Final Research Report on OTKA grant K124068:

Non-destructive, spatially-resolved element analysis of structured samples

1.) Introduction

Prompt-gamma activation analysis (PGAA) is an elemental analysis technique, where the representative bulk composition is obtained non-destructively. The sample is irradiated with a beam of slow neutrons and the resulting characteristic gamma radiation is detected. PGAA, when applied to the analysis of small and regular-shaped samples, is free of matrix effects and provides elemental mass fractions of high volumetric representativity and metrological quality [1]. When non-homogeneous or heterogeneous objects are measured, a pencil beam is formed by a neutron slit, and concentrations representative to a smaller part of the sample are measured at several spots in a row: this approach was named prompt-gamma activation imaging (PGAI).

The PGAA laboratory of the Budapest Neutron Centre (BNC) is an open user facility, therefore the samples to be analyzed are highly variable in their compositions, sizes, and shapes. Many are of irregular shapes (whole-rock geological samples, meteorites, ancient stone tools) and/or of inhomogeneous composition (composite artifacts, objects with decoration, gilding, or industrial items). Any sampling, coring, or powdering is in obvious conflict with the requirement of non-destructivity. The competing non-invasive or micro-destructive element-analytical techniques are inappropriate for this measurement task either due to their limited information depths and excitation spot sizes [2].

To match this sustained need from our user community for bulk-representative or position-sensitive elemental composition analysis of voluminous, complex-shaped, structured, or inhomogeneous objects, a significant improvement in the PGAA analysis protocol and data processing was necessary. In particular, the deep integration of the PGAA with imaging and computer simulation techniques had been identified as the main goal of the present project. The analytical method development, i.e. the generalization from the ideal point-source geometry to the most complex cases was made in multiple steps, allowing careful validation and exploring the related applications.

2.) Matrix effect of homogeneous samples

At first, analytical formulae of standard PGAA to correct for the matrix effect of homogeneous slabs, or powders sealed in flat rectangular Teflon bags were scrutinized. These methods require the knowledge of the sample dimensions, the (packing) density, the measurement geometry (e.g., the placement angle relative to the beam axis), as well as the linear neutron and gamma-ray attenuation coefficients of the material. For mixtures or compounds, these coefficients are derived iteratively from the composition via the mixing rule. For powder targets, the concept of equivalent thickness was introduced to deal with the variable pile density of packed powders [3]. We have proven that neutron tomography can successfully map the density variation inside of an object [4], even in the case of high-Z materials, where the attenuation and beam hardening effects are significant.

The linear attenuation coefficients of discrete gamma energies could be calculated using available databases; these needed only local validation. The neutron attenuation coefficient of a material, however, differs for every beamline, so those had to be obtained for various materials by a systematic

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series of measurements at the cold-neutron beamline of the NIPS-NORMA station. Transmission factors of thin, pure metal layers of known thicknesses were measured by white-beam neutron radiography, and the experimentally measured coefficients were confirmed by computer simulations. These data were used later in the segmentation of the neutron tomograms, where the different attenuation coefficients indicate the spatial distribution of different constituents. X-ray imaging of these layers was also accomplished to generate raw data for bimodal material classification (i.e., the discrimination between materials based on their neutron and X-ray attenuation coefficients), but here very severe beam hardening effect was experienced, making the quantitative conclusions unreliable.

3.) Stack of layers, 2D/3D structured samples

In the ideal case, the attenuation of a neutron beam by a material layer can be approximated with the Beer-Lambert law. We generalized the formulae for stacked layers of metal plates [5], as well as for circularly symmetric flow reactors used in in-beam catalysis measurements [6], but these could not take into account the beam hardening and the neutron (back)scattering, making the corrections for some highly-absorbing materials imprecise.

Therefore, a more general solution, the Monte Carlo calculation was employed. We applied the MCNP 6.2 code in our calculations. The geometries of the BNC's PGAA and NIPS-NORMA stations were implemented in the simulation environment. The energy distribution of the cold neutron beam was taken from our earlier experiments. The neutron flux density fields and the pointwise neutron capture rates of the selected nuclides were calculated with the FMESH functionality of the MCNP6. These discretized 3D distributions were used to assess the transmission of the neutron beam through the sample and define an emission map of prompt-gamma rays for the subsequent gamma self-absorption calculations [5]. The transmission of the neutrons and the emission rates of the layers in the metal stack could be well reproduced [5]. After the correction, the element ratios of stacked metal layers could be made consistent if the layer sequence or the orientation of the stack was varied [5]. This model is applicable to metallic cultural heritage objects covered with a corrosion layer, patina, metal coating, multi-component industrial products, or cast alloy items where in-depth segregation can take place.

The next level of complexity arises when position-sensitive PGAA measurements are performed on structured samples made of a few distinct materials. When raster scanning such an object, both neutron- and gamma-attenuation factors are position-dependent, since geometry, composition, and material thicknesses impact the propagation of radiation differently at each measurement spot. We assembled two test objects, a 1×8 tower and a 3×3×3 cube, from 7×7×7 mm^3 unit cubes made of limestone, tile, graphite, Fe, Pb, Sn, Cu, Al, and PTFE. This assembly was measured at 18 positions, and for the first time, highly consistent results could be achieved for the masses of the representative components [7]. We compared the cases when the sample was defined analytically in the Monte Carlo simulation or it was derived from the segmented neutron tomogram [7]. We concluded that the segmentation quality strongly determines the accuracy of the voxelized correction, while the analytical geometry definition proved to be very reliable.

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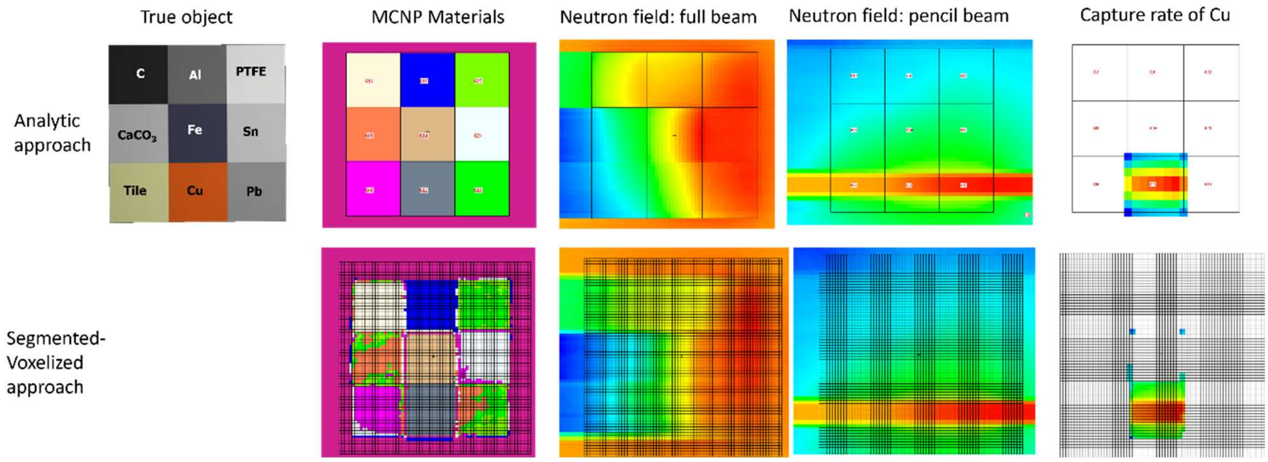

Figure 1. The simulated neutron field and capture rate of a 3×3×3 structured cube assembly

4.) Homogeneous, bulky, irregular-shaped samples

In the case of bulky and/or irregular-shaped objects, the larger sample size increases the matrix effect. This correction procedure requires detailed object geometry. Structured-light optical 3D scanning is a simple, cheap, productive, and non-invasive procedure for digitizing the three-dimensional surface geometry of objects [8-9]. We purchased a RangeVision SMART 3D scanner and integrated its use into our analytical workflow. When this dataset is used for matrix-effect correction, we imply homogeneity. If this is not the case, volumetric neutron or X-ray imaging techniques have to be used.

The 3D digital geometries are useful in creating plastic replicas of the object for tuning the measurement setup and producing gentle custom sample holders for valuable samples [8]. Further, they can be loaded into the Monte Carlo simulation framework to reproduce the interactions of neutrons and gamma rays in the specific geometry. We have programmed a conversion utility to convert a surface mesh to volumetric voxels, in the form that is loadable to MCNP, and fill them with a material whose composition is taken from the uncorrected composition of the PGAA measurement. The other functionality of this utility is to merge voxels of a high-definition 3D tomogram, loaded in the form of a TIFF image stack. In practice, we have chosen 0.5 or 1.0 mm unit cells for simulation voxel size [10, 11]. Each of these voxels has its materials assigned based on the tomogram's grayscale intervals.

We have demonstrated the consistency of this method first on the horizontal scan of a rectangular pavement stone block, where the neutron attenuation was the same in all cases, but more and more layers of materials were between the beam and the detector. After making the suitable corrections, a good overall agreement was found between different analytical lines of an element within the same spectrum, as well as between spectra taken at the different horizontal positions.

Later, an irregular-shaped 1.5-kg bulk stone sample was measured at multiple positions. The object's geometry was defined in MCNP using tomogram-converted voxels, and the measurement positions were simulated. The measurements on the as-received sample were validated with the standard PGAA analysis of destructively-taken powder samples that exactly corresponded to the measurement positions [10].

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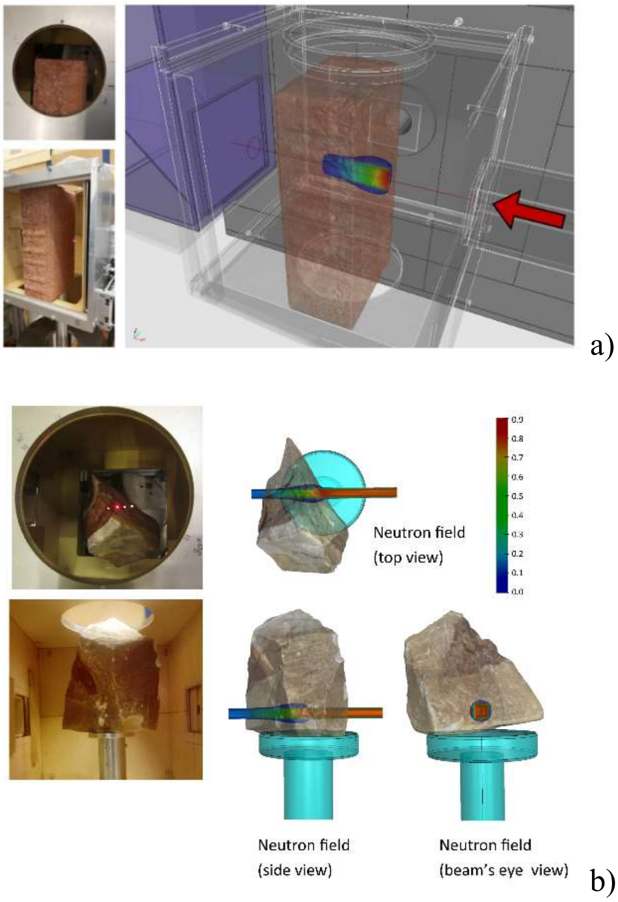

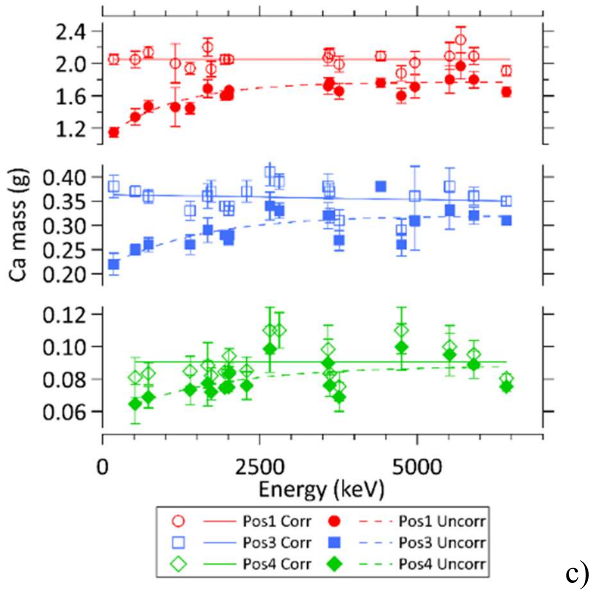

Figure 2. The visualization of the neutron beam as it penetrates a rectangular block (a) and irregularly-shaped bulky stone object (b), where the correction of the negative matrix effect resulted in consistent masses from multiple analytical peaks of element Ca (open symbols) (c)

<u>5.) Non-homogeneous, irregular-shaped samples</u>

In a collaboration with Japanese colleagues, we determined the elemental compositions of volumes of interest enclosed within a complex-shaped art object, an articulated iron lobster artifact from the mid-Edo period (17^{th} century) Japan. Many details of the manufacturing process and the materials used in these objects are unknown, as the knowledge was passed on within the families. Using synchrotron X-ray and neutron imaging, we revealed that it has been constructed from numerous hammered plates. Rivets and two kinds of solder were identified based on the contrasts observed in the XCT images; these were selected for local composition analysis. The adequate correction of neutron- and gamma-attenuation effects made it possible to obtain consistent and quantitative compositions of parts that are inaccessible from the outside. It was found that one soldering material consisted of Cu63Zn37 brass, while the other was a eutectic tin and lead alloy Sn39Pb61. The joint consideration of position-sensitive PGAA element analysis and imaging data allowed a more reliable explanation of the so far independently treated results [11]. This study has been highlighted as the "publication of the month" in April 2022 by the Chemical Sciences Section of the Hungarian Academy of Sciences.

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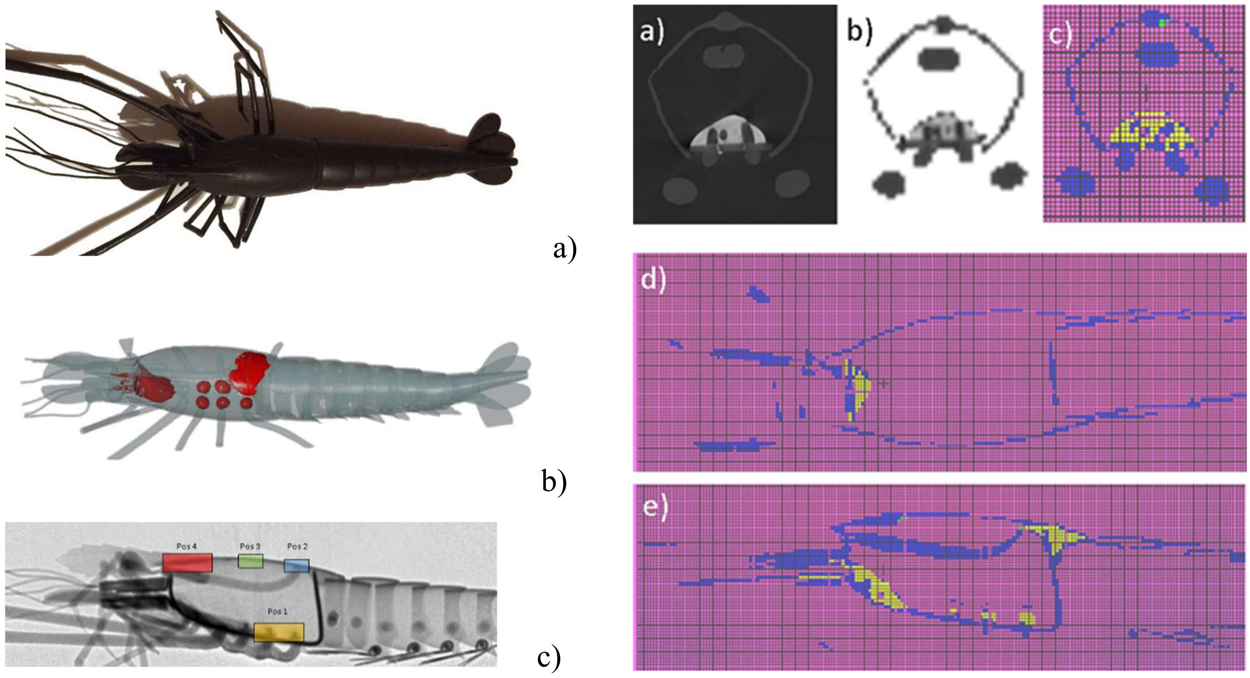

Figure 3. Left column: the photo, the segmented XCT, and the neutron-radiography-driven measurement positions of PGAA of the articulated lobster. Right column: The XCT slices (a) were segmented to discrete materials (b) and converted to MCNP geometry, shown at cutting planes (c-e). Materials are color-coded: air (purple), metal body (blue), solder1 (yellow), and solder2 (green).

PGAI, neutron imaging, and neutron diffraction studies were completed on the iconic sculpture "The Budapest Horse and Rider" of the Museum of Fine Arts, Budapest, attributed to Leonardo da Vinci. Earlier, X-ray-based measurements failed to deliver information on the manufacturing technology, while the present study visualized the remnants of the casting template, the pores of the bronze, and proved the perfect mechanical balance of the sculpture [12].

We contributed to the comprehensive, multi-method characterization of a bronze hoard from the West Hungarian archaeological site Velem-Szent Vid [13]. The identification of the finds' production technologies, functions, and the provenance of their raw materials are now supported by quantitative methods, i.e. non-destructive analytical and structure analysis techniques. These complement well the museological point of view.

In paleontology, the morphology and composition of fossils provide essential knowledge about the classification and development of the species, and about the environment during and after the life of the exemplar. We applied a beyond-state-of-the-art combination of three-dimensional surface and volumetric digital imaging techniques, as well as position-resolved element composition analysis on *Parascutella gibbercula* species [14]. The study of the sediment encapsulated within the sea urchin opens the perspective to a better understanding of the sedimentation conditions of the Paratethyan realm in the Miocene.

The technical experience we gathered since the introduction of the position-sensitive PGAI method in 2006 and the cultural heritage applications of the technique have been summarized in the form of a book chapter in the Springer Handbook of Cultural Heritage Analysis [15].

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6.) Surface-bulk contrasting

In collaboration with the AGLAE PIXE facility of the Louvre Museum, Paris, and the ceramic manufacturing workshop Sevres, a decorated ceramic benchmark object was studied [16-18]. We have turned our handheld pXRF into a basic element mapping device by mounting it on a 2D sample stage. To facilitate the measurement of non-flat objects, an elevation map based on optical 3D scanning can be used. We have confirmed that position-sensitive PGAA is only marginally influenced by the decoration, while XRF or PIXE are appropriate tools to characterize the surface features [18].

7.) Improvements in the prompt-gamma spectroscopy

To efficiently and precisely evaluate a large number of PGAA spectra, we have programmed a utility called Gammafit [19]. Later, a commercial gamma spectrometry software package, Hyperlab 2021, has been purchased. Both were made compatible with the 64k energy histograms created by our new ORTEC DSPEC 502 digital spectrometers. These programs brought a threefold speedup compared to the old spectrum evaluation practice. Our Monte Carlo simulation experience also stimulated the development of nuclear physics applications [20].

8.) Dissemination

We presented lectures at domestic and international conferences. The capabilities and applications of our methods were disseminated in popular science journal articles [21-23], in three television broadcasts [24-26], as well as to the students of the CETS and CERIC-ERIC HERCULES training schools. A video loop of the Budapest Horse and Rider study has been on display at the Leonardo special exhibition of the Museum of Fine Arts.

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