

STATUS AND PERSPECTIVES AT THE IFIN-HH CYCLOTRON FOR MATERIALS ANALYSIS AND CHARACTERIZATION

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Abstract. This paper will discuss several nuclear methods for the characterization of materials, developed at the Cyclotron Laboratory. The nuclear methods considered, depending on the specific materials, are the methods that allow the identification of multilayer structures composition and thin layers stoichiometry by Rutherford Backscattering Spectroscopy (RBS) as well as the concentration and distribution of vacancy-type defects and space distribution of electronic densities in the bulk (Positron Annihilation Spectroscopy – PAS). The Cyclotron Laboratory team has a long standing experience in Thin Layer Activation (TLA or Ultra-UTLA) technique, which is a nuclear method used mainly for different types of wear (corrosion) investigations for different engine parts or biomaterials. A dedicated fast neutron irradiation stand (maximum fluency: 10^{13} n/cm²) allows researches on the modification of the specific parameters of optical components. The discovery of new materials, processes and phenomena at nanometer scale, asks for the development and adaptation of new experimental techniques for materials analysis and characterization. This can be covered by using a low energy positron beam and the Coincidence Doppler Broadening Spectroscopy (CDBS), an infrastructure under construction in our institute.

Key words: nuclear methods, TLA, UTLA, RBS, FNIS, PAS.

1. INTRODUCTION

The materials science and its technological aspects are a major problem for any society and for this reason a multidisciplinary cooperation is necessary.

In the last six decades, in the international community, both conventional and nuclear methods have been used in the development of new materials. The nuclear methods considered in this paper are those which can be promoted in agreement with characteristics and parameters of the IFIN-HH Cyclotron. The principles, experimental set-ups and examples of typical applications for the following methods and techniques a) Rutherford Backscattering Spectroscopy-RBS; b) Thin Layer Activation-TLA-and Ultra –UTLA; c) Fast Neutron Irradiation Stand –FNIS and d) Positron Annihilation Spectroscopy-PAS, will be presented.

2. PRINCIPLES AND THE EXPERIMENTAL SET –UP

a) **The RBS method.** A very useful method for non-destructive material and surface analysis is using elastic scattering of ions from a well defined, medium high energy beam at the atoms in the probe, better known as Rutherford Backscattering (RBS) Spectroscopy [1]. The energy of the scattered particle is strongly dependent on the mass of the target ion and eventually reduced by the energy loss due to depth location of the scattering partner, whereas the intensity (counting rate) is given by the cross section ($\sim Z$) and the angular distribution. Fig. 1 illustrates a schematic principle of the RBS (Fig 1a) and its main parameters (Fig. 1b).

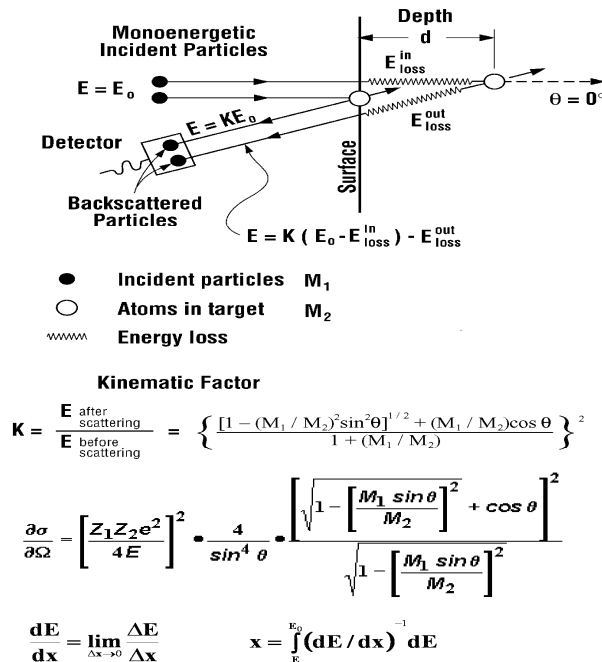


Fig. 1 – a) The RBS principle; b) main relations in RBS, K – kinematic factor, $d\sigma/d\Omega$ – differential cross section, dE/dx – stopping power.

We are performing such measurements and tests at our Cyclotron Laboratory mainly by means of a 3MeV He^+ beam. Further measurements, using heavier ions (e.g. Nitrogen) have also been successfully performed. The RBS laboratory is in the final stage of the ISO17025 approval, for which we had to improve our Quality Management to the highest international standards. One of the requirements for this approval is to show, that we are capable to precisely analyze the structure of a reference etalon as shown in picture (Fig. 2).

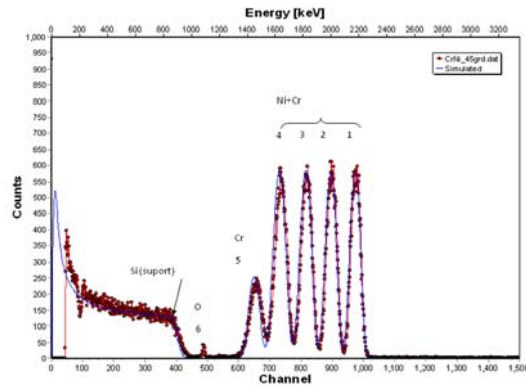


Fig. 2 – Spectrum of a periodic structure based on Cr (56nm)/Ni (56nm) as specified in the NBS certificate (National Bureau of Standards-USA).

Groups 1-4 show the superposition of Cr and Ni layers, due to their mass difference: each buried Ni layers appears at the same channel as the Cr layers in front of it. The probe consists of five Cr layers with four Ni layers in between. Group 6 shows the surface oxygen. The results of the fit/simulation from this measurement are within 2% of the specified values.

b) The T.L.A. and U.T.L.A methods. The principle of wear/corrosion determination by nuclear methods consists of a radioisotope induction upon the component to be studied and the development of a specific spectrometric measuring method in order to relate nuclear data to wear/corrosion data. The Thin Layer Activation (TLA) technique is an accelerator-based method, mainly performed using cyclotrons because this kind of machine usually delivers μA -current beams of basically light particles at an advantages price / μAh ratio.

The first publication on TLA, containing its principles and basic applications, appeared in the early 1970s [2, 3]. The principle of TLA is shown in Fig. 3.

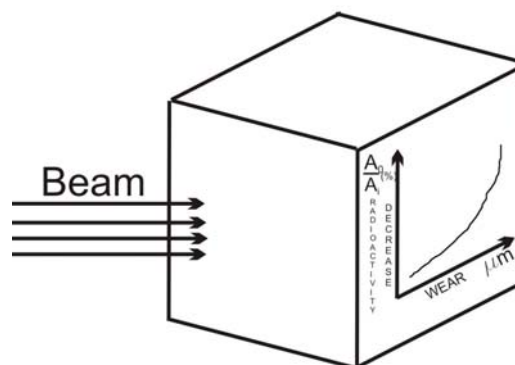


Fig. 3 – The principle of the Thin Layer Activation (TLA).

For these kind of studies, a dedicated beam line has been developed in our laboratory for in-air irradiation where the beam is extracted through a 50 μm Al foil. The most suitable nuclear reactions that can induce on basically-used machine construction metals (Fe, Cr, Cu, Zn, Ti, V, and Sn), by our U-120 Cyclotron medium energy beams, are tabulated and discussed in a previous work [4], considering the requirements of the determination of wear by activation. Also, taking into account nuclear data such as yields, γ -ray energies and half-lives, penetration range etc. General statements on the optimum irradiation and measuring condition can be found in [5, 6]

Two methods are available in order to establish a correlation between the decrease of the radioactivity and the wear /corrosion level:

1) The concentration measuring method [7] implies measurements of the radioactivity spread in the lubricant exposed to the washing wear/corrosion part. When the activation is made with charged particles from the cyclotron, the labelled zone of the exposed-to-wear machine part's surface must have a constant specific radioactivity. Also, for more accurate results a few other working conditions such as no filter retention, no sedimentation of the radioactive particles and no lubricant losses in the oil circuit, must be evaluated. A dedicated procedure and a mechanical-spectrometric arrangement have been successfully performed into account with metrology conditions.

The experimental wear determination uncertainties are approximately $\pm 10\text{--}15\%$, and the sensitivity threshold is $40 \mu\text{g}/\text{cm}^2$ for the most commonly used radioactive markers (^{56}Co , ^{57}Co , ^{65}Zn , ^{51}Cr , ^{48}V , ^{124}Sb). These values have been estimated considering the contribution of both filter retention and lubricant losses (usual processes for any thermal engine).

2) The remanent measuring method [2, 3] is based on the radioactivity decrease of the labelled zone vs. the thickness of the removed material. The activity of the irradiated machine part is measured by a γ -ray detector set close to it. Special attention must be paid to the detector position reproducibility near the labelled piece. Also, the wear/corrosion particles must be totally removed from the investigated region. For this method, experimentally obtained wear determination uncertainties are between $\pm 10\text{--}20\%$ and the sensitivity threshold is approximately 1% for a depth activation range of 20–200 μm .

The Ultra Thin Layer Activation (UTLA) method based on recoil implantation of radioactive heavy ions on the near surface of materials has been developed with the intention of having access to nanometric sensibilities without fluid detection (like in the concentration measuring method). This method enables "on line" detection on the experimented piece for nanometric wear or corrosion rates. The principle of the UTLA is illustrated in Fig. 4.

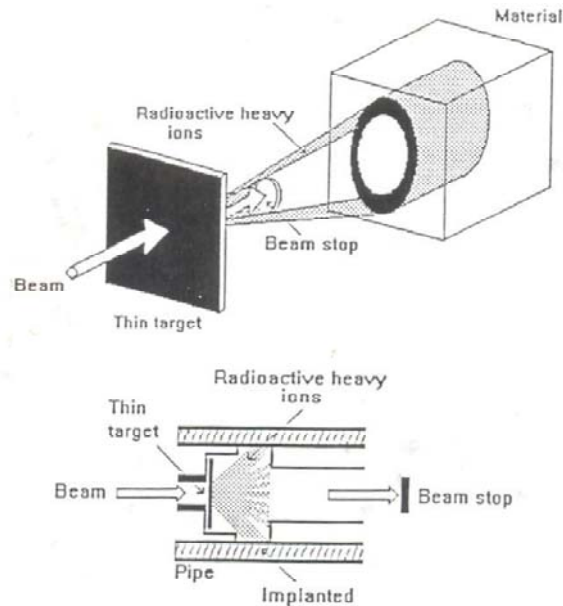


Fig. 4 – The schematique representation of U.T.L.A.

A thin target (a few micrometers) of elementary composition A is bombarded by the primary beam and is activated following the nuclear reaction $A(a,b)B$. Some general radioactive heavy ions B acquire sufficient kinetic energy to recoil out of the target and lodge in the material.

The implantation can be realized according to the piece of interest in frontal (Fig. 4a) or in tubular geometry (Fig. 4b). In 1980, T.W. Conlon [8] introduced the UTLA and gave a general treatment. The irradiation of various thickness films enables to establish the correlation between the remanent radioactivity and the surface loss $A_0/A_i = f(x)$. The experimental calibration methods implies the using of thin layer deposition methods to deposited metallic material on a silicon substrate whose roughness does not exceed 2 nanometres. Each film thickness is measured by RBS technique and can obtain calibration curves on depths ranging from a few tens to several hundreds nanometres. The theoretical value concerning the kinematic of the nuclear reaction coupled with dedicated software give essential indications to the choice of the nuclear reaction, the incident particle energy, the implantation geometry and therefore facilitates the application of the UTLA method.

There are several advantages compared to direct activation methods:

- The activation being independent of the activated material composition and the deposition methods permitting to deposit a wide range of materials, the UTLA method can be applied to all kinds of materials. Moreover, the potentially damaging effects are far less important than those induced by direct activation techniques using light or heavy ions. This method can be thus applicable to polymers.

– The general activities are very low (a few kBq). Radioprotection precautions are therefore considerably reduced.

Nevertheless, since the implantation set-up takes place in a vacuum chamber, the application fields of this method are limited to reduced dimension pieces. The experimentally obtained wear determination uncertainties range between $\pm 10\text{--}20\%$ and the sensitivity threshold is approximately 1% for a depth activation range of 20–200 nm.

c) The fast neutron irradiator. The fast neutrons irradiator at the U-120 Cyclotron in Bucharest (Fig. 5) is based on the reaction ${}^9\text{Be} + d \rightarrow n + X$, using a deuteron beam (13 MeV) and a thick beryllium target (165 mg/cm²). To obtain the desired neutrons fluencies, the samples are located downstream at distances between 10 to 40 cm of the Be target. The fast neutrons facility is provided with a biological shield built from borated paraffin bricks of 20 cm thickness, leaving a free volume (100×50×50 ccm), for neutron irradiation. From the induced activity of the metallic foils, using an unfolding procedure [9], we obtain the neutron energy spectrum.

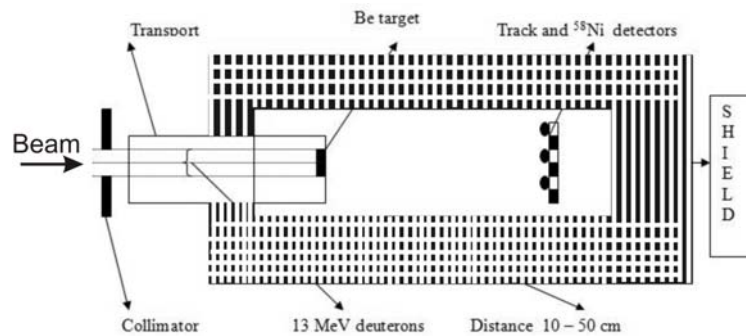


Fig. 5 – The scheme of the fast neutron irradiation.

The spectrum has a bell shape distribution around a mean energy of 5.2 MeV. The higher part of the energy spectrum was derived from the time of flight (TOF) measurement. The neutrons flux above 1 MeV is estimated with a relative error of about 20 %. The measured production yield, at 10 cm distance from the Be target, is $2.13 \cdot 10^8$ neutrons/cm².s.μA. The maximum neutron flux achievable in our set-up, at a distance of 10 cm from the target, is $2 \cdot 10^9$ neutrons/cm².s.μA, corresponding to a deuteron beam intensity of 10 μA. The neutron and gamma components of the mixed radiation dose are 138Gy/C respectively 2.38 Gy/C, at 30 cm distance from the Be target. In practice, a neutron fluency up to 10^{13} n/cm² can be obtained in about 1-6 days of irradiation, depending of the position of the samples. The heat (≈ 100 W) released in the Be target is removed by a flow of distilled cooling water.

At maximum beam power, the highest temperature of the target does not exceed 50°C. The Be target is electrically insulated, allowing on-line monitoring of the beam current.

d) The PAS methods. Compared with the electron which is a stable particle and can live forever in a free state, the positron interacts immediately after slowing down with an electron, producing 2 gamma photons, each with 0.511 MeV ($e^+ + e^- \rightarrow 2\gamma$). This phenomenon is the positron annihilation and based on it, a series of techniques for the study of vacancy and vacancy cluster type defects have been developed. In condensed matter, positrons loose their energy in a short time, of the order of picoseconds. The precise time of annihilation is announced by the 511keV photons whose energy, momentum and time can be measured with accuracy. Due to their positive charge, the positrons are repelled by the positive ions in the substance. The empty volumes of atomic dimensions are capture centers for the positrons, giving rise to measurable changes in the annihilation characteristic. The lifetime of the particle is longer due to capture on sites with lower electron densities near vacancies or vacancy clusters. As such, techniques like PLS (Positron Lifetime Spectrometry) have become useful methods of study. The development of gamma spectrometry with HPGe detector of high resolution brought about also another PAS technique, based on the Doppler broadening (Doppler Broadening Spectrometry – DBS). This allows fast detection of the presence of defects in various materials studied under different conditions: temperature, stress, radiation etc.

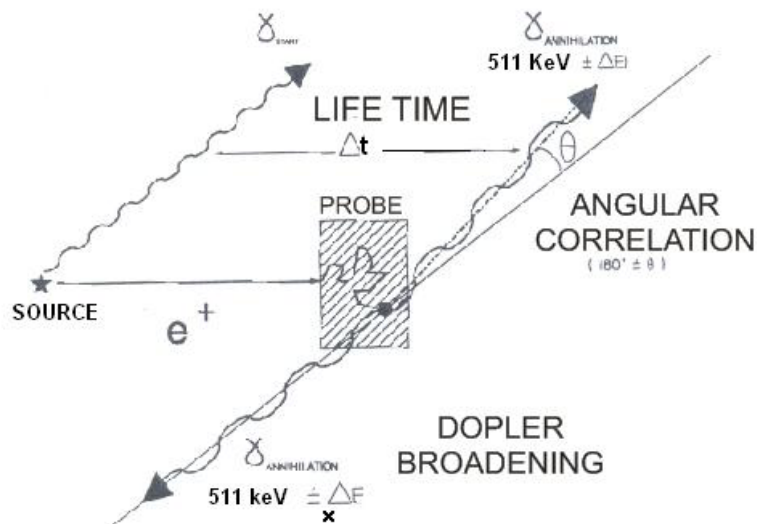


Fig. 6 – The schematic principle of the PAS techniques.

2. RELEVANT RESULTS

a) The RBS method. In the research and development of materials with new physical and electrical characteristics, indium nitrate (InN) is of interest for the realisation of electro optical devices, due to its semiconducting behaviour.

The semiconductor behaviour of InN is correlated to the impurities introduced into the lattice. In fact, this material is in the form of a nearly 2 dimensional structure placed on different supports (substrates), where the layer thickness, its composition and the substrate has influence of the behaviour.

In this context, it is evident that in order to establish an appropriate production technology, it is vital to be able to analyse structure and elemental composition of individual (production) probes and RBS is one of the suited analysis methods, to do that.

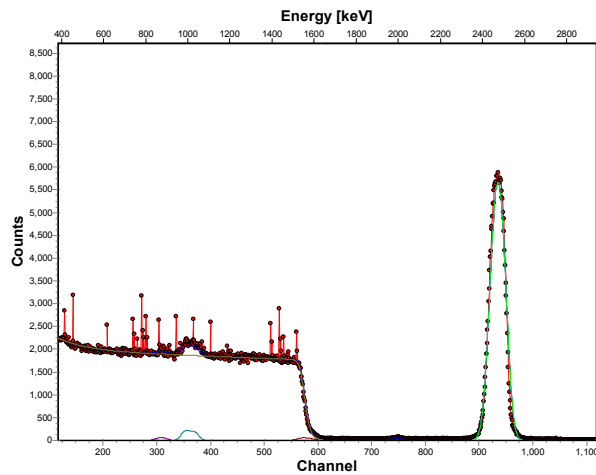


Fig. 7 – Spectrum of an InN structure on Si as described in Table 1 below.

Table 1

Layer No.	Composition	Thickness	
		[10^{15} at/ cm ²]	[nm]
1	In:33%, Al:4,8% N:16,2%, O:46%	621	150
2	In:42%, Al:5,7% N:19,3%, O:30% Ti:3%	85	24
3	In:3%, Si:56% O:38%, Ti:3%	183	50
4	Si:100%		30000

Table 1 illustrates the possibility of elemental and structural analysis of thin layers on different substrates. The samples show that the active layers (doted InN) are not homogeneous and that especially the Oxygen content varies significantly with the depth of its location in the probe. The achieved results can be used to re-evaluate the production procedure and optimize it.

b) TLA and UTLA. Since 1980, when the TLA technique has been introduced for the first time in our laboratory, more than 30 applications have been performed at Romanian customer's request.

One of the most interesting types of a TLA application is the optimization of an engine's running-in program. For this application the tribologic parts of interest are the cylinder jacket and the piston ring because their matching is considered to influence significantly the performances of the engine. Being interested in obtaining the wear diagrams for both Cr-plated and phosphated steel piston rings we have labelled them with 8 MeV deuterons inducing the ^{51}Cr and ^{57}Co radioisotopes, respectively. After activation, the parts have been mounted on an improved Hoffman engine test bench. The wear determination has been made by the concentration measuring method and both resulting radioisotopes have been simultaneously recorded Fig. 8 a, b.

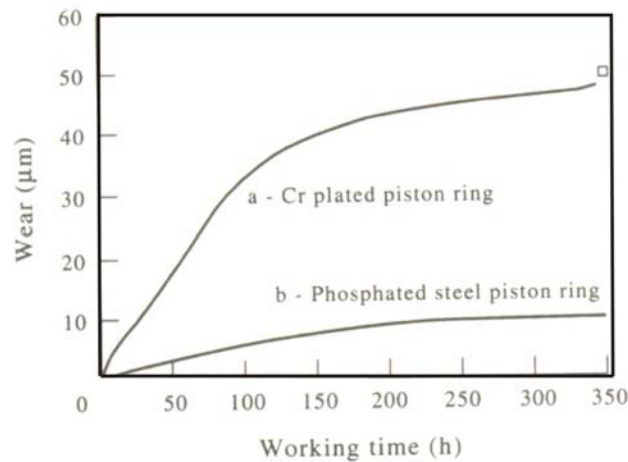


Fig. 8 – Wear diagram for: a) Cr-plated; b) phosphated steel of a M30 diesel engine.

c) Facility for fast neutron irradiation. Our original intention was to use this facility for neutron irradiation of optical components (laser diodes and optical fibers samples).

In preparation of this irradiation, the neutron fluencies were measured by activated foil detectors (^{58}Ni (n,p) ^{58}Co reaction) and mica track detectors. The Ni detectors were chosen because of appropriate sensitivity, for long irradiation time

($2.5 \cdot 10^9$ neutron/cm² Bq). The accuracy of the measurements is 20%, due mainly to uncertainty in activation cross-sections, but results are typically reproducible to within a few percent.

By measuring the integrated beam current, the time-stability of the neutron source was checked every hour. The deuteron current, on target, was roughly constant (2-4 μ A) over the irradiation period. We measured the neutrons fluencies at different distances from Be target on the symmetry axis using pairs of mica and ⁵⁸Ni detectors.

The results obtained [9, 10] for fluencies measured in a plane perpendicular on the symmetry axis and at 30 cm distance from the Be target are presented in Fig. 9.

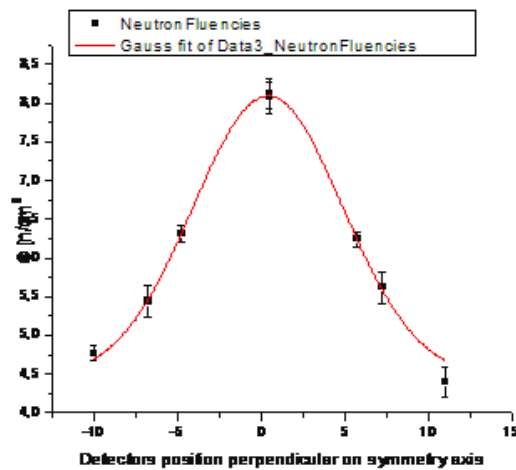


Fig. 9 – Neutron fluencies measured at 30 cm distance from Be target.

The calculated k constant used in the formula for fluencies evaluation: $\Phi = k \cdot \Lambda / m$ on ⁵⁸Ni gamma activity (Λ) measurement is: $k = 2.53 \cdot 10^9$ n·cm⁻²·Bq⁻¹·g.

d) Facilities for the PAS techniques. The PAS techniques were introduced for the first time in Romania as an analytical tool by the members of our group. [11]. Even if these techniques do not belong to ion beams techniques, their development was strongly influenced by the possibility to obtain a ²²NaCl source using the U-120 cyclotron facility [12]. A series of Doppler Broadening technique tests were performed on Al samples coming from the IFIN-HH VVR-S reactor, currently under decommissioning. Using a positron source of about 1.7 μ Ci, we used both DBS and CDBS, in the evaluation of our PAS samples to study radiation damage. The samples are still active (about half the activity of our source), which introduces a high background in the spectra, and as such the analysis is practically impossible in DBS. The bi-parametric acquisition system for the coincidence

measurements was developed around the ORTEC AD413 quad ADC. We developed a dedicated interface based on a Microchip PIC 18F4455 type micro-controller to master the CAMAC communication with the ADC. The data furnished by the ADC is sent further to a PC over the USB 2.0 interface: the maximum transfer rate is 6 kHz, which is quite good for the purpose of our coincidence acquisition system. The micro-controller software and a Visual C++ program for data acquisition and display (a MCA emulator with every ADC channel display and bi-parametric visualization) were also developed in our group. The coincidence setup is of standard type, with an ORTEC TAC 567 for the quad ADC opening gate [13].

The Time Differential Perturbed Angular Correlation Method (TDPAC) in connection with long-lived Positron Life-Time Spectroscopy (PLTS) has been used to observe “quantum beat” spin oscillations of a positronium atom in an external magnetic field. Time Positron Annihilation Distribution spectra for 3γ decay of Positronium show the oscillations in an external magnetic field. The measurements were done using one START and four STOP detectors and thus four time spectra were simultaneously registered. The detectors used are 2” by 2” BaF₂ crystals mounted on XP2020 photomultipliers. The positron polarization vector was perpendicular on the plane STOP detectors. The START signal is given by the 1275 keV gamma ray emitted by a ²²Na β⁺ source. The STOP signals are produced by annihilation rays with the energies in the range 140 keV–520 keV [14].

3. PERSPECTIVES

The increase in sensitivity and the shorter time for measurement and data acquisition in the PAS experiments was obtained in the 1980’s by increasing the intensity of the positron fluxes. To obtain the required parameters, the new equipments consisted of a primary positron source (on-line with a reactor or particle accelerator), a conversion system /moderator to obtain positron energy in the thermal range (eV), a focusing and transport line for the monochromatic positron beam, an accelerator in steps in the 0.8-100 keV range, a target chamber and the measurement set-up for PAS. Except the primary source, all the beam line components need to work in vacuum of $10^{-6} - 10^{-10}$ torr.

In the framework of a national R&D project extended over 3 years, we will build a magnetically guided slow positron beam with variable energy up to 50 keV. This slow positron beam implantator will evaluate the concentration of defects by the PAS techniques, begging from the surface and continuing deeper and deeper in the probe with a 5 keV step until reaching 50 keV.

At the beginning, the system will be coupled to a Doppler Broadening Spectrometer. After the ISO 17025 approval, the RBS laboratory will improve the ERDA technique in order to estimate and concentration in the light elements (H, O, N, etc).

Concerning the extension of the UTLA application in wear/corrosion studies for biomaterial we intend to modernize the existing experimental set-up.

4. CONCLUSION

Since materials science is truly multidisciplinary and not just involving simple connections with other sciences (chemistry, physics, engineering etc.), all sciences contribute their expertise to develop new materials with specific applicability. All nuclear methods presented in this paper can be used as complementary techniques to the usual conventional methods, if the obtained data are useful for achieving the main goal, that is to obtain materials with specific properties.

REFERENCES

1. Wei-Kan Chu, *Backscattering Spectrometry*, Academic Press, 1978, pp. 9–14.
2. A. Gerve, *Die wichtigsten Verschleißmeßmethoden der Isotopentechnik*, *Kertechnik*, **14**, 204 (1972).
3. I.O. Konstantinov and N.N. Krasnov, *Determination of the wear of machine parts by charged particles surface activation*, *J. Radioanalyt. Chem.*, **8**, 357 (1971).
4. B. Constantinescu et al., *Thin layer activation technique at the U-120 cyclotron of Bucharest*, *Nucl. Instr. Meth.*, **B89**, 82 (1994).
5. P.M. Racolta, *Nuclear methods for tribology*, *Appl. Radiat. Isot.*, **46**, 663 (1995).
6. O. Lacroix, G. Blondiaux, T. Sauvage, P.M. Racolta, L. Popa-Simil, and Alexandreanu, *Metrology conditions for thin layer activation applied in wear and corrosion studies*, *Nucl. Instr. Meth.*, **A396**, 427 (1996).
7. P. Fehsenfeld, A. Kleinrahm, H. Schweikert, *Radionuclide technique in mechanical engineering in Germany*, *J. Rad. Nucl. Chem.*, **160**, 141 (1992).
8. T.W. Conlon, *The UTLA technique*, *Nucl. Inst. And Meth*, **171**, 297 (1980).
9. Fl.Tancu, M.T. Magda, S. Dima, M. Macovei, E. A. Ivanov, R. Dumitrescu, C. Stan-Sion, *Energy Spectrum of Neutrons Produced by Deuterons on Thick Be Target*, *Rev. Roum. Phys.*, **28**, 10 857–865 (1983).
10. Ana Danis and M. Oncescu, *High neutron fluence measurement using simultaneously mica muscovite as track detectors*, *Nucl. Instr. and Meth.*, **173**, 143–146 (1980).
11. P.M. Racolta, L. Popa-Simil, N. Miron, C.I. Muntele, *Project of positron source at the U-120 cyclotron Bucharest*, *Nucl. Instr. and Meth.*, **B 139**, 461–465 (1998).
12. Catalina Campeanu et al., *The manufacturing and the chemical separation of Na²² radioactive isotope used in the obtaining of Na²² Cl positron source*, *Revista de Chimie*, **56**, 5, 499–501 (2005).
13. Angela Vasilescu, A. Ionica, O. Ghita, L.S. Constantinescu, F. Craciun, Catalina Constantin, Chiojdeanu and P.M. Racolta, *CDBS technique studies of samples from a VVR-S reactor under decommissioning*, presented at SLOPOS-11 Conference, 8–13 July 2007, Orleans, France (to be published in Applied Surface Science).
14. E.A. Ivanov, I. Vata, D. Dudu, S. Nitisor, I. Rusen, *Quantum Beats in the 3γ Annihilation Decay of Positronium Observed by Perturbed Angular Distribution*, presented at SLOPOS-11 Conference, 8–13 July 2007, Orleans, France (to be published in Applied Surface Science).