# Developments of measuring technology of X-ray spectrometry and its analytical applications

Summary of the Ph.D. thesis

Gerényi Anita

Supervisor: Dr. Imre Szalóki

Department of Nuclear Techniques
Budapest University of Technology and Economics

2018

# Introduction

Since the first application of the X-Ray Fluorescence (XRF) analytical technique this method has been developed significantly that based on the synchrotron X-ray beams, the new type of low-power air-cooled X-ray tube, the compact energy dispersive SD detectors and X-ray optical elements. The other main direction of the methodological progress is theoretical models described the X-ray spectrometric atomic processes and the fast solutions of numerical calculation methods using the novel computing techniques [West2016]. In the last two decades the published results in XRF referred to improved energy and lateral resolutions of the micro XRF methods, moreover their absolute and relative minimum detection limits. The main tendencies in micro XRF analytical techniques are the "detection of the lowest concentrations of chemical elements in the smallest amount of material during the shortest measuring time as low as possible". One of the results of the progress in micro XRF methods is that nowadays the chemical elements in macro-sized objects and very small volume of materials can be analysed. These methods are called confocal micro X-ray fluorescence (μXRF-CI) and emission micro tomography (μXRF-CT). The essential measuring parameters of these techniques are lateral and energy resolutions that frequently are the ultimate targets of the scientific research in this field. Significant tendency can be recognized in development of the quantification models and algorithms for numerical solutions of the mathematical models in XRF analytical techniques used for 2D/3D microanalysis based on synchrotron radiation.

However, the above mentioned principle of "the faster and the lower" can be applied for laboratory XRF spectroscopic equipment, improving the development of compact XRF spectrometers, in order to build specialised and unique designed XRF spectrometers for laboratory purposes [Tsuji2011].

My research work presented in my PhD Thesis follows the previously described development and research trend in X-ray spectrometry published in the last 15 years that mainly deals with the methodical development of X-ray fluorescence analytical technique and its application on wide range of samples. One of the unique properties of the XRF method is its non-destructive nature, that allows it to apply for industrial purposes and in most cases the sample preparation steps can be neglected. One of the possible fields of industrial utilization of the XRF techniques is the nuclear industry, since during the maintenance period in nuclear power plan often arises the necessity of quick, non-destructive and in-field or in-situ analysis on unknown objects without use of standard samples.

Comparing the X-ray fluorescence analysis with other analytical methods, the usage of standard samples is not required, which is useful in laboratory environment, and during in-field measurements as well.

Based on the preliminary research of the Nuclear Analytical Research Group of the Institute of Nuclear Techniques at BME in the field of XRF, we were invited by the MVM Paks NPP to develop a mobile XRF+Raman equipment for the above mentioned industrial analytical problem in the scope of R+D project. Another similar request was received from the Hungarian Atomic Energy Agency for developing a new XRF+gamma spectrometer for safeguard purposes. With this equipment it should be also possible to analyse radioactive solid substances or objects. In this R+D project we developed a new FPM model that is capable to describe mathematically the complete spectroscopy processes. By solving the system of the equations, the concentration of the sample elements can be calculated numerically. For these model calculations I have developed and constructed a software in MATLAB environment [5], [9], [10].

Based on the relevant publications issued in X-ray emission spectrometry it can be concluded that the μXRF-CI, μXRF-CT and XANES techniques gained more-and-more importance. In the first two methods, applying single bounce and polycapillary X-ray lenses in the path of the excitation X-ray beam, and placing the second one as acceptance lens the lateral distributions of elements can be recorded with 10-100 μm resolution [Servin2012]. Later, it was recognised that these micro-analytical methods can be applied for measurement on a wide range of materials for determination of 2D/3D elemental map and the microstructure. Therefore, these μXRF analytical techniques spread quickly in the co-sciences such as biology [7], geology [Laforce2014], archaeology and arts [Dik2008]. The FPM theoretical model can be adapted to the μXRF-CI methods applied at synchrotron beamlines especially for monochromatic excitation [Mantouvalou2014]. In research cooperation with Department of Plant Physiology and Molecular Plant Biology in ELTE we developed 2D/3D μXRF methods for plant samples in order to measure the quantitative distribution of toxic chemical elements (especially As) in plant tissues and the oxidation states of arsenic. For this analytical purpose we applied the XANES technique in-vivo measuring conditions.

# Research goal

Our research group in the Institute of Nuclear Technique received two invitations from the Paks NPP and the Hungarian Atomic Energy Authority to develop new X-ray fluorescence spectrometers for quick quantitative analysis of atomic and molecular compositions of nuclear waste materials, safeguards samples with non-destructive method, independently from their physical-chemical form. In order to solve these R+D analytical tasks, one of the aims of our research activity was to design a new combination of XRF and Raman spectroscopy in the same individual spectrometric unit. The spectrometer should be capable of analyse identically the same point of the sample with XRF and Raman method. The X-ray spectroscopical systems used at synchrotron beamline HASYLAB L and in our XRF laboratory in Institute of Nuclear Techniques involve a wide range of different equipment's (detectors, X-ray optical units, sample motion devices etc.). However, the main principle in our development activity is to plan and design a modular structure for the FPM calculation models. This property offers a possibility of flexible adaptation of the FPM calculation model to any type of XRF measuring set-up: conventional XRF with using X-ray tubes and monochromatic μXRF-CI with synchrotron radiation [7].

In the Department of Plant Physiology and Molecular Plant Biology in ELTE the biologist colleagues investigated the influence of arsenic and other toxic elements to the plant physiology processes and the possible way to decrease the level of this toxic effect. In addition to the visible biological changes on the plants it is more important information how the toxic elements are distributed in different tissues (root, hypocotyls) and what is the intensity of biological accumulation. Therefore, the aim of the XANES study at HASYLAB L beamline was to help the biological researches for discover how the biological resistance can be increased of cucumber plan against toxicity.

One of the key difficulty of the XRF technique is the quantification i.e. to determine the concentrations of the chemical elements in a sample material. This problem also appears at the case of μXRF-CI and μXRF-CT methods where the analysis is carried out a relatively small part of the sample. For solution this rather complicated theoretical and numerical task several research is continuously performed in different research institutes [Mantouvalou2017], however these solutions sometimes are very complicated and those can be applied only in very special experimental conditions. Therefore, we set as a research goal to construct a new model and numerical approximation algorithm that capable of producing convergent iteration of the concentrations in monochromatic measuring conditions.

# Experimental methods

X-ray tubes in the Institute of Nuclear Techniques and synchrotron radiation of DORIS-III HASYLAB beamline L in DESY were applied for the X-ray emission and absorption analysis, model calculations and the measurement technique developments. Important tool of the research work was the two different X-ray spectrometer developed in the NTI. Both devices involved low-power air cooled transmission X-ray tube and compact SD energy dispersive detector and connected electronics unit. Both of the spectrometers are operated as macro XRF-CI equipment. Calculation of the concentrations of the sample elements were performed by an own developed FPM based software.

In collaboration with the Department of Plant Physiology and Molecular Plant Biology in ELTE we investigated the lateral distribution and the chemical form of arsenic in hypocotyls of cucumber plant grown in nutrient solution. These experiments were carried out in-vivo and in-vitro mode. The preliminary studies of the biological samples were performed with the own developed and constructed laboratory XRF devices. The results of these experiments contributed to the design and optimization of the μXRF-CT and μXRF-CI measurements before the synchrotron beamtime. All the synchrotron experiments were done in cooperation with the colleagues of the X-ray Microspectroscopy and Imaging Group at the Gent University. During these research works we have developed and tested various sample preparation procedures and cryogenic sample cooling methods. Huge number of energy dispersive X-ray spectra was evaluated for that task the MICROXRF2 software and different versions of the core procedure AXIL code were applied such as the WinQXas, WinAxil and bAxil. For the preliminary evaluations of the XANES spectra the ATHENA (part of the software package IFEFFIT) was used. For the final calculation in the XANES i.e. the weight ratio of different oxidation numbers, and the reconstruction calculations in 2D and MA-XRF-CI were performed by own constructed software written in MATLAB environment.

Beamtimes at the Deutsches Elektronen-Synchrotron, DORIS-III HASYLAB L beamline:

1. 2010 May 24 - 28, *Confocal X-Ray fluorescence imaging on cucumber hypocotyls*.
2. 2010 November 26 - December 2. *Confocal X-Ray fluorescence imaging on cucumber hypocotyls*
3. 2011 May 24 - 30, *Three-dimensional micro-XRF/XANES studies on metal toxicity in biological model systems***.**
4. 2011 July 19 - September 8, Development of *wavelength-dispersive detection at beamline L, Hasylab Summer Students Program, L and A1 beamline*.

5. 2011 November 24 - December 2, *μXRF-CI experiments on cucumber hypocotyls for mapping of 2D As distribution*.
6. 2012 May 15 - 22, *XANES experiments for determination of oxidation number of As in cucumber samples in-vivo*.
7. 2012 October 6 - 10, *Three-dimensional micro-XRF studies on metal toxicity in biological model systems*.
8. 2012 November 24 - December 2, *3D μXRF-CI experiments on metal toxicity in biological model systems*.

# New scientific results

1. I have extended the applicability of the basic theoretical model so called Fundamental Parameter Method (FPM) for X-ray sources that radiate continuous spectra. I have proved with theoretical calculations and the results of XRF experiments that this type of continuous X-ray source can be replaced equivalently for FPM calculations by any number of fictive X-ray sources having discrete energy and the sample elements are excited by this great number of source. For the numerical solution of the system of the FPM equations I have developed a new calculation methods and software in MATLAB programing environment.
   Related publication: [5], [6], [10].

2. I have designed and constructed the optical and mechanical positioning system of the XRF-Raman combined spectrometer. I have developed the applicability of the spectrometer with He gas, which measuring method extended the analytical sensitivity down to the range of atomic number of $11<Z<15$. Performing experiments I have determined the minimum detection limits (MDLs) depending on the atomic number and excitation X-ray energy for biological matrix and proved that those MDLs values can be improved by using He gas for elements with light and medium atomic number.
   Related publications: [5], [6], [9], [10].

3. For the μXRF-CI analytical method I have developed a new algorithm for numerical solution based on the FPM theoretical model calculations and a code for performing the numerical solution at the case of excitation by monochromatic synchrotron radiation. The new method capable of reconstruct the quantitative elementary distribution from the μXRF-CI

2D/3D dataset. The applicability of the whole analytical procedure were tested and validated by result of μXRF-CI that experiments were performed on NIST SRM samples at HASYLAB beamline L of the DORIS-III synchrotron in Hamburg.
Related publications: [3], [7].

4. I have demonstrated that the lateral resolution of the 3D-μXRF-CI analysis can be improved significantly by the variation of the step sizes, the fine tuning the excitation X-ray energy and the voxel sizes depending on the atomic number of the analysed chemical elements. Performing experiments at HASYLAB beamline L with monochromatic synchrotron radiation in cryogenic measuring conditions I have proved that the focused, monochromatic synchrotron radiation and in-vivo μXRF-CT combination the elementary maps can be determined in small (1-5 mm) biological samples without damaging the biological structure.
Related publications: [1], [2], [11].

5. With application of synchrotron radiation I have developed a new XANES measuring and data evaluation method for determination of oxidation number of arsenic in plant tissue. I have carried out in-vivo and in-vitro XANES experiments at HASYLAB beamline L for determination of the oxidation number of arsenic in hypocotyls of cucumber plants. I have developed a new algorithm of the mathematical solution and calculation method for the quantitative evaluation of the XANES data to determine the quantity of the possible oxidation numbers in MATLAB programing environment.
Related publications: [4], [8].

# Publications

[West2016] M. West, A. T. Ellis, P. J. Potts, C. Streli, C. Vanhoof, P. Wobrauschek, 2016 Atomic Spectrometry Update - a review of advances in X-ray fluorescence spectrometry and its applications, *J. Anal. At. Spectrom.*, 2016, 31, 1706-1755.

[Servin2012] A. D. Servin, H. Castillo-Michel, J. A. Hernandez-Viezcas, B. C. Diaz, J. R. Peralta-Videa, J. L. Gardea-Torresdey, Synchrotron Micro-XRF and Micro-XANES Confirmation of the Uptake and Translocation of TiO2 Nanoparticles in Cucumber (Cucumis sativus) Plants, *Environ. Sci. Technol*. 2012, 46, 7637−7643.

[Laforce2014], Schmitz S, Vekemans B, Rudloff J, Garrevoet J, Tucoulou R, Brenker FE, Martinez-Criado G, Vincze L., Nanoscopic X-ray fluorescence imaging of meteoritic particles and diamond inclusions, *Anal. Chem.*, 2014, 86, 24, pp. 12369-12374.

[Dik2008] J. Dik, K. Janssens, G. Van Der Snickt, L. van der Loeff, K. Rickers, M. Cotte Visualization of a Lost Painting by Vincent van Gogh Using Synchrotron Radiation Based X-ray Fluorescence Elemental Mapping, *Anal. Chem.*, 2008, 80, 6436-6442.

[Mantouvalou2014] I. Mantouvalou, T. Wolff, C. Seim, V. Stoytschew, W. Malzer, B. Kanngießer, Reconstruction of Confocal Micro-X-ray Fluorescence Spectroscopy Depth Scans Obtained with a Laboratory Setup, *Spectrochim. Acta B*, 2014, 97, 99-104.

[Tsuji2011] K. Tsuji, K. Nakano, Development of a new confocal 3D-XRF instrument with an X-ray tube, *J. Anal. At. Spectrom.*, 2011, 26, 305–309.

[Mantouvalou2017] I. Mantouvalou, T. Lachmann, S. P. Singh, K. Vogel-Mikus, B. Kanngießer, Advanced Absorption Correction for 3D Elemental Images Applied to the Analysis of Pearl Millet Seeds Obtained with a Laboratory Confocal Micro X‑ray Fluorescence Spectrometer, *Anal. Chem.* 2017, 89, 5453-5460.

## Utilization of the scientific results

We have developed a new XRF-Raman combined spectrometer and a calculation method based on the general FPM model. This device is routinely applied in the Radiochemical Laboratory of Paks NPP for quick determination of atomic and chemical compositions of unknown solid objects and materials. The newest version of this type of XRF device without Raman probe is applied for similar analytical tasks in the Training Reactor.  It is also applied in various joint research projects such as other Departments, research institutes Energy Research Institute of the Hungarian Scientific Academy, Hungarian Atomic Energy Authority or Ferenzcy Museum in Szentendre and Paks NPP-II. This equipment is continuously improved technically in order to extend the analysed atomic range, to improve the minimum detection limit and the lateral resolution of the microanalysis.

The results of the synchrotron based micro-analytical studies on biological objects helped the better understanding of the physiological processes in cucumber as model plant. The conclusions of these X-ray micro-analytical empirical investigations were utilized in biological projects dealing with the biochemical processes in plant tissues. Dr. Victoria Czech (ELTE) used these results in her PhD thesis.

Before publishing our new quantitative FPM based micro-analytical model [7] developed for μXRF-CI, a simple FPM model was available only for a specialized sample of homogeneous layers. Our new model offers possibility for analysis of heterogeneous samples.

# List of publication of Anita Gerényi related to the new results:


[1] I. Szalóki, V. Czech, B. De Sambers, A. Gerényi and L. Vincze, Confocal X-Ray fluorescence imaging on cucumber hypocotyls, *HASYLAB Annual Report* 2010.
http://hasylab.desy.de/annual_report/files/2010/20101198.pdf

[2] A. Gerényi, V. Czech, J. Garrevoet, B. De Sambers, L. Vincze and I. Szalóki, Confocal X-ray fluorescence micro-imaging on cucumber hypocotyls, *HASYLAB Annual Report*, 2011.
http://photon-science.desy.de/annual_report/files/2011/20111711.pdf

[3] A. Gerényi, I. Szalóki, Micro-XRF studies on biological samples using synchrotron radiation, *PhD Conference of the Doctoral School for Physics*, pp. 63-66, ISBN 978-963-313-065-0, Budapest, 22. June, 2012.

[4] A. Gerényi, V. Czech, K. Appel, J. Garrevoet, L. Vincze and I. Szalóki, Study of arsenic uptake in cucumber by XANES at HASYLAB Beamline L, *HASYLAB Annual Report*, 2012.

http://photon-science.desy.de/annual_report/files/2012/20122445.pdf

[5] Gerényi Anita, Szalóki Imre, Röntgenfluoreszcens spektrométer fejlesztése, *Őszi radiokémiai napok*, pp. 82-86, ISBN 978-963-9970-42-7, Eger, Október 16-18, 2013.

[6] A. Gerényi, G. Radócz, I. Szalóki, Simultaneous application of X-Ray fluorescence and gamma spectrometer for analysis of radioactive waste material, *26th Symposium of AER on VVER Reactor Physics and Reactor Safety*, pp. 617-624, ISBN: 978-963-7351-27-3, Helsinki, Finland, 10-14., October, 2016.

[7] I. Szalóki, A. Gerényi, G. Radócz, A. Lovas, B. De Samber, L. Vincze, FPM model calculation for micro X-ray fluorescence confocal imaging using synchrotron radiation, *J. Anal. At. Spectrom.*, 32, 334-344, 2017.

[8] A. Gerényi, V. Czech, F. Fodor, L. Vincze, I. Szalóki, In-vivo XANES measuring techniques for studying the arsenic uptake in cucumber plants, *X-ray Spectrom.*,Vol. 46, pp. 143-150, 2017.

[9] I. Szalóki, A. Gerényi, G. Radócz, Confocal macro X-ray fluorescence spectrometer on commercial 3D printer, *X-Ray Spectrom.*, 46, 497-506, 2017.

[10] I. Szalóki, G. Radócz, T. Pintér, jnr. I. Szalóki and A. Gerényi, Development of mobile macro XRF spectrometer and FPM algorithm for surface analysis of solid objects, *J. Anal. At. Spectrom.*, (under reviewing).

[11] I. Szalóki, A. Gerényi, V. Czhech, F. Fodor, L. Vincze, XRF micro-tomography and confocal imaging of 2D distribution of toxic elements in biological objects, (under construction, planned to submit to *Analytical Chemistry*).

## Other publication of Anita Gerényi

[12] A. Gerenyi, M. Borchert and K. Appel, Wavelength-dispersive detection at beamline L, *HASYLAB Annual report* 2011.
http://photon-science.desy.de/annual_report/files/2011/20111547.pdf

[13] I. Szalóki, G. Radócz, A. Gerényi, FPM model for quantitative determination of surface contamination on Si wafers by TXRF analysis, (submitted, to *Spectrochim. Acta B*, 2018).

[14] G. Radócz, A. Gerényi, Sz. Czifrus, I. Szalóki, Determination of 137Cs content in fuel assemblies of a zero power reactor by Monte Carlo based efficiency calibration, (submitted to *Annals of Nuclear Energy*, 2018)

The number of presentations on X-ray analytical conferences in the time duration of 2011-2018: 26 ( the full list can be found in the Thesis).

## Abbreviations:

| | |
|---|---|
| DESY | Deutschen Elektronensynchrotron |
| μXRF | micro X-ray fluorescence |
| CT | computer tomography |
| CI | confocal imaging |
| XANES | X-ray Absorption Near Edge Structure |
| FPM | Fundamental Parameter Method |
| HASYLAB | Hamburger Synchrotronstrahlungslabor |
| 2D/3D | 2 dimension/3 dimension |