

# RECENT APPLICATIONS AND DEVELOPMENTS OF NEUTRON ACTIVATION ANALYSIS AT THE NUCLEAR PHYSICS INSTITUTE AS CR, CZECH REPUBLIC

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## Abstract

Facilities for neutron activation analysis (NAA) at the Nuclear Physics Institute (NPI) are described. Applications and developments of NAA achieved at NPI within the last five years are briefly discussed. These involve geochemistry, mycogeochemistry, food and agriculture, archaeometry, certification of new reference materials, and methodological development of  $k_0$ -INAA. The purpose of NPI participation in the interlaboratory testing organized by the IAEA and the lessons learned are reviewed, and future plans are outlined.

## 1. INTRODUCTION

NAA has been traditionally pursued at NPI since the end of the 1960s, after the advent of Ge semiconductor detectors for high-resolution  $\gamma$  ray spectrometry [1]. Presently, neutron irradiation is carried out in the LVR-15 research reactor of the Research Centre Řež, Ltd. operated at 9-10 MW thermal power, in which thermal, epithermal and fast neutron fluence rates of up to  $5 \times 10^{13} \text{ cm}^{-2} \cdot \text{s}^{-1}$ ,  $3 \times 10^{13} \text{ cm}^{-2} \cdot \text{s}^{-1}$  and  $1 \times 10^{13} \text{ cm}^{-2} \cdot \text{s}^{-1}$ , respectively, are available in vertical channels. The position of vertical channels used for NAA in the reactor active core is schematically depicted in Figure 1. One of these channels (H1) is equipped with a pneumatic transport system for short-time irradiation, in which polyethylene containers can be irradiated for 10 s – 3 min. with the transport time of 3.5 s. In three other channels long-time irradiation in Al cans can be carried out for several hours to several weeks.

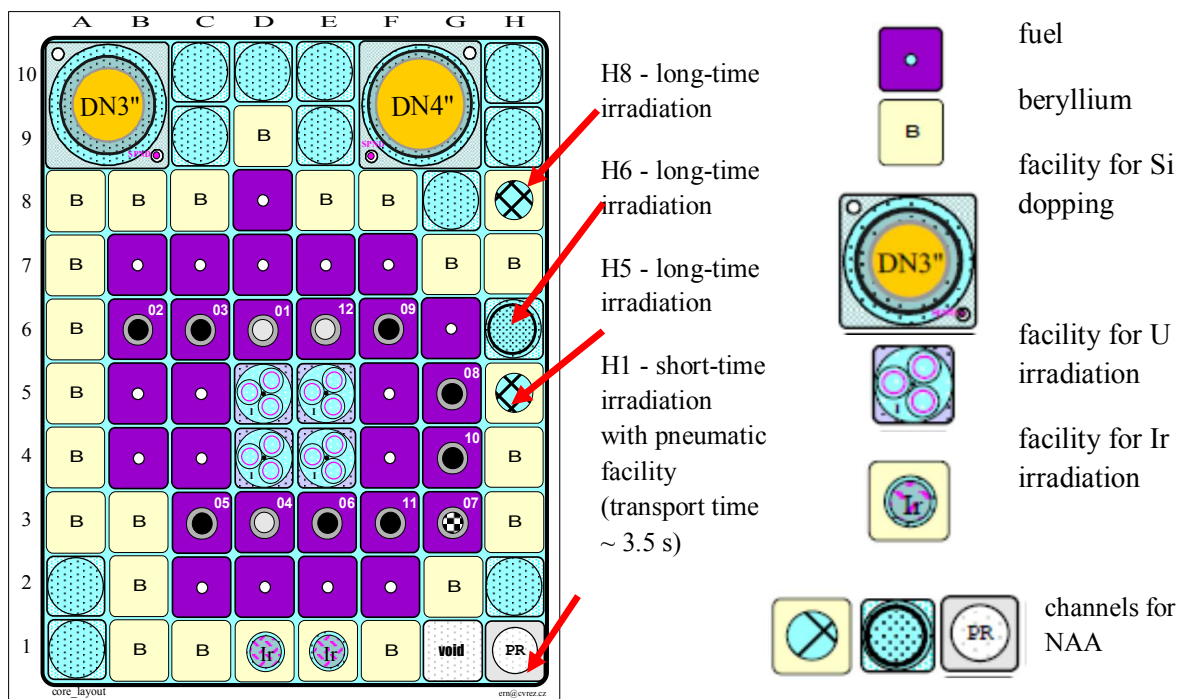


FIG. 1. Example of configuration of active of the LVR-15 reactor.

Both short- and long-time irradiation can be performed in special containers made of or inlaid with a 1 mm Cd shield to screen out thermal neutrons and to achieve selective activation with epithermal neutrons and/or fast neutrons. For measurement of the induced activities, the laboratory is equipped with a Canberra Genie 2000 computer controlled  $\gamma$  spectrometric system, which comprises four coaxial HPGe detectors with relative efficiency in the range of 20-78% and FWHM resolution of 1.75-1.87 keV for the 1332.5 keV photons of  $^{60}\text{Co}$ , two planar HPGe detector with the effective area of 500 mm<sup>2</sup>, thickness of 15 mm, FWHM resolution of 550 eV at 122 keV, and one well-type HPGe detector with the active volume of 150 cm<sup>3</sup>, FWHM resolution of 2.02 keV at 1332.5 keV, well dimensions 16 × 50 mm<sup>2</sup>. For a dynamic correction of the dead-time and pile-up effects, Canberra 599 Loss Free Counting modules are used. The Canberra Genie 2000 software is used for data reduction. Both relative and  $k_0$ -NAA standardization can be performed at NPI, the latter with the use of Kayzero for Windows program. To facilitate counting of large batches of solid samples, two coaxial HPGe detectors are equipped with a pneumatic sample changer. Contamination-free sample preparation is carried out at a clean bench, which provides Class 10 working environment. Ordinary chemical laboratories, as well as radiochemical laboratories with disposal systems for both solid and liquid radioactive waste are integral parts of the laboratory of NAA at NPI.

## **2. SCOPE OF CURRENT ACTIVITIES AND INTERESTS**

The advantages of NAA for highly accurate determination of up to 40 elements at levels ranging from several percent down to the sub- $\mu\text{g g}^{-1}$  level by non-destructive, so-called, instrumental NAA (INAA) have traditionally been used at NPI in geo- and cosmochemistry, environmental control and monitoring, biomedical, nutritional, material and archaeological research and in quality control analyses and preparation of reference materials of chemical composition. For determination of very low levels, down to the ng g<sup>-1</sup> level, of several elements, such as V, Cr, Co, Ni, Cu, As, Se, Mo, Sb, I, rare earth elements, Re, and Hg, procedures of radiochemical NAA (RNAA) have also been developed [1, 2]. These and the previously developed INAA procedures allowed us to further employ NAA, and also photon activation analysis (PAA), in studies concerning geo- and cosmochemistry, mycogeology, archaeology, agriculture and nutrition, quality control of other analytical methods and certification of new low-level reference materials. The main methodological development concerned implementation of  $k_0$  standardization in NAA.

### **2.1. GEOCHEMISTRY**

#### **2.1.1. Characterization of sediment profiles at the Jurassic-Cretaceous boundary**

The tectonic movements at the end of Jurassic initiated physicochemical, climatic, and temporarily biological differentiation of the Boreal (northern, cold) and Tethyan (southern, warm) realms. Differences in the taxonomic composition especially in marine biota between both realms complicates reliable determination and biostratigraphic correlation of a global Jurassic-Cretaceous (J/K) boundary. For a detailed and precise correlation of the J/K boundary interval in the Tethyan and Boreal regions based on high-resolution magnetostratigraphic, micro- and macropaleontological, and geochemical data, key profiles in both the Boreal and Tethyan realms were selected. For geochemical characterization, NAA methods combined with instrumental photon activation analysis (IPAA) were employed.

In geochemical characterization of limestone samples from the Brodno section (Slovakia - Tethyan realm), nickel and antimony anomalies exceeding almost twenty times the levels in neighbouring beds were found near the beds assigned to the J/K boundary. Geochemical

characterization of a vertical profile around the supposed J/K boundary situated on the Nordvik Peninsula (Middle Siberia, Russia - Boreal realm) has shown a sharp geochemical distinction between the central layer of phosphatized limestone and the surrounding argillite beds. A RNAA procedure was employed for assaying platinum group elements (PGE), which did not confirm significantly elevated PGE levels reported previously for the Nordvik J/K boundary. Only slightly elevated levels of Pt and Ir were found in pyrite aggregates inhomogeneously distributed throughout the profile. Concentrating of the elements in sulphides and phosphates in the beds near the J/K boundaries in both realms might be explained by diagenetic reductive processes following decomposition of buried organic matter, connected with volcanism or possibly with an isochronous meteoritic impact [3, 4].

### **2.1.2. Study of tektites and impact glasses**

Impact glasses and tektites are formed as a result of the impact of large meteorites on the Earth's surface by melting of surface materials, particularly sedimentary rocks and unconsolidated surface sediments. The Central European tektites – moldavites – and impact glasses from the Zhamanshin crater were studied by various modes of NAA and PAA, with the aim to contribute to the identification of their parent materials and elucidation of the processes which participated in their formation.

Formation of the Central European tektites - moldavites - has been associated with a large meteorite impact to Ries region in Germany 14.7 million years ago. Unambiguous assigning all source materials of moldavites and processes of their chemical differentiation still remains open. Some differences in chemical composition between moldavites and sediments of the corresponding age from the vicinity of the Ries crater could be explained by a hypothesis, according to which the ash from biomass burned during the impact contributed to the parent materials. Geochemical characterization of a large collection of moldavites has shown that the unconventional biogenic component could be indicated by the enrichment in elements essential for plants (e.g., K, Ca, Mg, Mn) and the depletion of nonessential elements (e.g., Na, Rb, Sr, Ba), similarly to redistribution of these elements during their transfer from soil to plants. Other evidence supporting the hypothesis has been obtained by analysis of carbon isotope composition, which corresponds to the composition of organic matter in the major part of terrestrial vegetation [5, 6].

Homogeneous, tektite-like impact glasses have been recovered from the one million years old Zhamanshin crater in Kazakhstan. Geochemical analysis of a large set of these glasses has shown that they can be divided into two geochemically different groups. The lustrous, silica rich (acidic) glasses with a high Ni content have been classified among the glasses conventionally denoted as irghizites. The dull, silica poor (basic) glasses with a very low Ni content have been classified as a separate type of impact glass, which should not be confused with the large, heterogeneous impact glass forms – zhamanshinites. Within both primary groups, further division has been suggested based on lower contents of Ni in a subgroup of irghizites, and evidence of mixing of source materials for both primary groups in a part of the basic glasses. Based on the high contents of Ni, Cr, Mn, Fe and Co in surplus over their background (terrestrial) levels, and on a rather convincing assignment of the impactor to ordinary chondrites, the fraction of the extraterrestrial component in the analysed irghizites has been estimated between 4 wt% and 21 wt%. Iridium was determined in a single irghizite in content more than ten times lower than corresponding to a chondritic component, which could be explained by significantly lower volatility of Ir compared to other extraterrestrial components such as Ni, Cr, Mn, Fe and Co [7].

## 2.2. MYCOGEOCHEMISTRY

Macrofungi (mushrooms) are heterotrophic eukaryotic organisms classified in the kingdom of Fungi. According to their lifestyle, they are recognized as parasites, saprotrophs and mutualists – ectomycorrhizal symbionts. Saprotrophic and ectomycorrhizal fungi are known as very effective accumulators of various trace elements including alkali metals (Rb, Cs), noble metals (Au, Ag), toxic heavy metals (Cd, Hg) and metalloids (As, Se). Concentrations of these metals in fruit-bodies can be much higher than those in underlying soils.

Bioaccumulation of Au in ectomycorrhizal and saprotrophic macrofungi was investigated in the vicinity of the Mokrsko gold deposit, Czech Republic [8]. Fruit-bodies were analyzed for Au by INAA and the highest concentrations were verified by ICP-MS. Ectomycorrhizal fungi yielded from 0.88-564 ng·g<sup>-1</sup> (d.m.) of Au in 79 samples. Saprobic fungi (75 samples) from the same locations yielded significantly higher concentrations: 3-7739 ng·g<sup>-1</sup> (d.m.) of Au, with the highest contents in *Lycoperdon perlatum*. These are the highest recorded concentrations of Au in naturally-occurring fungi/vascular plants. Concentrations of Au in ectomycorrhizae were approximately 4-10 times higher than those in fine roots. It appears that saprobic fungi, namely several terrestrial saprobes of the genera *Agaricus* and *Lycoperdon*, are more efficient than ectomycorrhizal fungi at taking up Au, probably assisted by other microbiota and/or by a range of naturally-occurring compounds that have yet to be identified.

Silver accumulation in macrofungi was studied in a large number of species [9] and the data obtained by INAA were thoroughly compared with those published in the literature. In pristine areas, the median Ag concentrations of ectomycorrhizal (ECM) and saprobic (SAP) macrofungi were 0.79 µg·g<sup>-1</sup> and 2.94 µg·g<sup>-1</sup>, respectively. In these areas, hyperaccumulation thresholds for Ag in ECM and SAP macrofungi are proposed as 100 µg·g<sup>-1</sup> and 300 µg·g<sup>-1</sup>, respectively. In the vicinity of Příbram (Ag-polluted area in the Czech Republic), the Ag concentrations in macrofungi (ECM and SAP) were significantly elevated with the median value of 24.7 µg·g<sup>-1</sup> and the highest concentrations in *Amanita* spp. of the section *Vaginatae* (304-692 µg·g<sup>-1</sup>).

In accumulating species, namely *Amanita strobiliformis* and *A. submembranacea*, the chemical form of Ag in fungal tissues was investigated [9, 10]. The Ag-speciation analyses showed that intracellular Ag was in wild-grown fruit bodies and cultured extraradical mycelia of *A. strobiliformis* sequestered by metallothioneins, cysteine-rich peptides involved in heavy metal tolerance of many eukaryotes. In *A. submembranacea*, virtually all Ag was found to be intracellular and sequestered in the major 7 kDa and minor 33 kDa complexes. The lack of glutathione and phytochelatin and the presence of a single 3 kDa sulfhydryl-containing peptide in the isolated Ag-complexes suggest that detoxification of Ag in *A. submembranacea* may also rely on metallothionein.

Interaction of Ag with communities of soil saprotrophic organisms was studied in two different soils using a metagenomic approach [11]. Silver was applied in mineral form as well as naturally bound in dry fruit-body biomass of the Ag-hyperaccumulating ectomycorrhizal fungus *Amanita solitaria*. Contrasting behavior of fungi and bacteria in reaction to Ag dosages was observed. The majority of bacterial ribotypes tended to prefer the soil with low doses of Ag, the ribotypes of fungi were more abundant in untreated soils and soils treated with the highest Ag concentration. Organically bound and mineral forms of Ag did not differ substantially in their effects on microbes in samples. The results indicate that decomposing Ag-rich fungal biomass can significantly alter the soil microbiota.

Macrofungi do not accumulate all heavy metals, however. Borovička et al. [12] measured concentrations of U, Th and rare earth elements (REE) in 36 species of ectomycorrhizal (26 samples) and saprobic (25 samples) macrofungi from unpolluted sites with differing bedrock geochemistry. Inductively coupled plasma mass spectrometry (ICP-MS) and epithermal neutron activation analysis (ENAA) were used and compared. It appeared that data recently published on these elements [13] are erroneous, in part because of use of an inappropriate analytical method (XRF); and in part because of apparent contamination by soil particles resulting in elevated levels of Th and REE. Macrofungi from unpolluted areas, in general, did not accumulate high levels of the investigated metals. Concentrations of U and Th were generally below  $30 \mu\text{g}\cdot\text{g}^{-1}$  and  $125 \mu\text{g}\cdot\text{g}^{-1}$  (d.m.) respectively. Concentrations of REE in macrofungi did not exceed  $360 \mu\text{g}\cdot\text{g}^{-1}$  (d. m.) and their distribution more or less followed the trend observed in post-Archean shales and loess.

## 2.3. FOOD AND AGRICULTURE

### 2.3.1. Selenium determination in cereal plants and cultivation soils by radiochemical neutron activation analysis

Selenium is an essential micronutrient for human health, but it is deficient in at least 1 billion people around the globe. Cereals are by far the most significant agricultural crops, not only on a gross tonnage basis, but also by what they represent in terms of energy supply and dietary intake for human nutrition worldwide. Therefore, in co-operation with three Portuguese institutions, namely CERENA-IST, Technical University of Lisbon, URSN-ITN, Instituto Tecnológico e Nuclear, Sacavém, and INRB/INIA-Elvas, National Institute of Biological Resources, Elvas, we studied Se status of major cereals and their cultivation soils. Two species of wheat—bread and durum wheat—were sown at the end of November 2009, and then sampled in different growth stages. Rye was collected during harvest season, and cultivation soils were analysed as well. The first attempts to quantify Se in wheat and rye samples through instrumental neutron activation analysis (INAA) at the Technological and Nuclear Institute (ITN) were unsuccessful, regardless using the long-lived  $^{75}\text{Se}$  or the short-lived  $^{77\text{m}}\text{Se}$  via cyclic INAA. The main reason was a high content of elements, mainly Al, Hf and Ta, which form interfering radionuclides. A high activity of  $^{28}\text{Al}$ , resulting either from the  $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$  reaction with thermal neutrons or from the  $^{31}\text{P}(n,p)^{28}\text{Al}$  reaction with fast neutrons, adversely affects the Se detection limit when the short-lived  $^{77\text{m}}\text{Se}$  is measured, due to an increased background below the 161.9 keV photopeak of  $^{77\text{m}}\text{Se}$ . On the other hand, when INAA is used for low-level determinations via long-lived  $^{75}\text{Se}$ , the most intense gamma-lines of this radioisotope—121.2 keV, 136.0 keV, 264.7 keV, 279.5 keV—are interfered by the gamma-lines of  $^{152}\text{Eu}$  (121.8 keV),  $^{181}\text{Hf}$  (136.2 keV),  $^{182}\text{Ta}$  (264.1 keV) and  $^{203}\text{Hg}$  (279.2 keV), respectively.

To overcome the above disadvantages of INAA, our RNAA procedure [14] was slightly modified and successfully employed for Se determination in both cereals and cultivation soils. Selenium levels were within the range of: 100–225  $\text{ng}\cdot\text{g}^{-1}$  for soils; 3–55  $\text{ng}\cdot\text{g}^{-1}$  for durum wheat; 6–80  $\text{ng}\cdot\text{g}^{-1}$  for bread wheat; and 4–30  $\text{ng}\cdot\text{g}^{-1}$  for rye. Accuracy of the RNAA procedure was proved by analysis of reference materials NIST-SRM 1515 and NIST-SRM 8433. Transfer coefficients relative to soil and to seed were also calculated. It has been shown that Se transfer from soil or seed to wheat plants increases as the plants go through the growing stages (tillering < booting < grain filling), and depends on the wheat variety. Overall, transfer coefficients from soils were lower for rye than for wheat in almost all plant parts [15].

### 2.3.2. Silicon determination in beer using INAA with fast neutrons

Silicon is an important element that is believed to be essential, especially for the proper functioning of connective tissues. Silicon intake can also affect the bioavailability of aluminium, a neurotoxin that has lately been implicated as one of the possible causal factors contributing to Alzheimer's disease. Thus, sufficient dietary intake of Si can affect the toxicokinetics of Al and thereby limit the Al neurotoxicity. Beer is claimed to be one of the best sources of bioavailable silicon, however, little is known about the impact of the brewing process on the concentration of silicon in beer.

Therefore, we studied the impact of the brewing process on the concentration of silicon in lager beer with INAA using the nuclear reaction  $^{29}\text{Si}(n,p)^{29}\text{Al}$  with fast neutrons. NAA is mostly recognised for its highly accurate determination of elements at trace and ultra-trace levels. It is also valued for its accurate determination of elements at much higher levels, especially for those, such as silicon, that cannot be assayed with a low uncertainty using other analytical methods. The Si concentration in beers brewed in several Czech breweries ranged from 13.7-44.2 mg·l<sup>-1</sup> and was highly dependent on the type and quantity of raw materials used, as well as on the brewing technology. The concentrations of silicon in beers of the same brands brewed by different breweries did not differ significantly. The silicon mass balance showed that the main silicon source in beer is barley malt, and that the concentration of silicon in solution significantly increases after mashing, whereas it decreases after fermentation. The majority of silicon remained in the spent grains and the resulting beer contained only about 10% of the silicon present in the raw materials. Our results confirmed that beer is a rich source of silicon in the human diet. In addition, we identified the most important factors that determine the silicon concentration in beer [16].

## 2.4. ARCHAEOOMETRY

### 2.4.1. INAA of sandstones from the Angkor monuments

Angkor temples in Cambodia, included into the World heritage list in 1992, were built during the golden age of the Khmer Empire (9<sup>th</sup> to 13<sup>th</sup> century). Apart from laterite and bricks, sandstone was the major material used in the construction of the Angkor monuments. Although the chronology of Angkor temples is relatively well known, very little information is available about the sandstone origin and petrology. Exact knowledge of the elemental composition of sandstone, including its petrological characteristics and provenance would help for better understanding of construction methods of Angkor monuments and stone deterioration processes. The aim of our investigation was to examine the properties (chemical composition using INAA and petrology) of Angkorian sandstones, hoping that it will be possible to characterize the sandstone collected in 19 Angkor temples and two different quarries accurately. Ultimately, we aimed at examining the possibility that a particular elemental and/or mineral composition of the building material is characteristic for a particular architectural style/building period in the history of constructing Angkor monuments. In every sample, we determined by INAA the contents of 35 major, minor and trace elements, namely Na, Mg, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Lu, Hf, Ta, Th, and U. However, no straightforward correlation was found between the sandstone features and a presumed construction period. The two possible reasons for the poor correlation between the chemical/mineralogical composition of the sandstones blocks and any particular construction period are as follows: (1) the inherent inhomogeneity of sandstone resulting from the effects of detritus recycling and fractionation by sorting and mixing in the Khorat basin; (2) sandstone building blocks were taken from

several sites (quarries) during the construction of a particular temple structure or its part. The latter explanation is a novel one and would alter some of the present presumptions about how the Angkor monuments were built. Its plausibility can only be tested from analysis results of the sandstone material taken from numerous and as yet undiscovered ancient quarries [17].

#### 2.4.2. Was Tycho Brahe murdered by mercury?

World-renowned Renaissance astronomer Tycho Brahe died in Prague on 24 October 1601, after 11 days of sudden illness. Several conspiracy theories regarding his death have been aired, the first shortly after his death. A key factor in the still lively debate is whether he was administered mercury—as medicine by his own hand, or as poison by an unfriendly hand. In 2010, Brahe’s grave was reopened by a Czech–Danish research consortium and samples of his remains, namely hair, beard hair and bones were procured and analysed. Hairs with well identified roots by optical microscopy were cut into 5-mm sections, washed by the IAEA recommended procedure [18], and mercury was determined by RNAA [19]. Results for three segmented hair samples are given in Figure 2. Each experimental point was obtained by analysis of 25-30 individual hair segments. Hair provides a lasting record of exposure to trace metals [21] over the last few months of life, depending upon the hair length. The hair samples analysed in this study reflect the Hg intake over approximately the last 2 months prior to the death of Tycho Brahe, assuming the most frequently cited hair growth rate of 10 mm per month [21]. Most of the Hg values found in hair of Tycho Brahe are in the normal range. However, the very highest value,  $16.4 \text{ mg}\cdot\text{g}^{-1}$ , is slightly higher than the present normal range, and a factor of four higher than the present median value. The Hg exposure decreased in the last 2 months prior to the death of Tycho Brahe, most markedly in the last 2 weeks (Fig. 2).

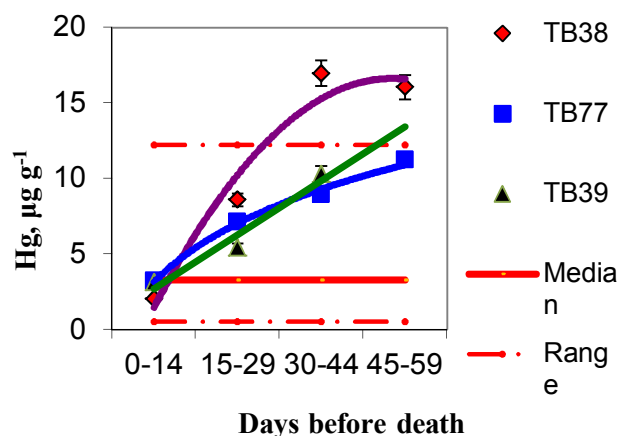


FIG. 2. Hg concentrations in three segmented hair samples from Tycho Brahe (TB38, TB39, TB77). The error bars show the combined uncertainties ( $k = 1$ ). Also shown are the range (dotted line) and the median (dash-dot line) of normal Hg concentrations in hair [20].

Thus acute exposure (poisoning) of Tycho Brahe can be excluded, as the Hg contents found are below the levels of  $200\text{--}800 \text{ mg}\cdot\text{g}^{-1}$  seen in cases of moderate intoxication [22]. The slightly elevated Hg levels suggest that Brahe could possibly have been exposed to small and relatively harmless doses of Hg during the last weeks prior to his death, possibly due to his own medication, *Medicamenta tria* [23]. Human bones concentrate Hg much less efficiently than hair, normally rendering bone Hg concentrations a factor of 10–100 less than the corresponding hair concentrations. The range of Hg bone value for Tycho Brahe determined by Cold Vapour Atomic Absorption Spectrometry (CV-AAS) in Denmark [24] was  $0.054\text{--}$

0.092 mg·g<sup>-1</sup>, which is in complete accordance with the non-exposed medieval and Renaissance individuals from the selection of Danish cemeteries [25]. Thus, we find it likely that Tycho Brahe was never exposed to excess levels of Hg during the last ca. 10–15 years of his life.

### 2.4.3. INAA of ancient glass and copper samples

INAA was used as the main method to determine the composition of La-Tène glass objects from two different localities in Czech Republic and Slovakia. The results of elemental composition allowed to divide the samples into several different groups according to both colour and elemental composition [26, 27] and contributed to the proper classification of the individual findings on the timeline. INAA was also used as a complementary method to XRF for analysis of 161 Early Bronze Age samples (total amount of approx. 210 artefacts). A part of this work was analysis of 14 samples of the chalcopyrites and malachites from the different part of Europe which were a potential source of Early Bronze Age copper. The primary aim - finding the place where the primary minerals originate from - has not been reached completely. Nevertheless, these minerals were probably used as a basic material for the metallurgy of Early Bronze Age [28].

## 2.5. CERTIFICATION OF NEW REFERENCE MATERIALS

The National Institute of Standards and Technology (NIST) has recently prepared a freeze-dried powdered bovine liver tissue material to renew the supply of the well-known Bovine Liver Standard Reference Material (SRM). In a co-operative approach, part of certification analyses was performed at NPI using RNAA procedures developed earlier for low-level determination of vanadium [29] and nickel [30]. Combining the values found in this work with ICP-MS values obtained previously at NIST resulted in a NIST certified value of 8.17 µg·kg<sup>-1</sup> ± 0.66 µg·kg<sup>-1</sup> for vanadium and 44.5 µg·kg<sup>-1</sup> ± 9.2 µg·kg<sup>-1</sup> for nickel. Although labor-intensive, the combination of chemical procedures with neutron activation analysis can elucidate problems and provide critical information for benchmark values [31].

## 2.6. METHODOLOGICAL DEVELOPMENT OF K<sub>0</sub>-INAA

The  $k_0$  standardization method in instrumental neutron activation analysis ( $k_0$ -INAA) has become increasingly used in many laboratories worldwide due to its favourable features. These involve mainly the possibility to determine a large number of elements without the need of irradiation and measurements of their calibration standards, which significantly increases the efficacy of NAA. Therefore,  $k_0$ -INAA has recently been successfully implemented and validated with the use of Kayzero for Windows program. To check the proper implementation of  $k_0$ -INAA, a set of synthetic reference materials (SMELS) was used, while to validate the method for analysis of real samples matrix certified reference materials, such as NIST SRM 1571 Orchard Leaves, NIST SRM 2704 Buffalo River Sediment, NIST SRM 1633b Constituent Elements in Coal Fly Ash were analysed [32]. Measurement of monitors was carried out considering the methodology of determination of neutron flux parameters  $f$  and  $\alpha$  using bare triple-monitor method employing the Au+Zr monitor set and Kayzero for Windows program. On comparing this evaluation software with the software package  $k_0$ -IAEA we have found that the declared advantage of  $k_0$ -IAEA program that the holistic approach of evaluation of results minimizes the need for user interaction with the routines, its robustness with respect to interference corrections, and its reliability in identifying the origin of peaks has not been fully confirmed [33]. We also noted significant differences between uncertainties evaluated by this and other programs. Therefore, we tested



several programs and proposed calculation of uncertainties of neutron flux parameters and uncertainties of analysis results with the Kragten spreadsheet technique that takes into account all important sources of uncertainties and their correlations [34]. We have also found that the well-known Au–Zr tri-isotopic monitor set as a tool for determining  $f$  and  $\alpha$  neutron flux parameters is not optimal for use in our reactor LVR-15. Hence, we proposed and validated a new monitor set for short-time irradiation consisting of the elements Au + Mn + Rb [35] and a new monitor set for long-time irradiation comprising the elements Au + Mo + Rb + Zn [36].

### 3. PURPOSE OF PARTICIPATION IN INTERLABORATORY COMPARISON, ORGANIZED BY THE IAEA

The main purpose was the laboratory preparation for future accreditation (within two years) in the field of assay of samples with various matrices by  $k_0$ -INAA. Thus, analysis of botanical and environmental samples of unknown composition provided by the IAEA through the Wageningen Evaluating Programs for Analytical Laboratories (WEPAL) was an optimal tool to verify the  $k_0$ -INAA procedures validated previously by analysis of certified reference materials with known composition.

### 4. EFFORTS AND MAIN RESULTS

The NPI laboratory participated in several runs of interlaboratory comparisons (ILC) as given in Table 1. It was not possible to participate timely in one run, because of the late delivery of samples in 2011 and limited operation of the LVR-15 reactor at the end of 2011. Thus, the samples ISE-2011/4 and IPE-2011/4 were analysed at a later date. Within ILC standard operation procedures have been extended and their documentation has been improved. Regular checks of all equipment used in the NPI laboratory have been established, as well as feedback sessions and communication within the analytical team. The results achieved in ILC were classified as belonging to the laboratories with a good performance. Details of the NPI results evaluation are given in the report of the ILC tests results [37].

TABLE 1. PARTICIPATION OF NPI IN ILC

Samples	Received	Analysis started	Analysis completed	Results reported
ISE-2011/4	11/2011	3.10.2012	16.12.2012	20.12.2012
IPE-2011/4	11/2011	3.10.2012	16.12.2012	20.12.2012
ISE 2013/1	6.12.2012	8.1.2013	20.3.2013	26.3.2013
IPE 2013/1	6.12.2012	8.1.2013	20.3.2013	26.3.2013

### 5. LESSONS LEARNED AND CORRECTIVE ACTIONS TAKEN

It surfaced during ILC that an assay of samples of unknown composition usually requires a trial analysis after which the existing standard operation procedures are to be finely tuned. Several mishaps occurred in the stage of reporting due to both human and software imperfections, e.g. typographical errors and incorrect spectra evaluation, respectively, which emphasized the need of improving the integrity checks of the data obtained and establishment of checklists before sending the results to a customer.

### 6. FUTURE ACTION PLAN TOWARD SUSTAINABILITY OF QUALITY

The preparation of NPI laboratory for accreditation of  $k_0$ -INAA for assay of natural and synthetic samples will continue with the goal to obtain the accreditation in 2015. This will involve to complete standard operation procedures for all analytical and reporting steps and to develop checklists for the individual operations. A part of these activities will also include training of the laboratory personnel in getting acquainted with ISO 17025 in detail and with the appropriate quality control measures. Participation in more interlaboratory comparisons is also foreseen.

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