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NUCLEAR TECHNIQUES BASED ON X-RAY AND PROMPT GAMMA-RAY EMISSION FOR THE ANALYSIS OF ENVIRONMENTAL MATERIALS

The distribution of elements in the environment, their concentration and dynamics can be seriously affected by human activities. Environmental pollution occurs through the introduction of various substances in soil, water and atmosphere by anthropogenic activities. Often this pollution produces imbalances in terrestrial and aquatic ecosystems, threatening the health of living beings. The complexity of study of the trace metal migration in the ecosystems requires the application of validated research methods and up-to-date techniques and equipment.

The attractiveness of non-destructive methods and the ability to perform simultaneous multi-elemental determinations has led to an extensive application in research laboratories of accurate, precise and sensitive atomic and nuclear analytical techniques for the investigation of different types of materials (industrial, geological, biological, environmental, etc.). Atomic and nuclear analytical methods, such as neutron activation analysis (NAA), X-ray fluorescence (XRF) and particle-induced X-ray emission (PIXE), play an important role in the frame of instrumental analytical methods, mainly for non-destructive characterization of solid samples. For complex examinations of materials of various matrices or research activities in life sciences, interdisciplinary cooperation is advantageous, mainly involving physicists and chemists, but also, e.g., biologists, medical researchers and material scientists.

X-ray based techniques (XRF, PIXE):

The monitoring of the polluting factors in natural environments requires the use of rapid, accurate and, not least, cheap detection methods. From this point of view, the XRF spectroscopy, using both energy-dispersive (ED-XRF) and wavelength-dispersive (WD-XRF) technique, is very suitable for the analysis of elements of the periodic table between boron ($Z = 5$) and uranium ($Z = 92$). XRF technique using stationary or portable ED or WD spectrometers is widely applied for the rapid analysis of the major, minor and trace chemical elements in complex samples for diverse interdisciplinary studies in the laboratory or in the field, with good reproducibility and at low cost.

For the elemental analysis of environmental samples XRF has the advantage of being a rapid and inexpensive method with a simple sample preparation. Quantitative and qualitative analyses are performed without acid digestion processes and a great number of elements can be determined simultaneously in a short time.

XRF and PIXE are two methods very different in terms of their information depth, excitation mechanism, and applied devices. They are based on the ionization of atomic inner shells of a sample/target by a photon (XRF) or charged particle beam (PIXE) entering the target, followed by emission of the characteristic X-rays. The X-rays spectrum is registered by means of an electronic chain based on a high-resolution semiconductor detector. The Z -dependence of the X-ray energy lines in the spectrum, as well as the dependence of the X-ray lines intensities (peak areas) by the element concentrations, allow a qualitative and quantitative determination of the elemental contents in samples. The fundamentals of both techniques in theory and in practice, instrumentation and sample preparation are presented, as well as the problems of matrix correction and secondary effects.

Numerous studies in the life and earth sciences and environmental monitoring on the application of XRF and PIXE techniques to the analysis of natural and environmental samples of various matrices (soils, sediments, fish, aerosols, vegetation, biological samples, food items, etc.) are presented in this course and some papers showing interesting cases in biology, biochemistry, geology, and environmental science are made available to students.

The elements of interest for PIXE in environmental matrices are: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr and Pb.

In order to extend the palette of chemical elements which can be analyzed in environmental samples, including

heavy metals, XRF and PIXE can be combined with other atomic and nuclear spectrometric techniques such as instrumental NAA or atomic absorption spectrometry (AAS).

Prompt gamma-ray emission technique (PIGE):

PIXE belongs to the group of Ion Beam Analysis (IBA) techniques which constitute a cluster of analytical techniques that use an ion beam for study of structures and composition of samples belonging to various classes of materials. Particle Induced Gamma-ray Emission (PIGE) is an IBA technique able to determine light elements, such as Li, B, C, F, Na, Mg, Al, P, S, and Cl, besides some heavier elements (e.g. Cr, Mn, Fe, Co, Cu), based on $(p,p'\gamma)$, (p,γ) , $(p,\alpha\gamma)$ or $(p,n\gamma)$ nuclear reactions of the projectile particles “p” on target samples. Detection limits are discussed in detail, in comparison with those obtained by PIXE and XRF. Advantages and limitations of each technique are highlighted.

The course presents some applications of IBA techniques, such as: i) simultaneously use of PIXE and PIGE ion beam analytical techniques for the determination of some major, minor and trace elements in selected environmental samples (animal tissues, aquatic plants, bottom sediments, soils), collected from polluted and natural protected areas in Lower Danube basin, Danube Delta and Black Sea; ii) applying IBA techniques for bioaccumulation studies of minerals and toxic elements from environment/substrate to related biological tissues in industrial areas.

Conclusion:

The determination of trace elemental levels in different matrices is a challenge for the entire spectrum of analytical techniques, including nuclear and atomic techniques. Due to the fact that all the employed techniques have own advantages and disadvantages, the choosing of one or another technique is dictated by its sensitivity, type of sample matrix under investigation, the range of chemical elements to be investigated in a single sample, rapidity of analyses (including sample preparation, automatisisation, and time of spectra evaluation), cost of instrumentation and level of matrix effects and spectral interferences.

Using a combination of these methods, a large number of microelements could be determined in environmental samples at part-per-million (ppm) level or even less, in the case of INAA. It is worth to mention the great advantage of non-destructivity of samples compared to other atomic spectroscopic analytical techniques, such as AAS.

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