## SUMMARY

- LA-ICP-MS – applicable for any type of material
- suppression of different ablation rate – crucial step for correct results
- elemental specific detector + immunochemistry = determination of specific proteins
- improving of distribution from single line scan of elements to imaging of specific proteins



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## OUTLOOK

- **elemental microscope** - improving of lateral resolution and shortening time analysis
  - 1 Mpx images of all elements with resolution 10  $\mu\text{m}$  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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Využití  
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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 kovu  
a mechanismus  
jejich čištění



GA101/08/1100  
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materiály  
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výměníků  
metodami  
plazmové  
spektrometrie



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



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**THANK YOU FOR YOUR ATTENTION**

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