Neutron activation analysis and imaging techniques in Romania-JINR cooperation in material and life sciences

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"Dunarea de Jos" (Lower Danube) University of Galati

- **A state university with:**
- more than 65 years of academic tradition;
- more than 12 500 students and 700 academics;
- **14** faculties, **55** undergraduate study programmes, **32** master's programmes and **2** doctoral schools (12 fields of study);
- more than 100 partner universities from 22 foreign countries;
- bilateral agreements with 13 EU countries and 15 non EU countries, out of which Erasmus with 22 countries;
- international full-time students enrolment: about 1626 from EU and non EU countries

Due to the increased demand for ultrapure metals and alloys and requirements for knowledge of toxic emissions, along with the increasing use of new sources of raw materials (new deposits, industrial by-products, wastes), it is necessary to carefully analyze the distribution of impurity elements between the main products and by-products of metallurgical processes.

Special attention should be given to the elements that are harmful both to metallurgical products and to the environment. Trace and minor elements existing in the raw materials (ores, coal and secondary resources) can remain in the final products as residual elements and influence their properties, so that their transfer during metallurgical operations must be thoroughly investigated.

Also, impurity analysis in Li-N, B-N and diamonds systems synthezised at different pressures became extremely important in materials research.

Nuclear methods were applied in combination with imaging techniques within the **Romanian-Russian joint projects** nos. 78/2014, 84/2015 and 104/2016 in the frame of the protocol no. 4113-4-11/16 between Frank Laboratory of Neutron Physics (FLNP) of Joint Institute of Nuclear Research (JINR) at Dubna, Russia, and Physics Division at Department of Chemistry, Physics and Environment, Faculty of Sciences and Environment, "Dunărea de Jos" University of Galati, Romania.

The **most used** analytical techniques for elemental analysis (metals, metalloids, trace elements) in environmental studies and materials research are **spectrometric** techniques:

Atomic techniques

X-ray Fluorescence (XRF) (ED-XRF and WD-XRF)

Energy-dispersive X-ray Analysis (EDX) in Scanning Electron Microscopy

Atomic Absorption Spectroscopy (AAS)

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

Inductively Coupled Plasma–Mass Spectrometry (ICP-MS)

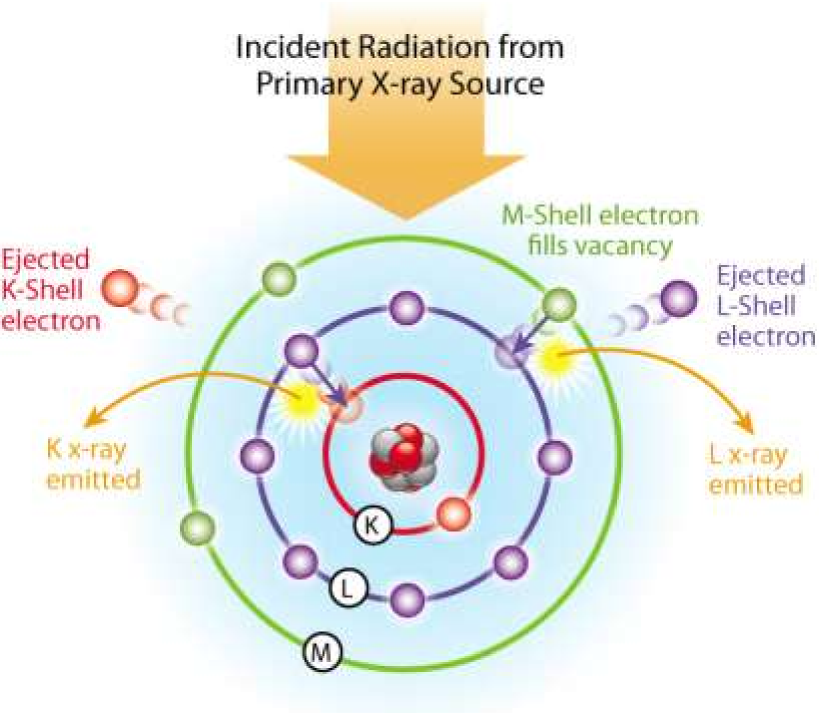
Nuclear techniques

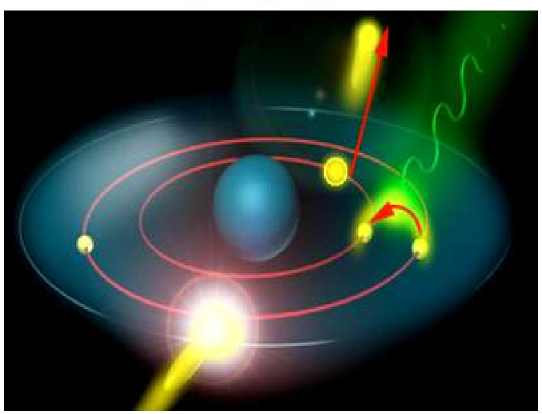
Instrumental Neutron Activation Analysis (INAA)

Particle Induced X-ray Emission (PIXE)

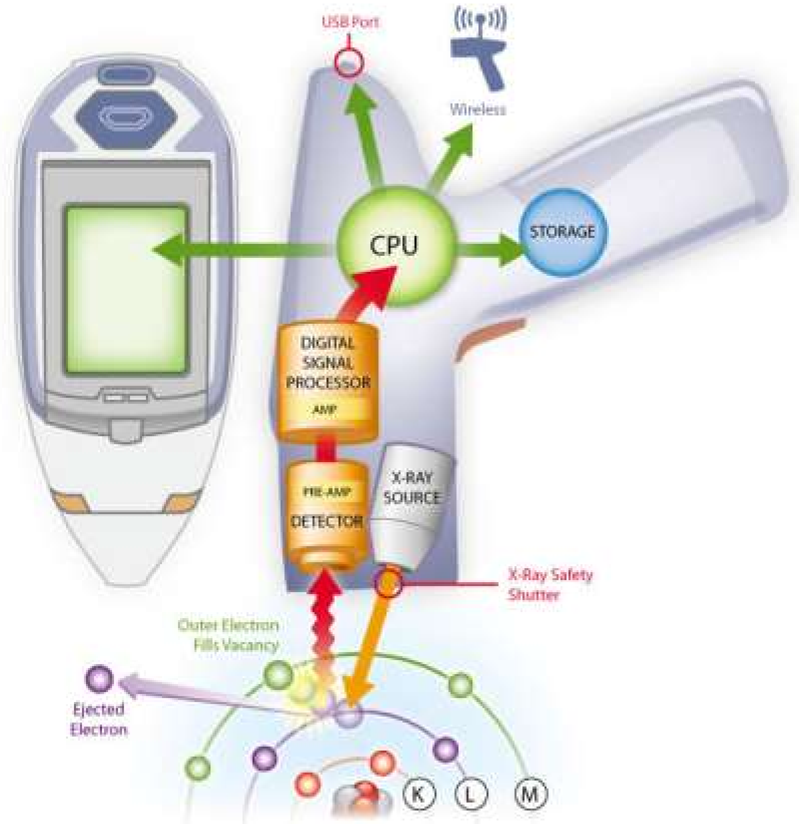
Particle Induced Gamma-ray Emission (PIGE)

XRF Excitation Model

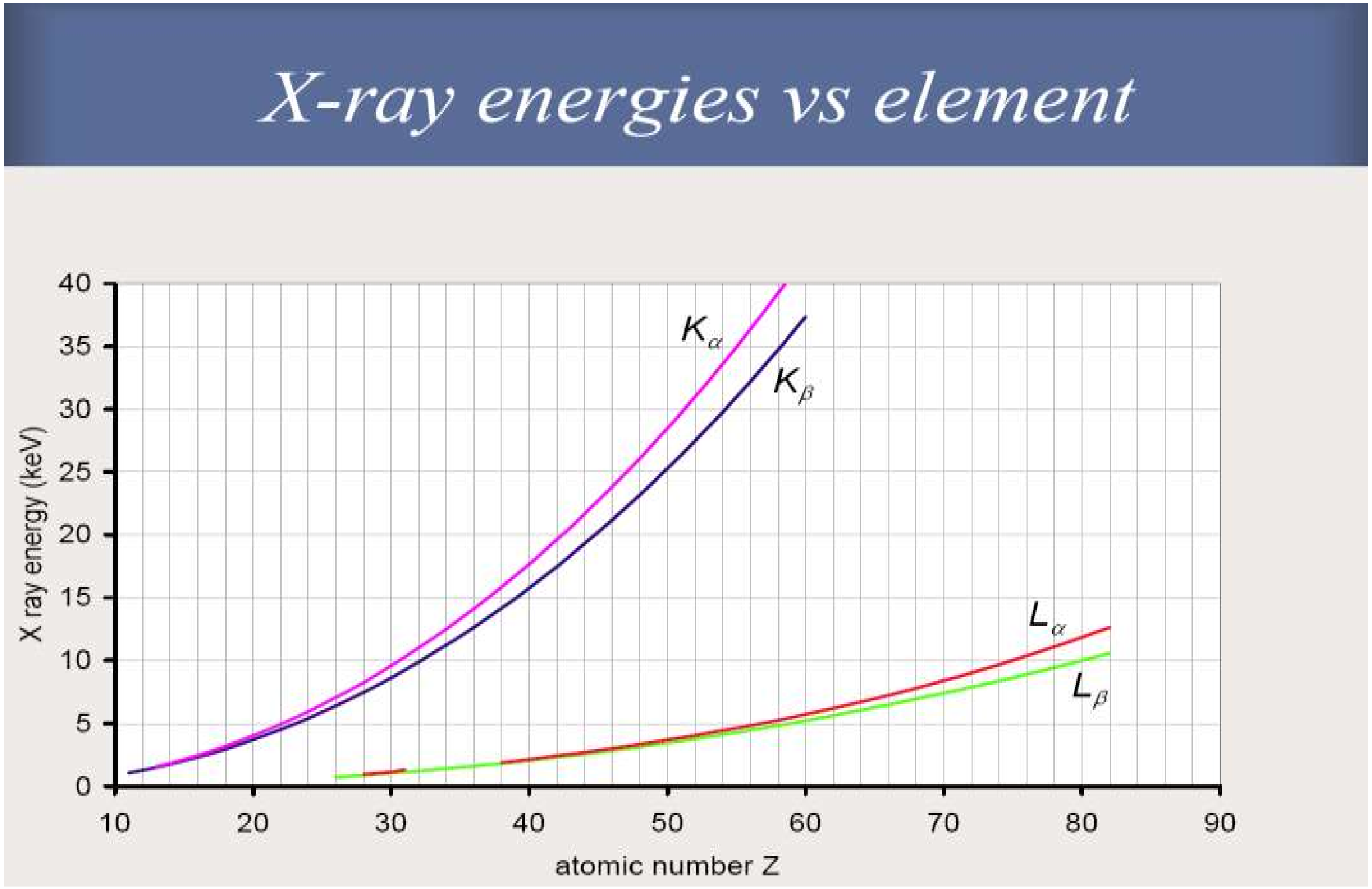




Portable XRF Spectrometer

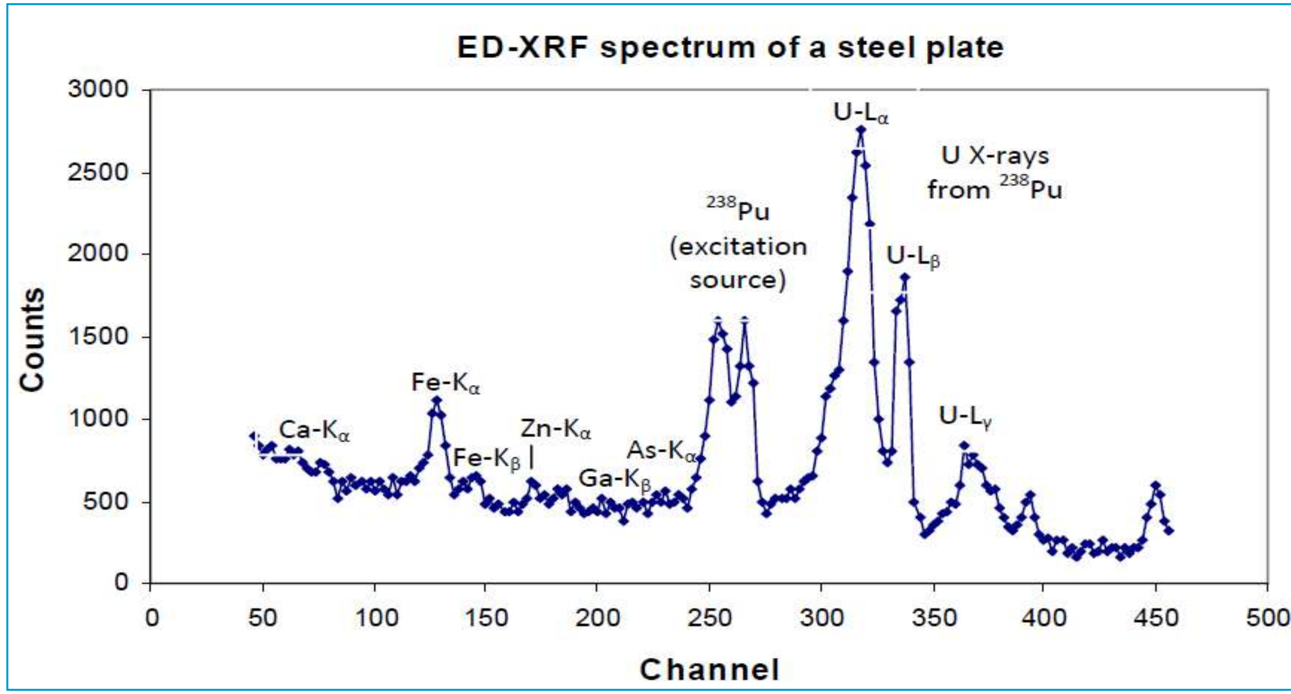


The monotonic increase of the **X-ray energies** with the atomic number Z of the element (energies known and tabulated in the literature) as well as the proportionality of the **X-ray intensities** (peak areas) with the element concentration in the sample allow a **qualitative** and **quantitative** determination of the elemental contents in samples.



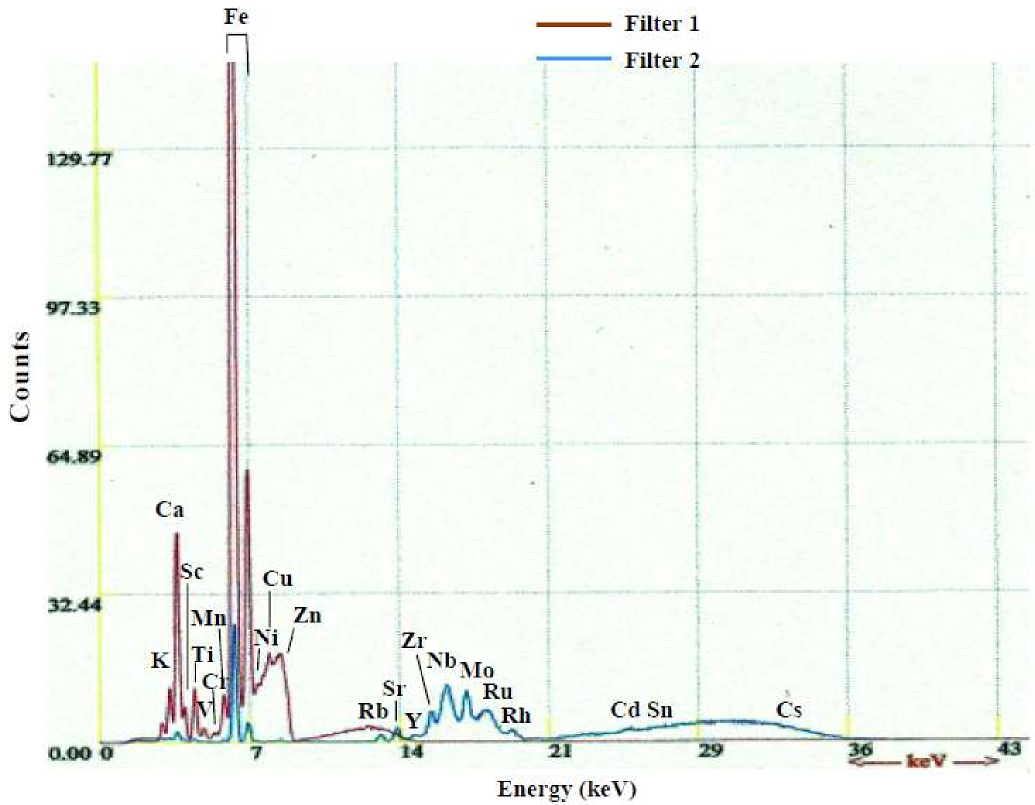
Characteristic elemental X -rays energies (K and L type).

ED-XRF spectrometer with primary radioisotope photons excitation

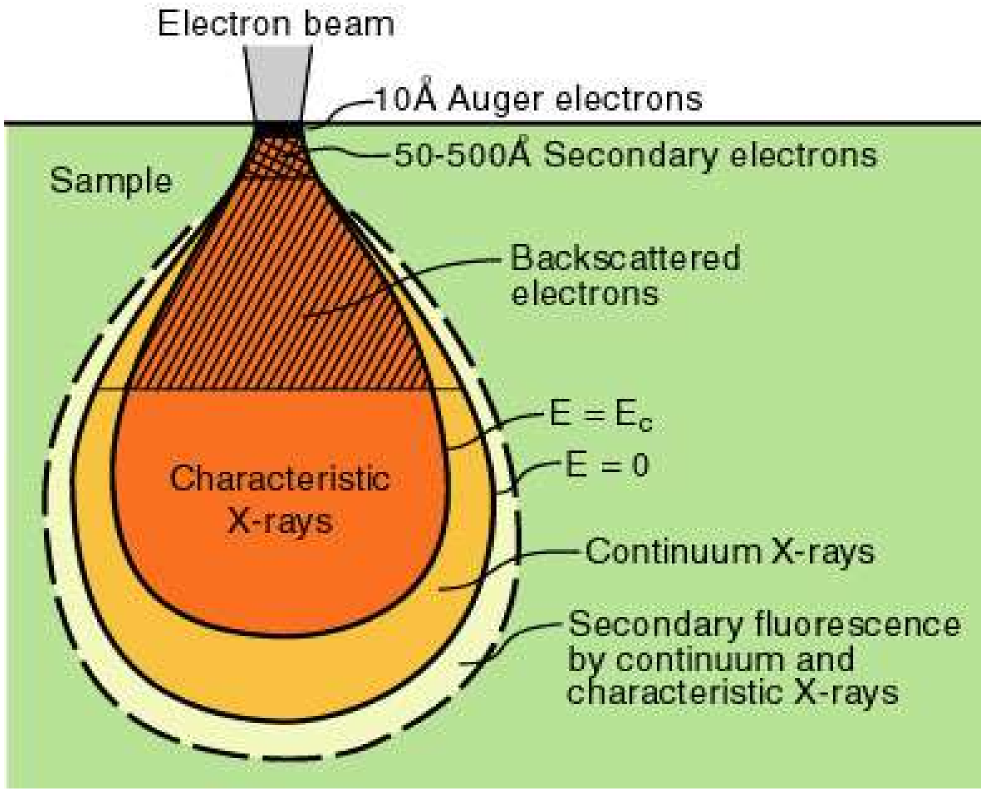


ED-XRF spectrum for a complex matrix – steel

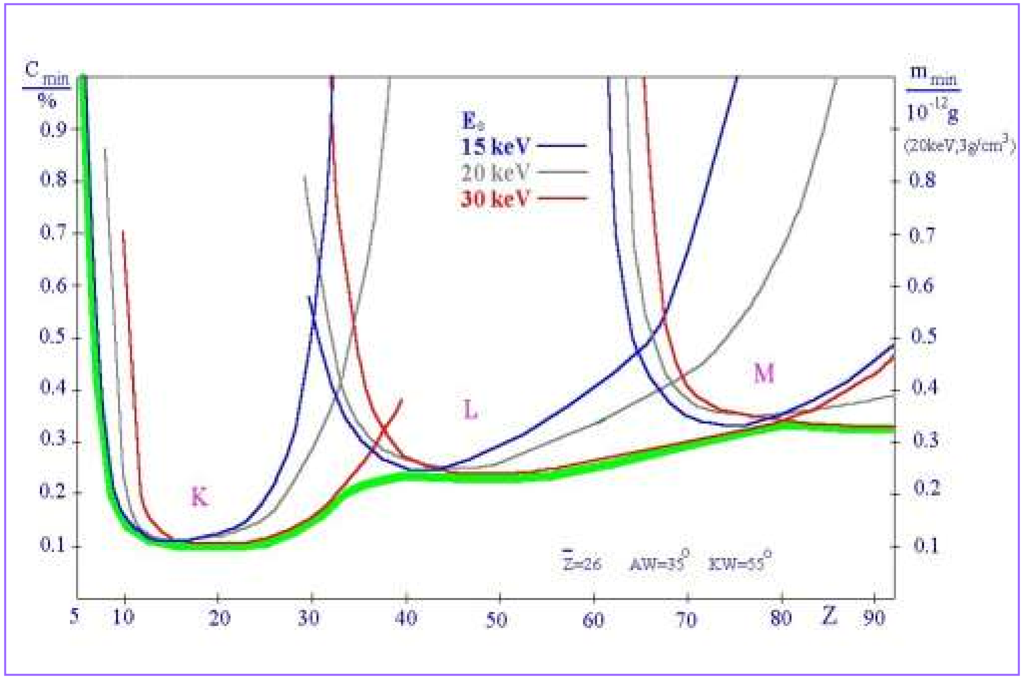
XRF Spectrum of a soil sample collected in the vicinity of an iron and steel enterprise



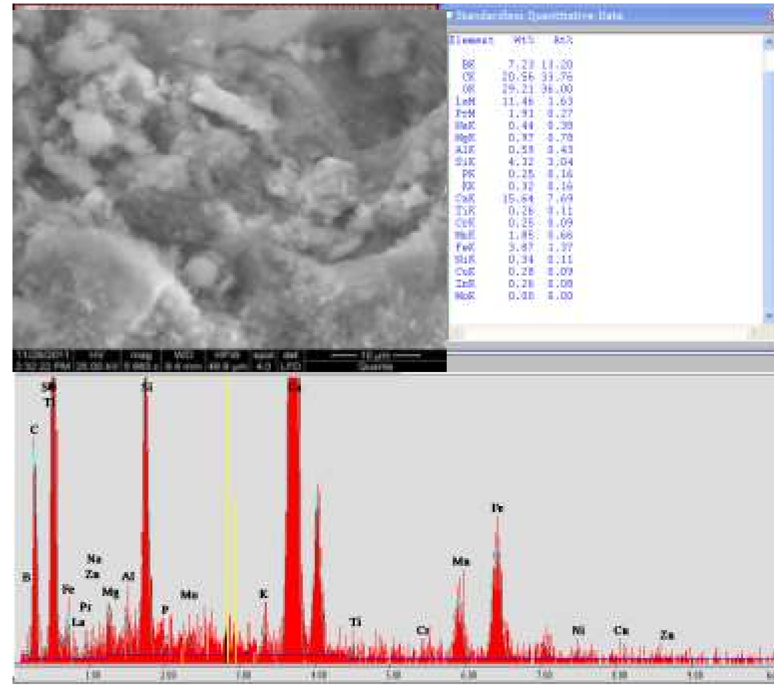
Over 20 elements determined by energy dispersive X-ray fluorescence (ED-XRF): K, Ca, Sr, Ti, Cr, V, Mn, Fe, Ni, Cu, As, Ga, Pb, Zn, Rb, Sr, Zr, Sb, Mo, Rh, Cd, Cs.



SEM Quanta FEI 200 and excitation of characteristic X-rays with electron beams



Detection limits of SEM-EDX technique



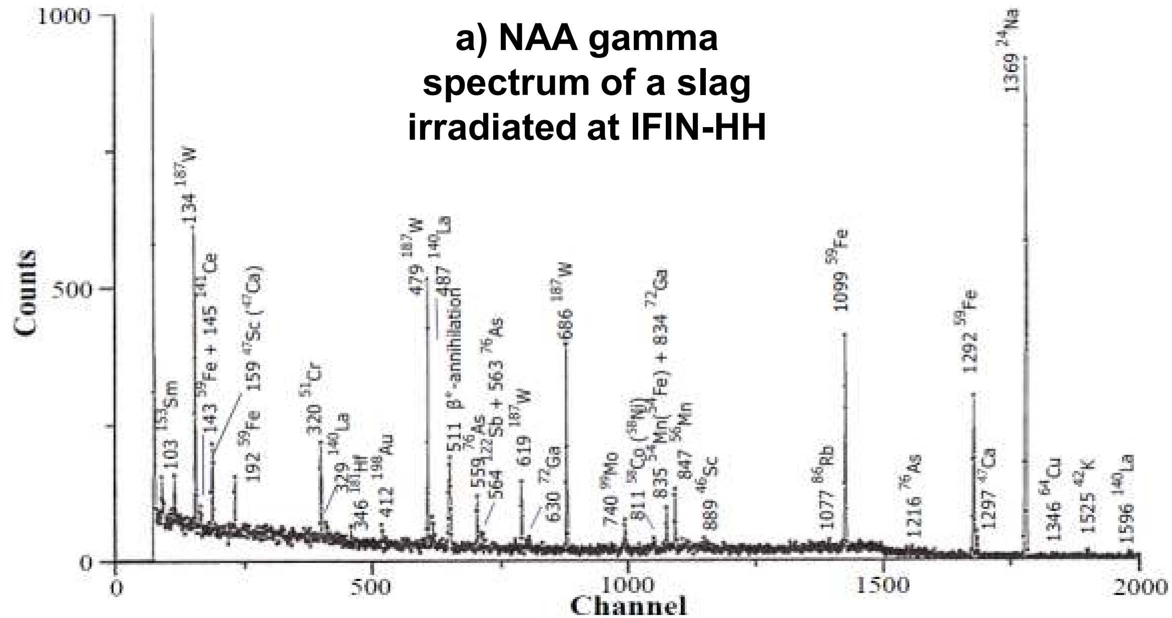
SEM-EDX spectra of a slag sample

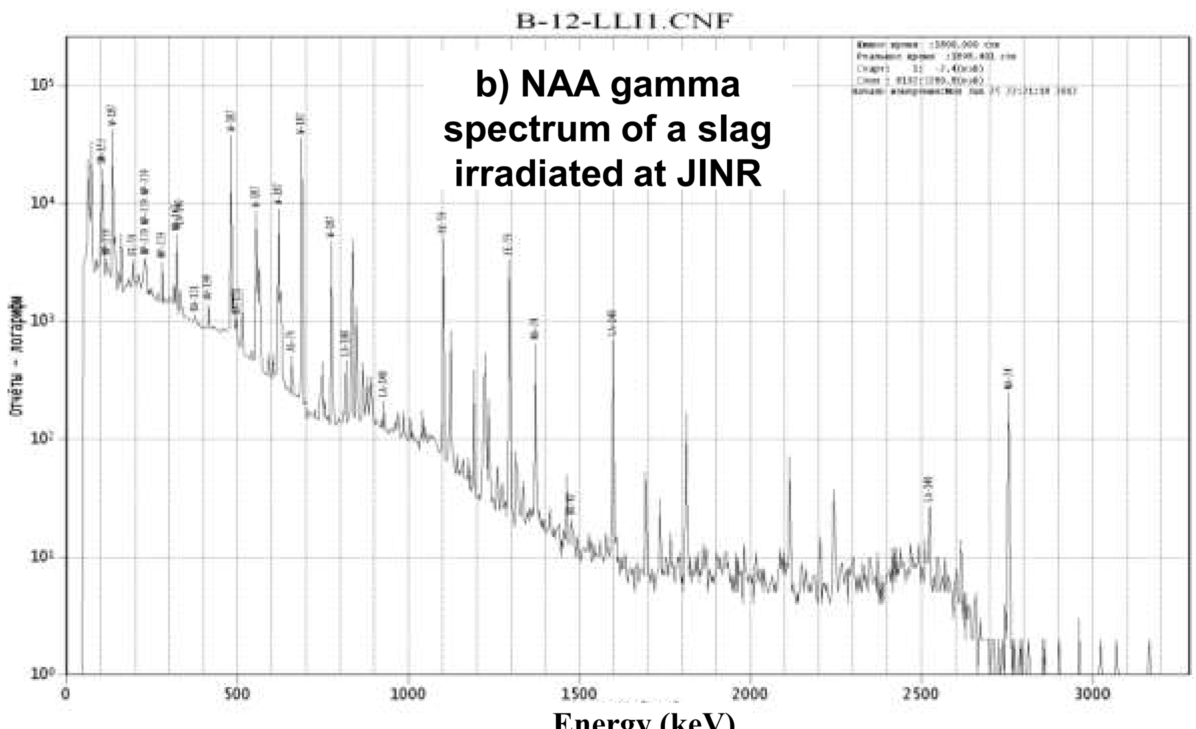
By scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) the following elements could be determined:

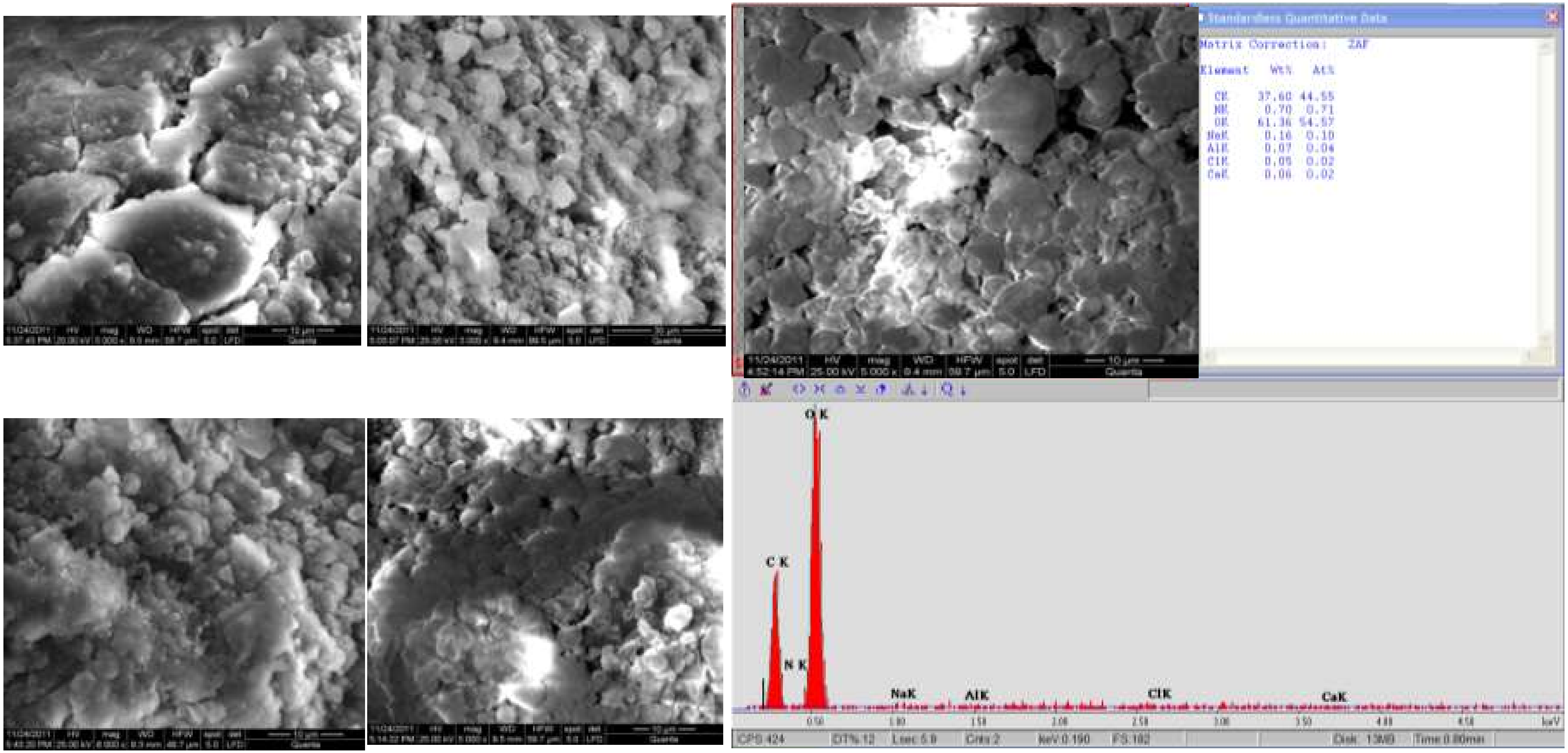
C, O, S, P, Si, Ca, Na, K, La, Ce, Nd, Ga, Mo, Pr, Rh, Sm, Sn, Mg, Al, Ti, V, Cr, Ni, Cu, Mn, Fe, Co, As and Zn

INAA carried out at JINR Dubna in two irradiation steps allowed determination of 40 elements (Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Co, Zn, As, Br, Rb, Sr, Zr, Mo, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Tm, Yb, Hf, Ta, W, Au, Hg, Th, U, etc.) in soil samples.

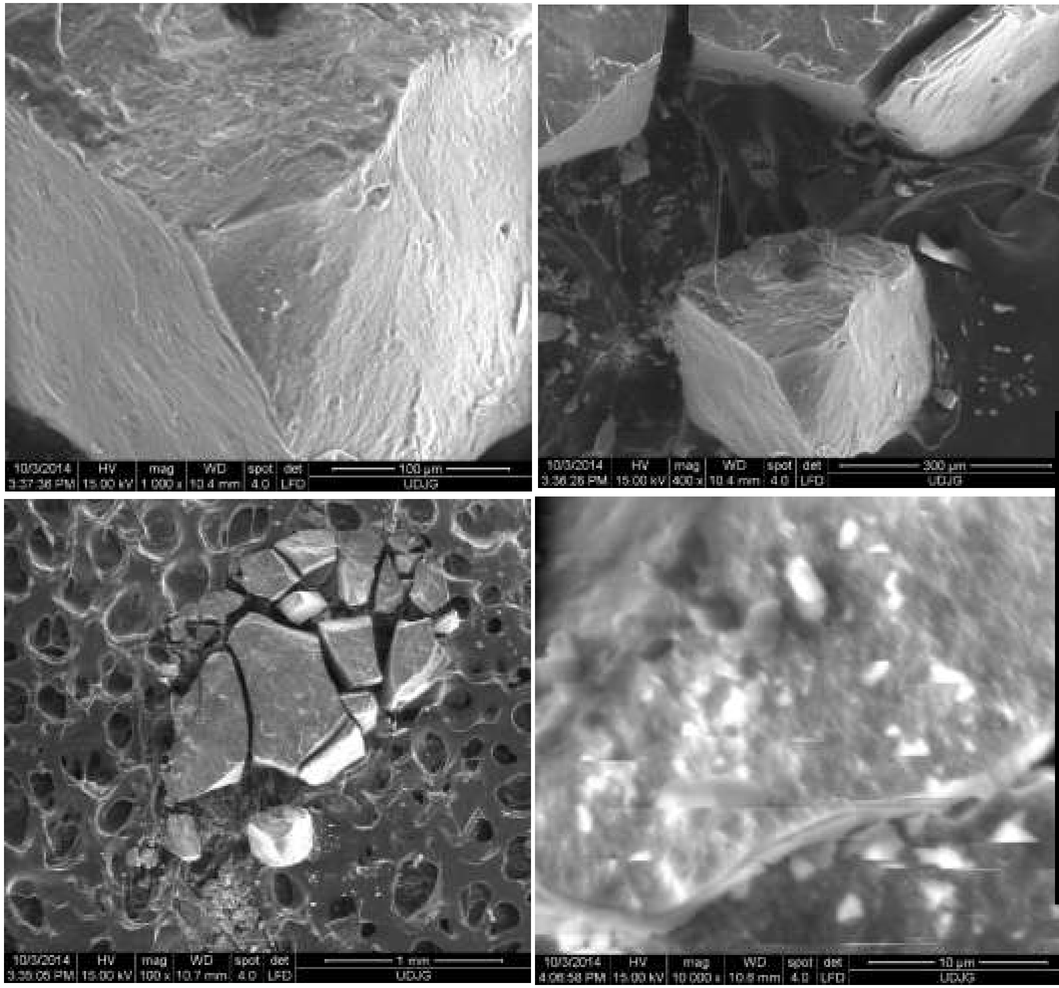
The influence of steel plant activity on occurrence of heavy metals in surrounding soils is obvious. It is observed a decrease with depth of metal levels.


a) NAA gamma spectrum of a slag irradiated at IFIN-HH
Counts
Channel
0
500
1000
1500
2000
1369 24Na
1099 59Fe
1292 59Fe
686 187W
479 187W
487 140La
511 β+-annihilation
134 187W
145 141Ce
143 59Fe
159 47Sc (47Ca)
192 59Fe
103 153Sm
320 51Cr
329 140La
346 181Hf
412 198Au
559 76As
563 76As
564 122Sb
619 187W
630 72Ga
740 99Mo
811 58Co (58Ni)
834 72Ga
835 54Mn (54Fe)
847 56Mn
889 46Sc
1077 86Rb
1216 76As
1297 47Ca
1346 64Cu
1525 42K
1596 140La

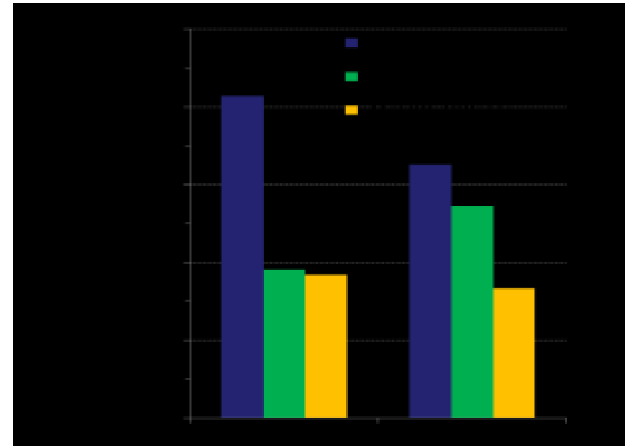

B-12-LLI1.CNF
b) NAA gamma spectrum of a slag irradiated at JINR
Energy (keV)
0
500
1000
1500
2000
2500
3000



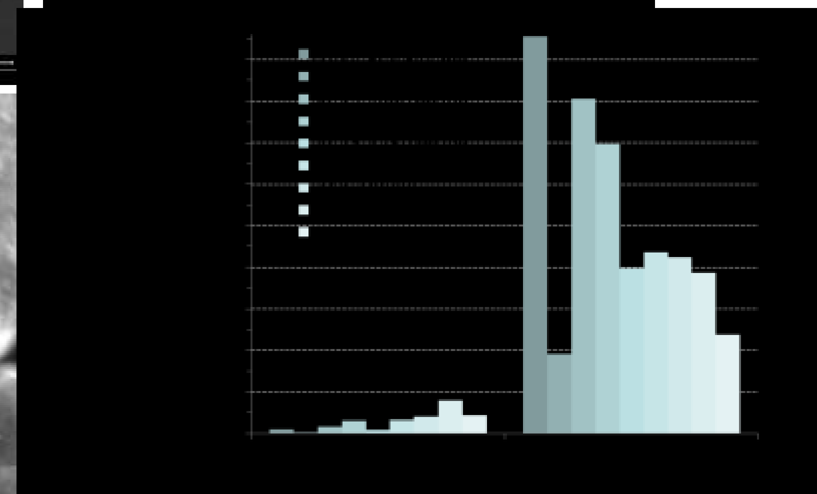
SEM images and SEM-EDX spectra for Li-N system



SEM images of diamond after application of synthesis pressure



a)



Distribution of process impurities (Al and Mn) for the diamond powder synthesized in the system Fe-Ni-C (a) and system Mn-Ni-C (b)

SEM highlighted the structural differences between the powder diamond samples with various grain sizes (160/125 mm, 500/400 mm, 400/315 microns and 250/200 microns), synthesized in different pressure and temperature conditions.

According to neutron activation analysis, the Fe-Ni-C growth system allows to synthesize diamond

2016 projects/grants

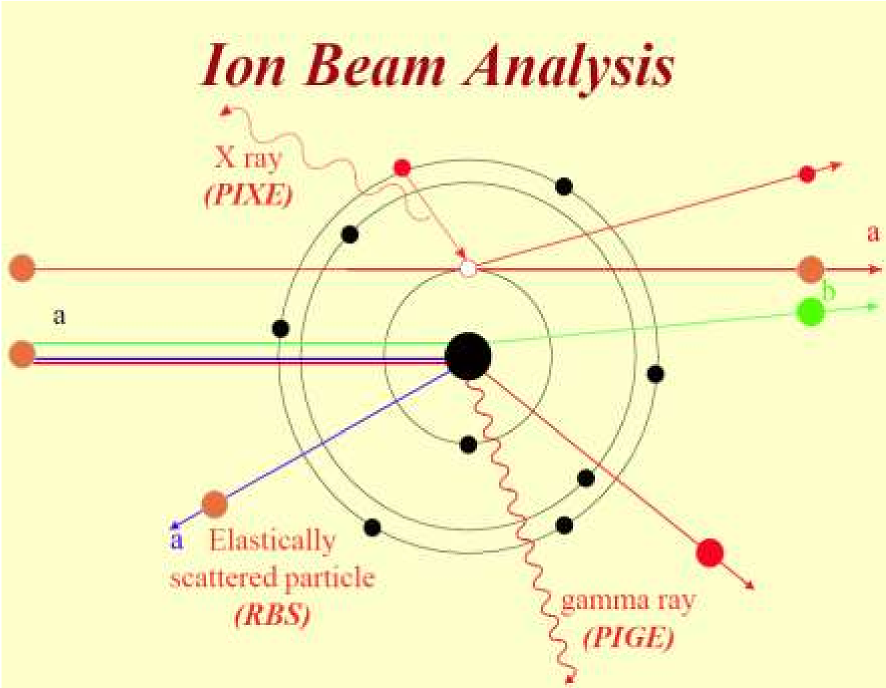
RESEARCH PROJECT 2016 JINR-Romania no. 104, **Investigation of crystalline materials (diamonds and boron nitrides) using atomic and nuclear analytical techniques and imaging microscopy,** Theme no. 03-4-1104-2011/2016, Investigations in the Field of Nuclear Physics with Neutrons, Protocol No. 4321-4-14/16,

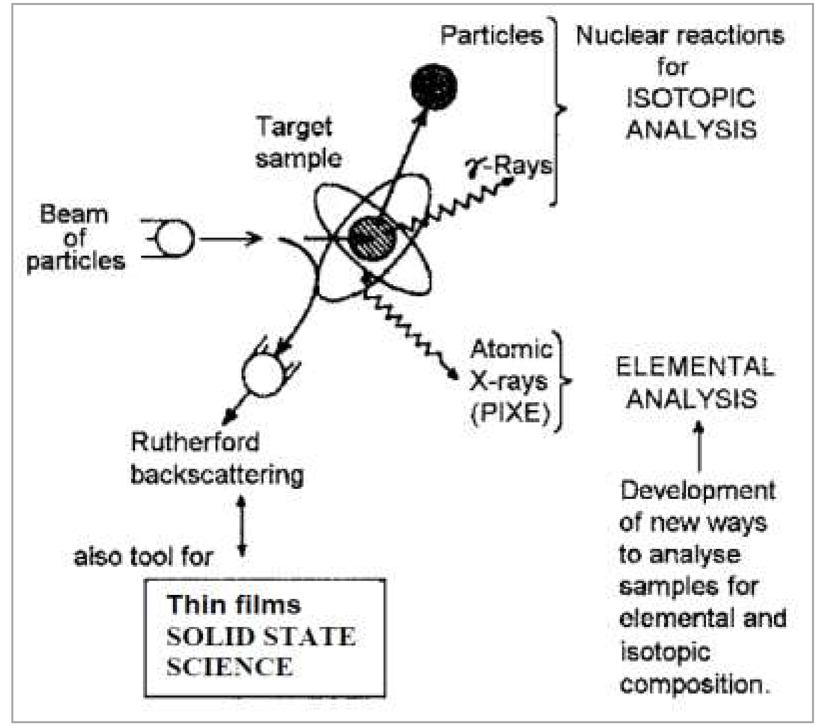
RESEARCH GRANT JINR-Romania no. 22/2016, **Development of infrastructure of spectroscopy and microscopy laboratories used for the characterization of environmental and crystalline materials,** Protocol No. 4321-4-14/16

This collaboration **will enforce the research partnership** of Romanian institutions (UDJG, IFIN-HH) with JINR and research institutes from other countries and will have in view **the enlargement of the research network** in order **to apply to European** and **international calls of proposals**.

Furthermore, it is foreseen that, beside the academic staff, **more scientists** (young and senior researchers, M.Sc. or PhD students) **will get benefit from these analytical tools**.

Complemenatry nuclear techniques applied at IFIN-HH:





The **particle induced X-ray emission (PIXE)** technique is based on the ionization of atomic inner shells of a sample/target by a charged particle beam (protons, in particular) entering the target, followed by emission of the characteristic X-rays.

PIXE can be coupled with other **ion beam analysis (IBA)** techniques, such as **particle induced gamma-ray emission (PIGE)** or **Rutherford backscattering (RBS)**, and can be completed by **neutron activation analysis (NAA)**.





Preparation of dried/lyophilized environmental samples for irradiation

PAC experiment 01-04 October 2015 – 3 MV Tandetron at IFIN-HH Bucharest





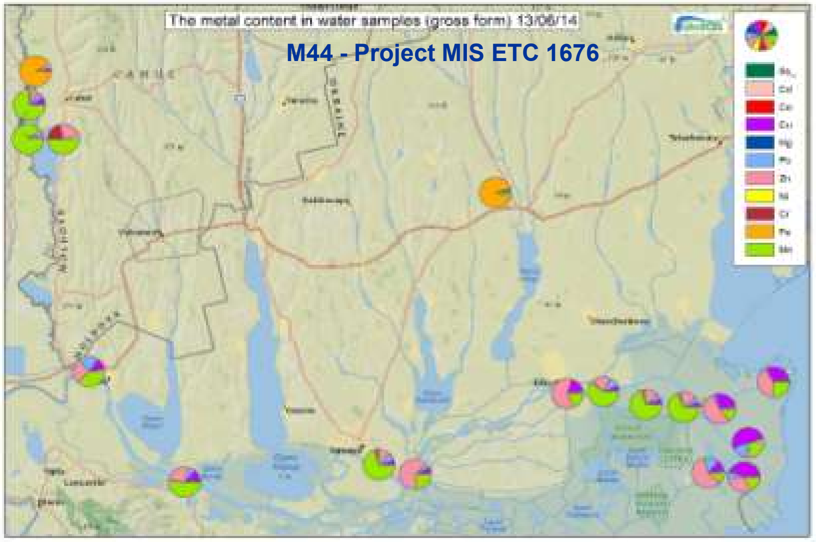




Sampling of environmental materials in Danube river region

The results obtained by application of combined nuclear and atomic techniques will permit:

- to **determine the regional extent of pollution** with heavy metals and toxic elements
- to **identify the specially affected areas** and local sources of pollution in RO-UA-MD border regions
- to **establish the background concentrations** for trace elements which are not of anthropogenic origin
- to **complete the database** obtained in the frame of the cross-border project and
- to **build new maps of pollution points** in the Lower Danube Euroregion.



Map of Danube River Basin and the sampling sites in Lower Danube Euroregion

Thank you for your attention !