International Symposium on Food Safety and Quality:
Applications of Nuclear and Related Techniques
IAEA, Vienna, Austria, 10–13 November 2014

Nuclear-physical methods for detecting pollutants and microelements in food

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Purposes of research

To develop, demonstrate and practically use effective methods of detecting different trace elements in food products including in the form of nanoparticles, for supporting safety control, risk assessment and management, biological experiments

General view

Currently different methods are used for detection of trace elements and pollutants in food and agricultural raw materials:

- **microscopy and related methods,**
- **atomic and X-Ray fluorescence spectrometry,**
- **nuclear-physical methods (NPhMs),**
- **nuclear magnetic resonance**
- **and others.**

Nuclear-physical methods

Development and application of NPhMs has a long and successful history

Examples of good review papers:

- **Frontasyeva M.V. Neutron Activation Analysis for the Life Sciences. A Review // Phys. Part. Nucl. 2011. V. 42, No. 2. P. 332-378 (in English).**
- **A.V.Gorbunov, S.M.Lyapunov, O.I.Okina, M.V. Frontasyeva, S.F.Gundorina. Assessment of human organism's intake of trace elements from staple foodstuffs in central region of Russia. Preprint of the Joint Institute for Nuclear Research. Dubna, 2004 (in English).**

A few NPhMs' options

- **Instrumental neutron activation analysis (INAA);**
  identification of elements is carried out with the gamma rays emitted by radioactive nuclei formed during irradiation of the sample in the neutron flux.
- **The neutron radiation analysis (NRA);**
  determination of elements is carried out with the gamma rays emitted by nuclei immediately after the capture of neutrons.
- **X-ray fluorescence analysis (RFA);**
  RFA is performed by the usual method of detection of the fluorescent characteristic X-rays of the sought-for elements.
- **Instrumental proton activation analysis.**

Trace elements in food

- **Essential (Fe, I, Cu, Zn, Co, Cr, Mo, Se, Mn);**
- **Conditionally essential (Br, B, F, Li, Ni, V, Si);**
- **Toxic (Al, As, Cd, Pb, Sb, Hg, Be, Bi, Tl).**

Ti - ?

Ag - There is a tendency to classify it as a toxic element.

The current level of NPhMs

the current high level of NPhMs is determined by the following important factors:

- **powerful neutron fluxes (10^{12}–10^{15} n/cm$^2\cdot$s) from research reactors,**
- **a combination of various versions of the technique,**
- **use of**
  - **modern high-resolution (≤ 2 keV) semiconductor detectors,**
  - **standard samples,**
  - **measuring and computing equipment,**
  - **advanced computer technologies for data processing and interpretation.**

Important features and advantages of INAA (1)

- **High sensitivity and accuracy;**
- **High reliability;**
- **High selectivity to a majority of elements due to their specific nuclear-physics' characteristics;**
- **A possibility of simultaneously determining a number of elements;**
- **Independence of the results on the form of chemical compounds;**
- **Easy procedure for preparation of samples for analysis;**

Important features and advantages of INAA (2)

- The extended area of applications in defining significant number of elements in samples of various nature, including biological ones (**with heterogeneous distribution**);
- **A nondestructive nature of the analysis;**
- The ability to measure the mass content directly in the volume of solid samples;
- Determination of the mass content of elements can be produced both in micro- and macro-samples up to several centimeters in all three dimensions;

Important features and advantages of INAA (3)

- **The ability of studying biokinetics of controlled substances in laboratory animals as they arrive from the environment, including with food products; thus it is possible to study biokinetics of essential elements (e.g., zinc, selenium), unlike many other techniques;**

- **The possibility to use charged accelerated particles to activate the detected elements.**

Important features and advantages of INAA (4)

Measurements' sensitivity with NPhMs largely depends on the isotopes' nuclear constants of studied elements (neutron capture cross section, half-life, etc.) and is significantly different for different elements of the periodic system. It also depends on the power of a neutrons' source.

Important features and advantages of INAA (5)

- The sensitivity can reach up to a few picograms per gram, varying from element to element. The sensitivity can be changed by selecting the mode of exposure, the choice of the best NPhM' variant and processing conditions of the sample after irradiation.
- To achieve high accuracy (5 – 15 %) the relative method is typically applied: the object is irradiated together with a standard sample containing a known mass of the detected stable isotope.

Shortcomings of INAA

- It is impossible to determine the valence state of the element,
- Method requires a complex equipment (e.g., a nuclear reactor).
- It is necessary to work with radioactive substances, that requires compliance with safety and work permit.
- Possibility of degradation and even destruction of the samples during irradiation by a powerful radiation flux.

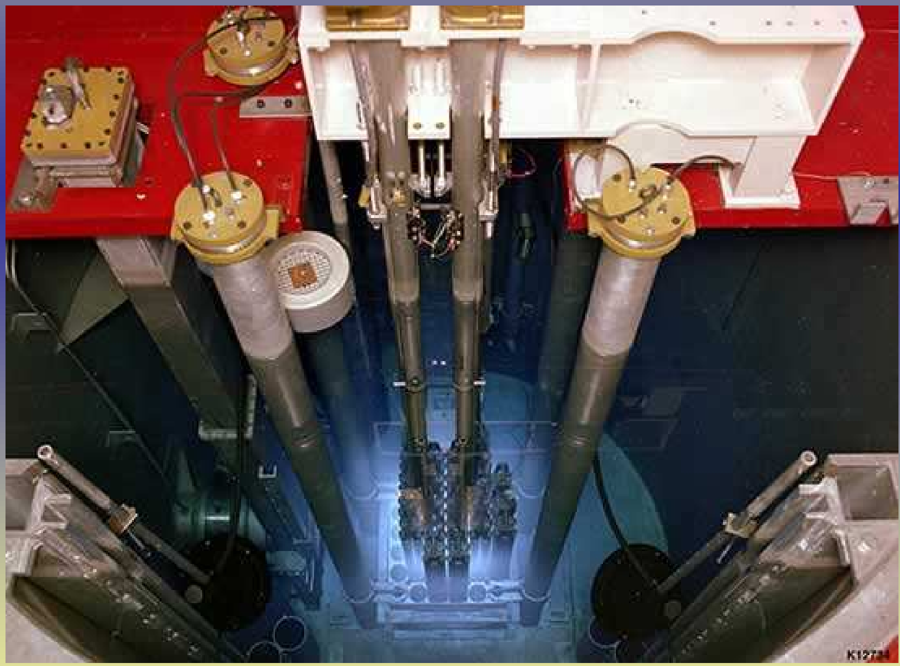
Installations and equipment in NRC "Kurchatov Institute", Moscow, for NPhMs

- **Research nuclear reactor IR-8 with the necessary characteristics to activate isotopes of studied elements, providing thermal neutron flux density to $3 \cdot 10^{12} sm^{-2} s^{-1}$,**
- **Isochronous cyclotron U-150 as a source of fast protons and other charged particles, providing particle flux density up to 10^{13} $p \cdot cm^{-2} \cdot s^{-1}$ and particle energy upto 60 MeV,**
- **Different gamma-spectrometry and supporting equipments, PC codes,**
- **and others.**

Main and Auxiliary Equipment, NRC KI

Source of neutrons of research reactor IR-8 with neutron flux of no less than 10^{12} $cm^{-2}c^{-1}$;

Gamma-spectrometer CANBERRA with the detector GC 3018 and analyzer DSA 1000, verification certificate № 03-13 2684 26



Measurements of nanoparticle concentration containing silver, gold or zinc with the gamma-spectrometric analysis of neutron activated samples.
Detection limit (metrologically provided) is 10^{-11} g.

Other Russian institutions with necessary installations and equipment

- **Joint Institute for Nuclear Research, Dubna,**
- **St. Petersburg Institute of Nuclear Physics with the best research reactors in Russia WWR-M with thermal capacity of 18 MW and the neutron flux density of up to $4 \cdot 10^{14} n / cm^2 \cdot s$,**
- **Tomsk Polytechnic University**
- **and others**

Russian institutions with necessary installations and equipment

- These institutions have accumulated a vast experience in the development and use of NPhMs for different applications, including food control.
- For nuclear research centers some shortages prescripted to NPhMs are really not drawbacks. In some sense they could be considered as advantages. Namely such centers have nuclear research experience and all possibilities to develop and effectively use of NPhMs for different applications.

Two different, but partly connected, research directions

- Supporting food control by developing and use of the effective methods of detecting trace element;
- Supporting biological research of biokinetics of nanoparticles in laboratory animals with special attention to overcoming biological barriers.

Some data and results on NPhMs' use for food control

Chem. element	Sensitivity limit δm, μg	Maximum allowable (MAC) and actual content, μg/g			
		Meat, eggs and their products		Dairy produce	
		MAC	Content	MAC	Content
As	10^{-2}	0.1 - 0.6	< 0.01	0.02 - 0.2	< 0.01
Pb	10	0.3 -1.0	0.04 ± 0.02	0.1 - 0.3	< 0.02
Cd	10^{-2}	0.01 - 0.05	< 0.05; 0.04 ± 0.01*)	0.03 - 0.1	< 0.01
Cr	10^{-2}	0.5	0.04 ± 0.02	0.1	0.04 ± 0.02
Se	10^{-2}	1	0.08 ± 0.01**); < 0.02;	0.5	< 0.02
Zn	10^{-1}	70	20-50 (±5)	5 - 10	5.0 ± 1.5
Ti	1	-	-	-	-
Ag	10^{-3}	70 μg/day	-	-	-

***) Eggs; **) meat**

Some data and results on NPhMs' use for food control

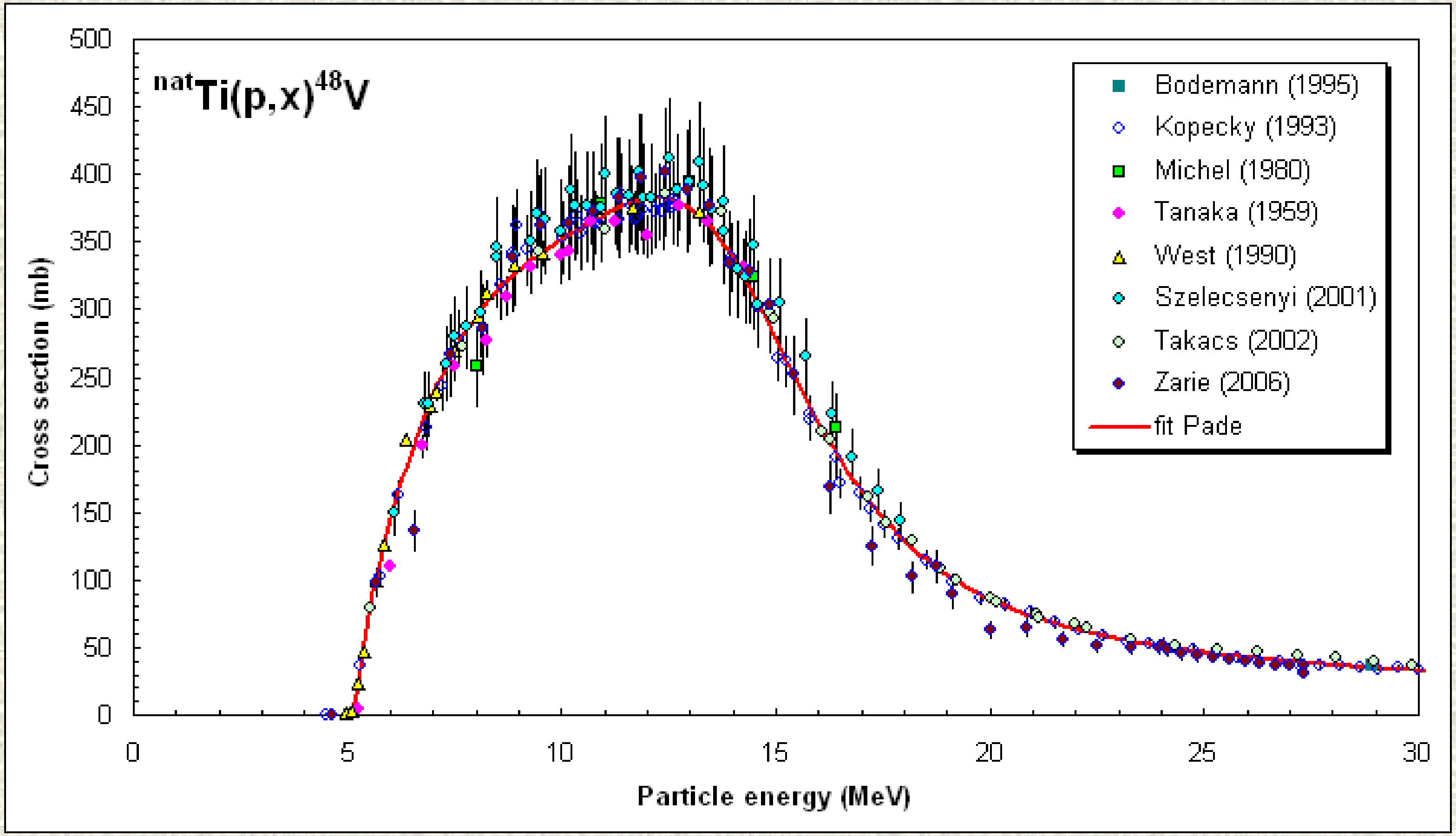
Chem. element	Sensitivity limit δm, μg	Maximum allowable (MAC) and actual content, μg/g				
		MAC	Content			
			Leafy vegetables	Maize	Potatoes	Apples
As	10^{-2}	0.2	0.02 ± 0.01	0.06 ± 0.02	0.01±0.002	< 0.005
Pb	10	0.5	0.23 ± 0.03	< 0.02	< 0.02	0.06 ± 0.01
Cd	10^{-2}	0.03	< 0.01	< 0.01	0.01±0.002	< 0.01
Cr	10^{-2}	0.2	0.32 ± 0.06	0.84± 0.2	0.06 ± 0.03	0.04 ± 0.01
Se	10^{-2}	0.5	< 0.05	< 0.05	< 0.05	< 0.05
Zn	10^{-1}	10	7 ± 3	16 ± 8	4 ± 2	0.3 ± 0.04

Supporting research of biokinetics of nanoparticles

The development of nanotechnology and the rapid increase of products containing nanoparticles (NPs) raises the problem of ensuring their safety for humans and the environment.

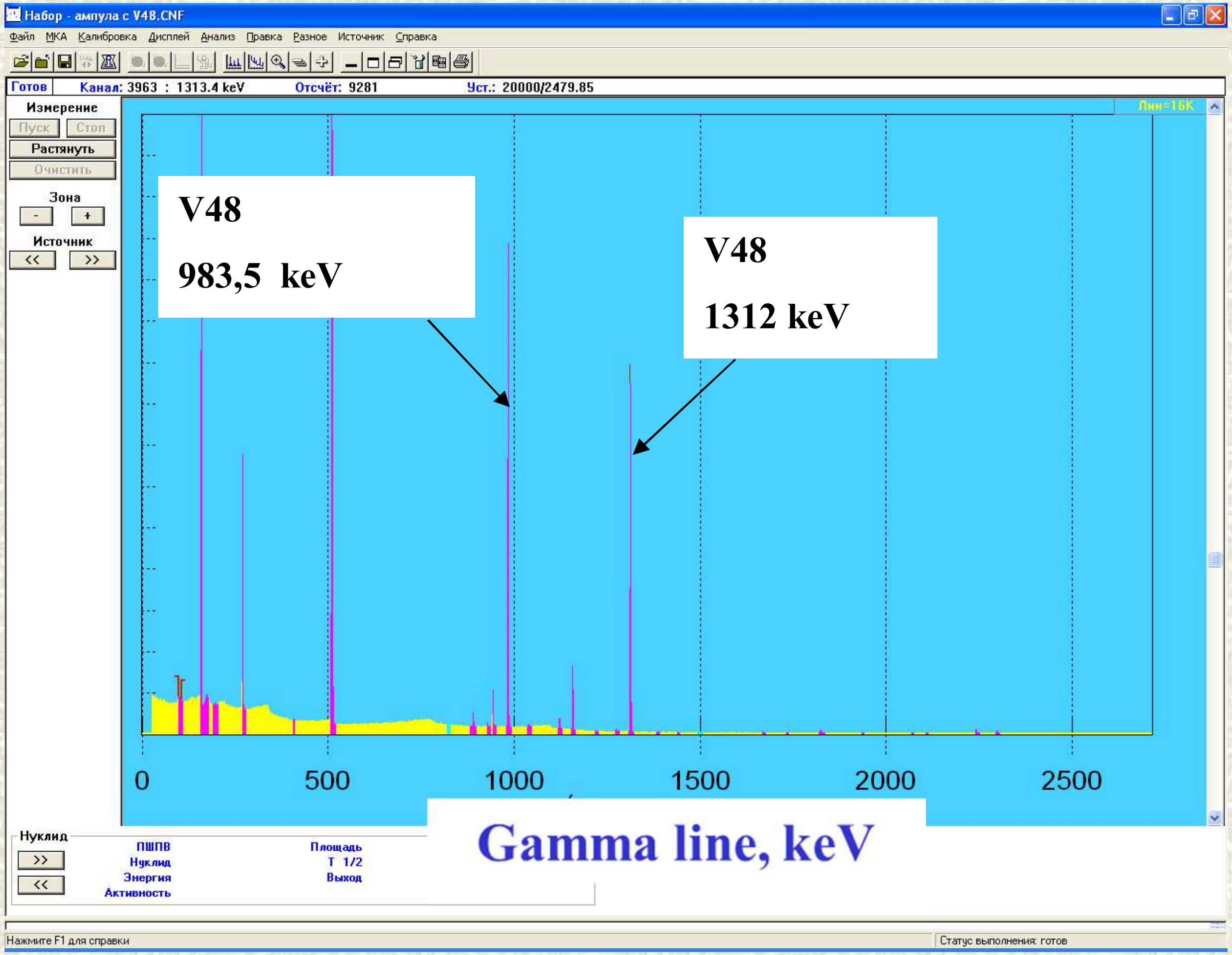
In the last 10 - 20 years the production and consumption of silver and titanium (in the form of dioxide TiO_2) nanoparticles has dramatically increased in various fields of industry, including food production, medicine, pharmaceutical and other fields of human activity.

Proton activation analysis



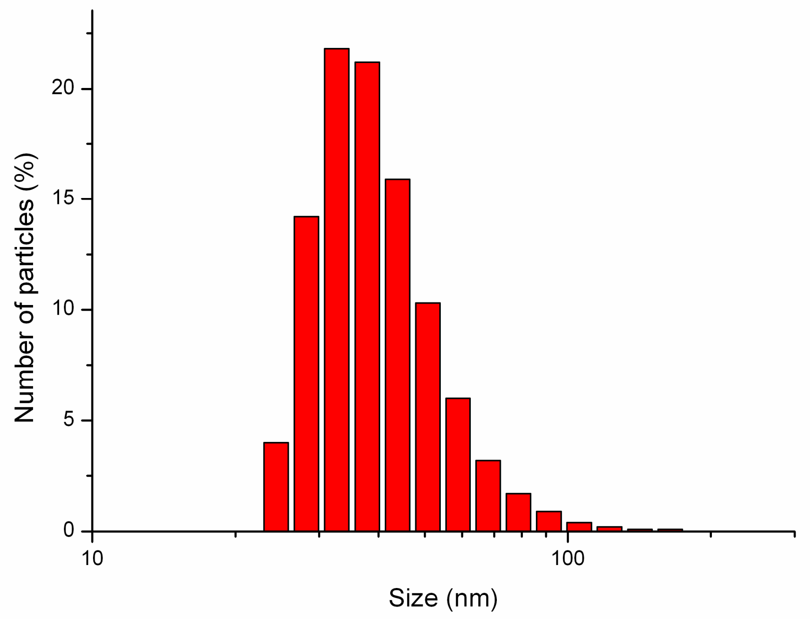
From IAEA nuclear data base

Proton activation analysis



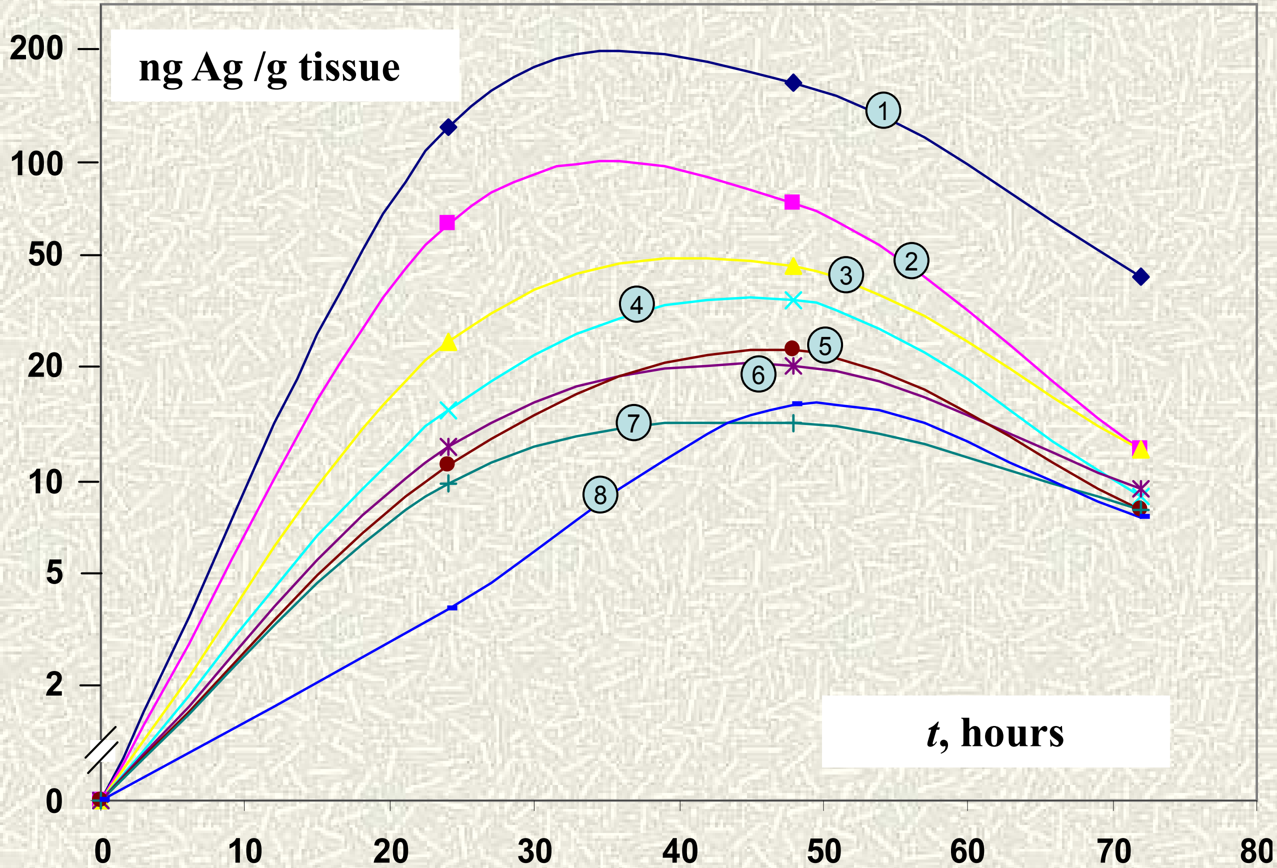
Study of biokinetiks of Ag NP in lab. animals (rats)

Silver nanoparticles Argovit stabilized with polyvynilpyrrolidone. An average size was 33,7 nm



Measurements of linear size of Ag NPs with dynamic light scattering

Studying biokinetiks of Ag NPs in lab. animals (rats)



Ag NP concentration in tissues of rats after single peroral probe administration (0.25 mg/rat); 1- liver; 2- spleen; 3- blood; 4 – kidneys; 5-lungs; 6- gonads; 7- heart; 8- brain.

Studying biokinetiks of NPs

Some other results

- **Methods of measurement of mass concentration of nanoparticles, containing silver or zinc, in different media and biological matrixes on the basis of gamma ray and optical spectroscopy, certified by Rosstandart**

- *E.A.Melnik, Yu.P.Buzulukov, V.F.Demin, et. al.*

Transfer of Silver Nanoparticles through the Placenta and Breast Milk during *in vivo* Experiments on Rats // Acta naturae. 2013; V. 5, # 3 (18), P. 45 – 53.

Purposes of research

To develop, demonstrate and practically use effective methods of detecting different trace elements, including in the form of nanoparticles, in food products for supporting safety control, risk assessment and management, biological experiments, development of mathematical models of NPs biokinetics in lab. animals and then in human body.