DETERMINATION OF TRACE ELEMENTS IN FOOD AND THE ENVIRONMENTAL SAMPLES

ОПРЕДЕЛЕНИЕ МИКРОЭЛЕМЕНТОВ В ПРОДУКТАХ ПИТАНИЯ И ОБРАЗЦАХ ОКРУЖАЮЩЕЙ СРЕДЫ

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The presentation shows three recent examples of the activity of the Laboratory of Nuclear Analytical Methods in the field of determination of trace elements in food and the environmental samples. Two of them demonstrate the results obtained for the environmental as well as for food samples.

The last part of the presentation describes the proficiency testing, including interlaboratory comparison, for the testing of accuracy that different laboratories can achieve.

В презентации представлены три примера деятельности Лаборатории Ядерных Аналитических Методов в области определения микроэлементов в пищевых продуктах и пробах окружающей среды. Два из них демонстрируют результаты, полученные для окружающей среды, а также для образцов пищи.

В последней части презентации описывается проверка квалификации, включающая межлабораторное сравнение, для проверки точности определения, которую могут достичь разные лаборатории.

Keywords: trace elements, food, environment, neutron activation analysis, mass spectrometry, interlaboratory comparison.

Ключевые слова: микроэлементы, пищевые продукты, окружающая среда, нейтронный активационный, анализ, масс-спектрометрия, межлабораторные исследования.

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The need for accurate chemical trace analysis is vital to answering industry problems, when rapid and accurate results are essential to addressing a question regarding a product's purity (e.g. in the food or pharmaceutical industry). Fast and precise methods for determination of the environmental contamination plays also an important role in human health, as presence of numerous trace elements, even at low levels, may cause harmful effects.

The Laboratory of Nuclear Analytical Methods of the Institute of Nuclear Chemistry and Technology specializes in nuclear and nuclear-related analytical methods for applications in many specific fields of high technology, especially nuclear technology, but also health and environmental problems. The main area of activity of the Laboratory includes inorganic trace analysis. For this purpose, new procedures of chemical analyses for various types of materials have been developed. The main analytical techniques, but not the only, employed in the Laboratory comprise: neutron activation analysis with the use of a nuclear reactor (instrumental and radiochemical modes), inductively coupled plasma mass spectrometry (together with laser ablation and HPLC) as well as gamma-ray spectrometry and alpha- and beta-ray counting.

Gamma neutron activation analysis (NAA) is a technique used for determining the presence and amount of many elements simultaneously in samples ranging in size from small to very large. The sample is continuously irradiated with a beam of neutrons The elements of the sample absorb these neutrons and emit prompt gamma rays which are measured with a spectrometer. Each element emits a unique gamma ray. The energies of these gamma rays identify the neutron-capturing elements, and the intensities of the peaks at these energies reveal their concentrations.

The LA ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) method profits the laser evaporation of small amounts of material from the sample surface in an inert gas atmosphere (usually argon), then the aerosol is

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transferred to the carrier gas stream (also argon) to the coupled plasma mass spectrometer. The plasma ionizes the analyte particles (particles). Positive ions are directed to the mass analyser, where they are separated due to the m / z ratio, and then they go to the detector.

In below, we present three recent examples of the activity of the Laboratory of Nuclear Analytical Methods in the field of determination of trace elements in food and the environmental samples. Two of them demonstrate the results obtained for the environmental as well as for food samples. The last part of the presentation describes the proficiency testing, comprising an interlaboratory comparison, for testing of the accuracy that different laboratories can achieve.

The black summer truffle (*Tuber aestivum*), the second-most commercially valuable vegetable, is harvested from May to August and is most often found in the Mediterranean climate areas of France, Italy and Spain. However, this fungus may be found in almost all European countries. Knowledge on the chemical composition of truffles until now is limited to the organic compounds forming its special taste and smell, but inorganic constituents so far have been rarely documented.

Recently, in cooperation with a group of German scientists, forty three elements present in the mushrooms were determined by three independent analytical techniques: two variants of the neutron activation analysis (PGAA, INAA) and ICP-MS [1]. Mature mushrooms of the black summer truffle were collected at four different locations in Germany: Bavaria, Thuringia, Lower Saxony and North Rhine Westphalia. From a few large fruit bodies additionally, the outer skin (peridium) and the inner soft part (gleba) was collected separately and dried as well.

Results of the analyses are presented in Table 1 and Figure 1.

Table 1 – Percent composition of main metals (more than 0.01 %) found in the summer truffle

	C	P	S	Ca	N	Si	Mg	K	Al	Na	Cl	Fe	Zn	Cu	Ti	V	Mn	Rb
%	43.20	20.91	9.91	5.43	4.79	4.48	3.07	2.90	1.82	1.18	0.60	0.50	0.39	0.15	0.10	0.07	0.05	0.01
SD	1.60	4.25	2.95	1.75	0.78	3.92	0.94	0.45	1.32	0.76	0.20	0.44	0.10	0.04	0.06	0.05	0.03	0.01

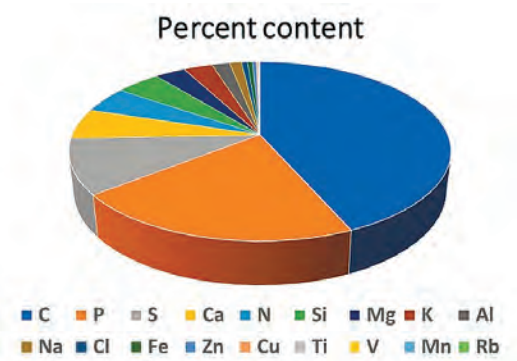

Figure 1 – Percent composition of main metals (more than 0.01 %) found in the summer truffle

Comparison of determination of Al, Fe, Zn and Cd in six samples of the summer truffle made by different analytical methods is shown in Table 2.

Table 2 – Comparison of the elemental analyses of Al, Fe, Zn and Cd (mg/kg [dry weight]) made by different methods in six samples of the summer truffle

Analytical techniques	Element	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	**Percent**
ICP-MS	**Al**	1575±627	811±269	640±468	847±914	393±89	490±237	1.82±1.32
PGAA		2175±189	2225±479	1725±263	1450±129	1600±115	1250±308	
ICP-MS	**Fe**	398±206	177±92.8	127±74	78.1±57.2	115±28.8	261±209	0.50±0.44
INAA		574±187	232±125	159±79.2	66.7±45.4	118±20.9	293±26.5	
PGAA		360±110	223±216	155±144	243±246	93.3±51.3	425±270	
ICP-MS	**Zn**	108±23.2	126±27.2	155±13.1	210±25.1	167±25.6	193±41.5	0.40±0.10
INAA		123±25.6	141±28.6	177±15.8	205±35	172±23.3	195±57.3	
ICP-MS	**Cd**	2.43±0.35	2.98±0.93	2.36±0.86	2.7±0.31	5.74±1.11	2.71±0.99	0.01±0.00
PGAA		2.07±0.3	2.44±0.7	2.07±0.72	2.13±0.24	4.43±0.84	2.13±0.79	

It is seen, that determination by more than one technique generally provides the results which agree within the experimental error of determination. The only exception is observed for Al, which showed systematically higher values in all samples by PGAA compared to ICP-MS.

Białowieża Forest is the last remaining primordial forest in Europe. It covers an area of over 1500 km^2 in the calm corner of Poland and Belarus. On the Polish side, part of the Białowieża Forest exists as the Białowieża National Park, with an area of about 105 km^2. The forest is home to several types of unique birds, insects and thousands of mushrooms. It is also known as the last sanctuary of the European bison - the largest land mammal in Europe. There are also numerous old specimens of oak, elm, lime or several other representatives of trees. For this reason, Białowieża Forest has been recognized by UNESCO as a Biosphere Reserve and World Heritage Site.

Existing literature inspection has shown that in 2009 the mean content of Mn, Zn, Cu, Pb, Cr, Ni and Cd in soils from the Białowieża National Park have been determined as 297, 29, 8, 12, 16, 10, and 0.29 mg/kg of soil, respectively [2].

To perform quick analysis of heavy metal content is relatively difficult due to existing analytical methods being time-consuming. Therefore, the aim of work performed in the Institute of Nuclear Chemistry and Technology in collaboration with the International Sakharov Environmental Institute of the Belarusian State University was to assess the concentration of several heavy metals in soils collected from different areas of the Białowieża National Park (Polish part) with possibly different types of anthropogenic impact.

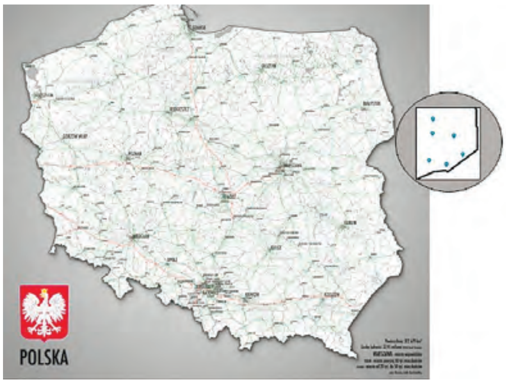

Figure 2 – Sampling locations of the Bałowieża Forest soil in this study

Six soil samples were collected in August 2019, twenty years after the measurements of Gworek *et al*, according to the IAEA guidelines [3]. Sampling locations of the Bałowieża Forest soil is shown in Figure 2. Before collection of the soil samples, flora was removed, and subsequent removal of forest bedding was carried out. Then, the samples were digested using a microwave assisted high-pressure system (Anton Paar Multiwave PRO, USA) equipped with temperature and pressure regulation, transferred into the PFA volumetric flasks and diluted. After addition of indium as an internal standard, metal content present in the samples was determined using ICP-MS instrument ELAN DRC II (Perkin Elmer) with crossflow nebulizer with Scott double-pass spray chamber and Ni cones.

Results of the analyses are presented in Table 3 and Figure 3.

Table 3 – Mean concentrations of metals in samples from different Bałowieża sites in (mg/kg) dry weight determined by the ICP-MS

Element	Mn	Zn	Pb	Ce	V	Ni	La	Nd	Cu	RE	Co	Th	U	Cd
Mean	294	24	17,53	9,79	9,55	5,82	5,18	3,94	3,09	1,41	1,33	1,32	0,59	0,11
SD	150	4	7,09	1,91	2,92	0,42	0,98	0,76	1,01		0,47	0,47	0,16	0,06

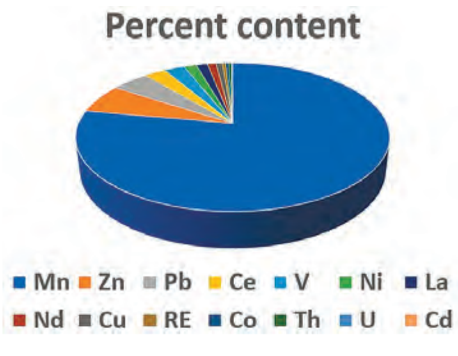

Figure 3 – Percent composition of metals found in the samples collected from different sites of Bałowieża Forest determined by the ICP-MS method

It may be seen, that the content of manganese and zinc found in present work do not differ from the literature data [2] by more than 10%. Copper and lead content are higher by 40% and 150%, respectively. Taking into account, that the determined values are low and the sample collection points are different in both studies, the ICP-MS method seems to be reliable method for analyses of the environmental samples. Considering the fact that the determined values do not differ significantly from the results provided by Goworek *et al* [2], it can be assumed that the content of metals in the Białowieża Forest soil has not changed in the last twenty years.

All measurement gives rise to inaccuracies, technically known as 'errors'. The term 'error' does not imply that a mistake has been made, merely that the outcome of the measurement process varies.

The measurement of chemical concentration requires far more complicated procedures than typical physical measurements, e.g. a length or time. If it is not a problem to measure the physical properties to an accuracy of one part in a million, chemical measurements can seldom be made with better accuracy. This is especially important if concentrations are very low, for instance trace elements determined in foodstuffs.

For this reason, periodic participation in the interlaboratory comparisons (ILC) and the proficiency testing (PT) is an important tool to assess the laboratory competence. It allows improving the quality of laboratory routine work and comparing its results with those of other laboratories. It can be also used to verify reliability of the data produced by a laboratory and provide confidence in measurement results to the users of laboratory services. Since 2004, the Institute of Nuclear Chemistry and Technology has been involved in conducting PTs on the determination of selected man-made radionuclides. The PTs were conducted on the request of the National Atomic Energy Agency (Poland).

The PTs were provided in accordance with PN-EN ISO/IEC 17043:2011 [4]. Results of the determination made by any laboratory have been expressed in terms of *z* and *zeta* scores [5,6]. The values of $z<3$ and $zeta<3$ have been established as the level of acceptance of the result in the PT.

The activity concentration of the following radionuclides: ^{137}Cs, ^{90}Sr, ^{3}H, ^{226}Ra, ^{241}Am and ^{239}Pu were determined in water, food samples and soil. Concentration of the radiation activity in the individual materials ranged from the natural level to 30 Bq/kg. Eleven leading laboratories involved in the radioactive contamination measurements in Poland participated in PTs. The results of the PTs, observed trends in laboratory performance and benefits for the laboratories participating in PTs were evaluated and presented every year. An example of *z* and *zeta* scoring of the results of ^{241}Am measurement in water (PT organized in 2019) is shown in Figure 4.

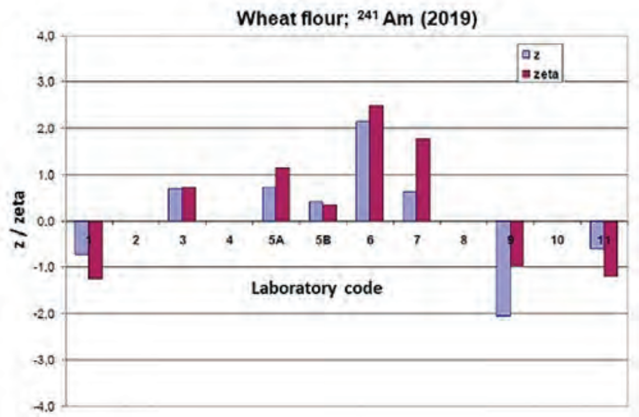

Figure 4 – An example of z and zeta scoring of the results of ^{241}Am measurement in water (PT organized in 2019)

Every year, any laboratory received a certificate of quality from the organizer. Institute of Nuclear Chemistry and Technology invites further laboratories to participate the PT for free of charge.

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