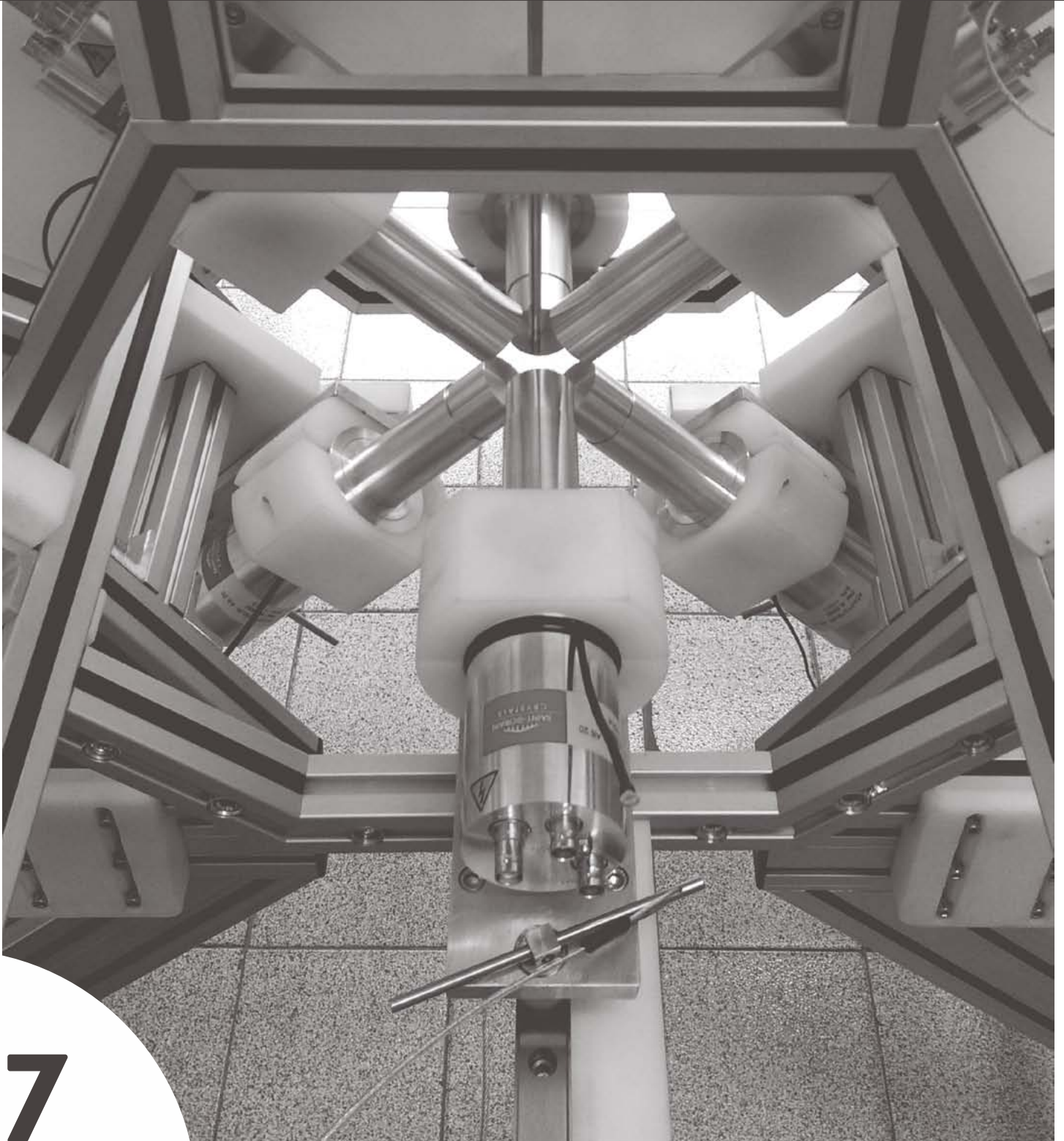


# Nuclear Science and Technology





## Introduction

The Program on Nuclear Science and Technology comprehends Nuclear and Condensed Matter Physics, Neutron Activation Analysis, Radiation Metrology, Radioprotection and Radioactive Waste Management. These activities are developed at the Research Reactor Center and the Radiation Metrology Center. The Radioprotection activities are developed at all radioactive and nuclear facilities of IPEN-CNEN•SP.

The Research Reactor Center at IPEN-CNEN•SP is responsible for the safe operation and maintenance of the Research Reactor IEA-R1 and has a three-fold mission: promoting basic and applied research in nuclear and neutron related sciences, providing educational opportunities for students in these fields and providing services and applications resulting from the reactor utilization.

Specific research programs include nuclear structure study from beta and gamma decay of radioactive nuclei and nuclear reactions, nuclear and neutron metrology, neutron diffraction and neutron multiple-diffraction study for crystalline and magnetic structure determination, perturbed -angular correlation (PAC) using radioactive nuclear probes to study the nuclear hyperfine interactions in solids and neutron activation analysis, with comparative or k0 standardization applied to the fields of health, agriculture, environment, archeology, reference material production, geology and industry. The research in the areas of applied physics includes neutron imaging, scientific computation and nuclear instrumentation.

The Radiation Metrology Center promotes the development, improvement and establishment of new methodologies and products in radiation metrology, with the goal of assuring radiological safety of IPEN workers, community and environment. The Center offers services to internal and external communities in the fields of personnel and environmental dosimetry, high dose and accident dosimetry, production of dosimetric materials, metrology in diagnostic radiology and radiotherapy, calibration of instruments and radioactivity determination in environmental samples, in foodstuffs and food commodities imported and exported by Brazil.

# **Experimental Nuclear Physics and Condensed Matter**

## Hyperfine interactions in solids, nanoparticles, and biomolecules

Zero-emission electric vehicles, data processing and storage based on spin, mega magnets, nanoparticles selectively delivering drugs to tumor without interacting with the normal body cells, all of these and much more new achievements will be available in the near future. Technological revolutions require incredible new materials. Synthesis and characterization of new materials requires unconventional techniques. Phenomena in solid materials and other substances, in general, originate from small differences in their electronic structure, which makes specifically interesting to investigate new material and compounds from an atomic view in order to understand the origin of such phenomena. Experimental measurements of hyperfine interactions (interactions between the nuclear moments and magnetic field or the electric field gradient) provide a very sensitive and accurate method to investigate condensed matter phenomena in many different solids, as well as dynamic parameters in biomolecules. The hyperfine interactions laboratory of IPEN is using the nuclear technique of Perturbed gamma-gamma Angular Correlation (PAC) to measure hyperfine interactions to investigate a series of intermetallic compounds, metal oxides and nanostructured materials which present interesting properties like superconductivity, magnetic order, phase transitions, etc. Biological materials like proteins and peptides are also a recent subject of investigation. The PAC technique uses radioactive nuclei implanted into the material to be studied that can probe magnetic hyperfine field (mhf) and electric field gradient (efg) in determined sites of crystalline structure of the material and provide information about the electronic



Fig 1. Closed-cycle He refrigerator at the center of a six-detector PAC spectrometer (left). He-vapor cryostat to cool samples down to 1.2 K (middle). Compact furnace at the center of a four-detector PAC spectrometer to measure samples in the range from 300 K to 1350 K (right).

charge and spin structure around the probe. This information makes possible to investigate properties of the crystal structure and or the origin of magnetic interactions in the material as well as the electronic structure around the probes. Due to the proximity of a nuclear research reactor, our laboratory can use a variety of special radioactive probe nuclei such as  $^{140}\text{La}$ ,  $^{111}\text{Ag}$ ,  $^{111\text{m}}\text{Cd}$ , that are produced by neutron irradiation in the IEA-R1 research reactor of IPEN, besides the usual ones like  $^{111}\text{In}$  and  $^{181}\text{Hf}$ . Three PAC spectrometers: two with 4-detectors setup and other with 6-detectors are available in the Hyperfine Interactions laboratory. The facilities for sample environment in the laboratory includes three closed-cycle He refrigerators, one specific He-vapor device to cool samples down to 1.2 K, and a compact furnace capable to reach 1350 K. A new fully digital PAC spectrometer is currently being set up with six new  $\text{LaBr}_3$  detectors.

A methodology using the  $^6\text{Li}$  ion beam from the Pelletron accelerator in the Physics Institute of University of São Paulo to implant  $^{111}\text{In}$

probe into the sample through  $^{108}\text{Pd}(^6\text{Li},3\text{n})^{111}\text{In}$  nuclear reaction is also available. A strong collaboration with the ISOLDE group from CERN is also under progress, which allows access to complementary probe nuclei.



Fig 2. Reversible fully digital PAC spectrometer set up in a configuration of six  $\text{LaBr}_3$  (left) and four  $\text{LaBr}_3$  (right) detectors.

### Materials which have been investigated are:

- 1 Oxide semiconductors: new families of semiconductors, which are doped with magnetic materials in order to use the electron spin information, are under intensive investigation as they can be used for spintronics. Effects of doping in ZnO,  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{TiO}_2$ , and vanadium oxides are being investigated by PAC in order to understand the local crystalline structure around the dopant and the its electronic structure.
- 2 Insulator oxides with large bandgap as  $\text{HfO}_2$ ,  $\text{ZrO}_2$  and  $\text{CeO}_2$  are promising materials to replace  $\text{SiO}_2$  as a gate dielectric to prevent leakage current in complementary metal oxide semiconductor (CMOS) transistors. Thin films and nano-structured powders of these materials are under investigation using PAC spectroscopy in order to obtain an atomic scale characterization of their properties under different temperatures.
- 3 Rare-earth based compounds: series of intermetallic compounds based on rare earth elements show different magnetic behaviors and exhibit very interesting physical phenomena like Fermi liquid behavior, Kondo effect, etc. These properties are not well understood yet, and nuclear techniques are very suitable to investigate the microscopic origin of such phenomena. In our laboratory, we have studied heavy fermions compounds such as  $\text{REIn}_3$  (RE = rare-earth element),  $\text{REMn}_2\text{X}_2$  (RE= rare-earth, X = Si, Ge) and  $\text{LaMnSi}_2$  with PAC technique using  $^{140}\text{Ce}$  and  $^{111}\text{Cd}$  probe nuclei.

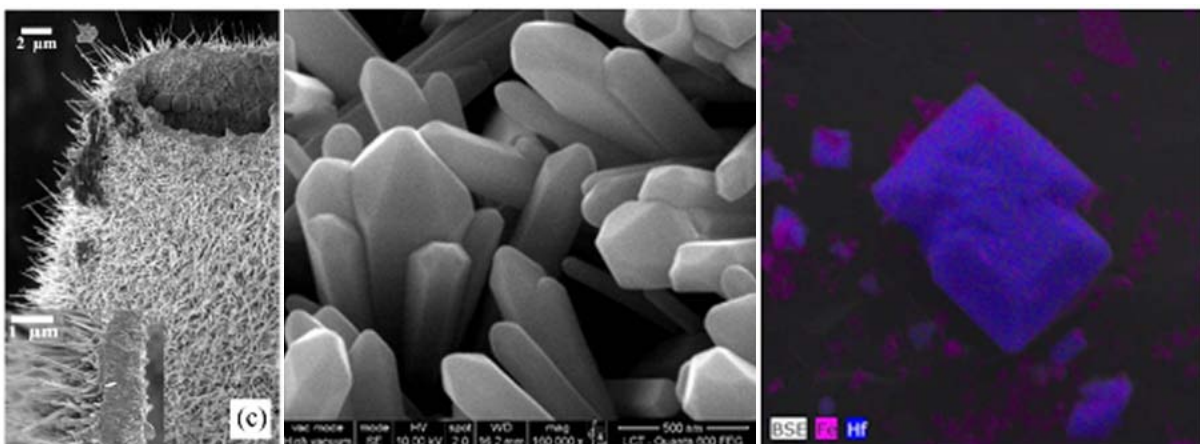


Fig 3. (left) Pencil-like particles of ZnO doped with Cr (M. R. Cordeiro, Ph.D. Thesis, IPEN, 2012). (Center) ZnO microtube decorated with nanowires on the surface (C. M. Rivaldo-Gómez et al. Scientific Reports 5, 15128, 2015). (right) Electron back scattering diffraction image showing the spatial distribution of Fe and Hf in Fe doped  $\text{HfO}_2$  (T. S. N. Sales et al. AIP Advances 7, 056315, 2017).

- 4 Magnetic nanoparticles of  $\text{Fe}_3\text{O}_4$  and  $\text{XFe}_2\text{O}_4$  (X = Mn, Co, Ni) with sizes homogeneously smaller than 30 nm are

also being investigated with PAC spectroscopy using  $^{111}\text{Cd}$  as probe nuclei. These nanoparticles are important materials for biomedical applications such as drug delivery, hyperthermia treatment of tumors and imaging.

- 5 Rare-earth nanoparticles such as  $\text{Gd}_2\text{O}_3$  and  $\text{Er}_2\text{O}_3$  are also being studied targeting imaging and radiotherapy enhancement.
- 6 PAC spectroscopy is also used to investigate biomolecules of EDTA, nucleobases, and peptides.
- 7 Very precise ab-initio method of electronic structure calculations based on the density functional theory using a local density approximation are being used to help in the interpretation of hyperfine interaction parameters through the WIEN2k code. The first-principles full potential linear augmented plane-wave (FP-LAPW) calculations of the electronic structure and hyperfine fields have been performed for the intermetallic compounds  $\text{RECd}$ ,  $\text{REIn}_3$  (RE = rare-earth element) and  $\text{LaMn}_2\text{X}_2$  (X = Ge, Si). Ab-initio calculations for oxides such as  $\text{HfO}_2$ ,  $\text{CoO}$  and  $\text{In}_2\text{O}_3$  are also being carried out.

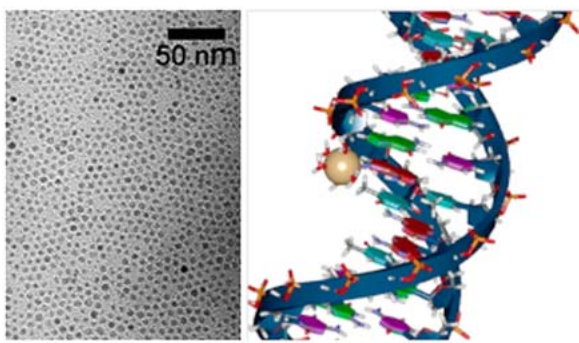
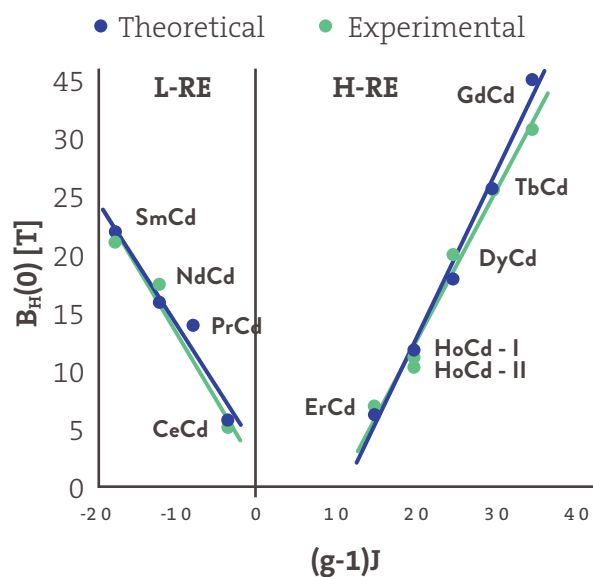


Fig 4. (left) TEM images for  $\text{Fe}_3\text{O}_4$  nanoparticles. (F. B. Effenberger, A. W. Carbonari, L. M. Rossi, . *Magn. Magn. Mater.* 417, 49, 2016). (Center) Experimental, measured by PAC, and theoretical, calculated by WIEN2k, spin dependence of saturation values of magnetic hyperfine field  $B_{\text{Hf}}$ . F. H. M. Cavalcante et al. *Phys. Rev. B* 94, 064417, 2016). Fig. 4 (right) Cd probes in DNA molecules of mice infected with the Y-strain of *Trypanosoma cruzi* used for PAC measurements and DFT calculations. P. A. D. Petersen et al. *Biochemistry* 53, 3446, 2014).





## Study of the crystalline and magnetic structures of materials by neutron and X-ray diffraction

The high-resolution neutron powder diffractometer Aurora, installed on the IEA-R1 research reactor at IPEN-CNEN/SP, has a position sensitive detector (PSD) which allows a quite fast measurement of powder patterns with good resolution. The PSD measures  $20^\circ$  of a pattern at once. An extensive pattern can be obtained by collecting data in contiguous  $20^\circ$  segments, in an angular interval ranging from  $5$  to  $130^\circ$ . A double-bent silicon monochromator permits measurements with four different wavelengths namely  $1.111$ ,  $1.399$ ,  $1.667$  and  $2.191$  (nominal values). The research staff at the IPEN Neutron Diffraction Laboratory, which is in charge of the operation of Aurora, has participated in several studies carried out in cooperation with other laboratories or by itself. In the following sections, papers published in the past three years are presented.

### Neutron multiple diffraction used as a tool for structural studies

During numerous years, neutron multiple diffraction (NMD) has been developed as a tool for structural studies in the Neutron Diffraction Laboratory at IPEN. Several papers have resulted from the application of NMD in structural crystallography. Recently, the Neutron News magazine dedicated a special issue to the development of neutron scattering in South America. A Scientific Review, condensing the results found in the papers published by the Neutron Diffraction Laboratory was published in this issue together with others from Brazil and Argentina. It presents a brief history of the development of neutron diffraction as a tool for structural studies and some

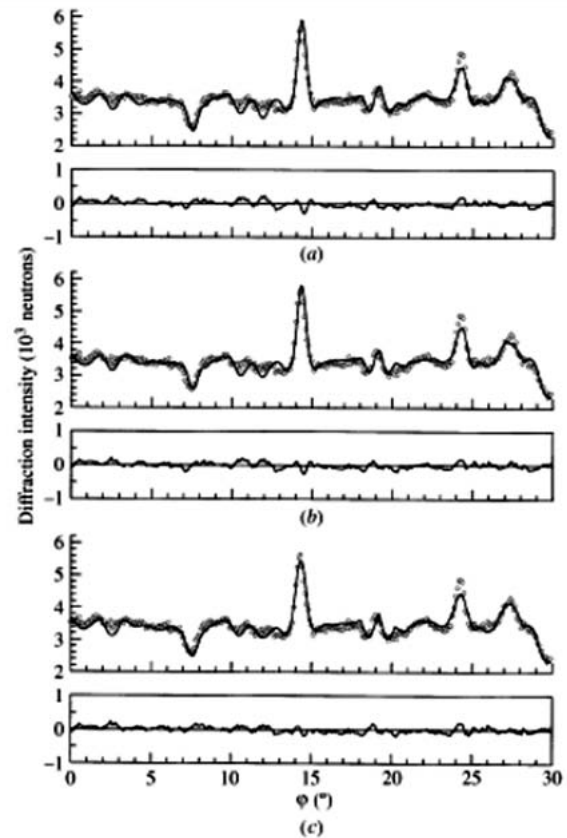


Fig 5. Experimental NMD pattern (small circles), obtained with magnetite in the paramagnetic phase ( $976$  K), compared with simulated patterns (continuous lines) simulated by MULTI for the three different cases mentioned in the text.

results of application to structural studies like, for instance, the refinement of the ferri- and paramagnetic phases of magnetite ( $\text{Fe}_3\text{O}_4$ ). At room temperature, magnetite ( $\text{Fe}_3\text{O}_4$ ) is a ferromagnet; above the Curie temperature ( $853$  K), it becomes a paramagnet. NMD patterns of a natural sample of magnetite were measured at room temperature and  $976$  K. With the patterns, lattice, positional and thermal parameters were refined in three different cases: assuming an overall isotropic thermal parameter, assuming different isotropic parameters and assuming anisotropic parameters. In this application and in the others reviewed in the work, the program MULTI, of simulation of NMD patterns, revealed to be an essential tool for the analyses. This program was developed by the staff of the Neutron Diffraction Laboratory in the nineties.

## Rietveld analyses of neutron and X-ray diffraction patterns

The Neutron Diffraction Laboratory is also involved in studies that employ the Rietveld quantitative phase analysis using neutron and X-ray diffraction patterns. The studies presented below were all made in cooperation with other groups. The X-ray diffraction patterns were measured at different laboratories, inside and outside IPEN, and the neutron diffraction ones in the high-resolution diffractometer Aurora.

### Oxygen stoichiometry in BSCF

In a co-operative study between the Science and Technology of Materials Centre and the Neutron Diffraction Laboratory, the compound  $\text{Ba}_{0.50}\text{Sr}_{0.50}\text{Co}_{0.80}\text{Fe}_{0.20}\text{O}_{3-\delta}$  (BSCF) has been studied. BSCF is a candidate for air electrodes in Intermediate Temperature Solid Oxide Fuel Cells (ITSOFC). This work deals with the oxygen vacancy in BSCF. The EDTA- Citrate method was applied to a solution of barium, strontium, cobalt and ferrite nitrate salts to synthesize the compound. Three portions of the product were calcinated at 700, 800 and 900 °C, for five hours in air. Rietveld phase analyses applied to the three samples found that only that calcinated at 900 °C showed to be a single-phase BSCF. Use of neutrons was fundamental for the determination of the oxygen stoichiometry in the sample. As a matter of fact, oxygen is a light atom and it becomes 'invisible' to X rays when associated to heavy atoms, like those in the formula of BSCF. This is a classical case where neutrons shall be used instead of X rays. Actually, a combination of X rays and neutrons was applied to this case. The stoichiometry in the single-phase sample was then determined by using a combined X-ray and neutron Rietveld refinement. The stoichiometric formula for the single-phase BSCF sample resulted

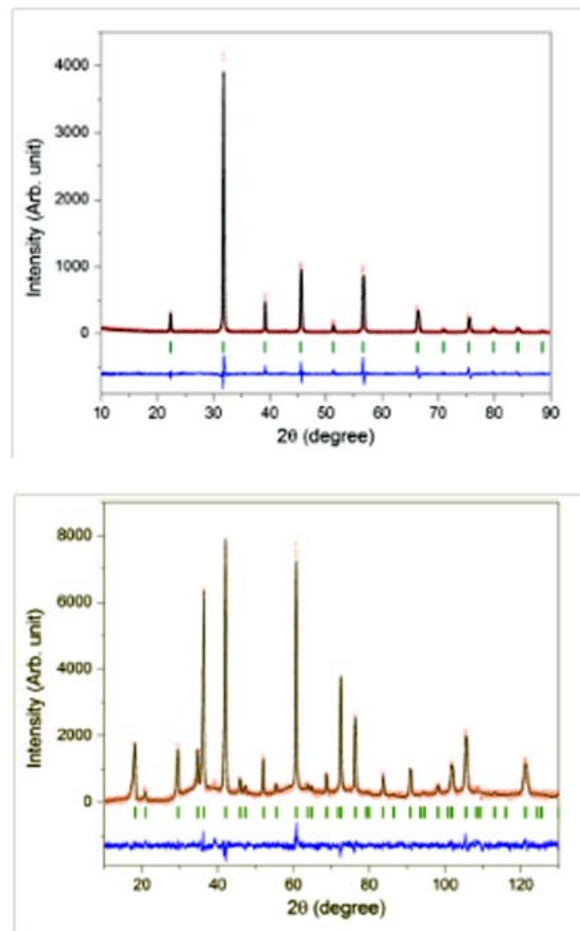


Fig 6. -ray (a) and neutron (b) diffraction patterns employed in the combined -ray and neutron Rietveld refinement.

### Thermal analysis and phase relations in the system $\text{La}_2\text{W}_2\text{O}_9$ - $\text{Li}_2\text{W}_2\text{O}_7$

The pseudobinary phase diagram  $\text{La}_2\text{W}_2\text{O}_9$ - $\text{Li}_2\text{W}_2\text{O}_7$  has been described, for the first time, in a co-operative work done in the Crystal Growth and the Neutron Diffraction Laboratories, both at IPEN, and in the Leibniz Institute for Crystal Growth, IKZ- Berlin, Germany. The phase diagram contains the intermediate tungstate  $\text{LiLa}(\text{WO}_4)_2$  which has been studied as a prospective laser host material.  $\text{Li}_2\text{CO}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{WO}_3$  powders were used as starting materials to synthesize the compounds  $\text{La}_2\text{W}_2\text{O}_9$  and  $\text{Li}_2\text{W}_2\text{O}_7$ . These two compounds were mixed

in different proportions, heated to the melting temperatures and cooled with a constant rate to produce annealed samples for the study. X-ray diffraction data for Rietveld analyses were collected at room temperature. Four different phases were identified in the system  $x\text{Li}_2\text{W}_2\text{O}_7 - (1-x)\text{La}_2\text{W}_2\text{O}_9$  for  $0 \leq x \leq 1$ , namely  $\text{LiLa}(\text{WO}_4)_2$ ,  $\text{La}_2\text{W}_2\text{O}_9$ ,  $\text{Li}_2\text{W}_2\text{O}_7$  and  $\text{Li}_2\text{WO}_4$ . In the interval  $0 \leq x \leq 1$ , phase  $\text{LiLa}(\text{WO}_4)_2$  is formed for all values of  $x$ . One, two or even three of the other phases coexist with  $\text{LiLa}(\text{WO}_4)_2$  in shorter intermediate intervals of  $x$ . The cell parameters of  $\text{LiLa}(\text{WO}_4)_2$  and the occupation factors of Li, La and O, in this phase, were also determined in the analyses. In order to complete the study, differential thermal analysis (DTA) and scanning electron microscopy (SEM) were applied to samples and single-crystal fibres grown by micro-pulling-down ( $\mu$ -PD) technique.

### Hydration mechanism in Portland cements

A study of the hydration mechanism in Portland cements has been initiated. The study results of a co-operation between the Polytechnic School at Sao Paulo University and the Neutron Diffraction Laboratory at IPEN. Neutron diffraction patterns of dry and hydrated Portland cement were measured in the high-resolution neutron diffractometer Aurora. Hydration was done with heavy water ( $\text{D}_2\text{O}$ ) owing to the high level of incoherent background in the pattern if light water is used. Rietveld refinement of the deuterated and dry cement samples gave as result the presence of several phases in different proportions. A list of the phases and their weight percentages (Wt. %) refined for the deuterated sample is as follows: 35.60 of Alite ( $\text{Ca}_3\text{SiO}_5$ ), 0.46 Portlandite ( $\text{CaO}_2\text{D}_2$ ), 19.60 Belite ( $\text{Ca}_2\text{SiO}_4$ ), 39.90 Calcite ( $\text{CaCO}_3$ ), 1.10 Anhydrite ( $\text{CaSO}_4$ ), 1.20 Tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ) and 1.30 Periclase ( $\text{MgO}$ ).

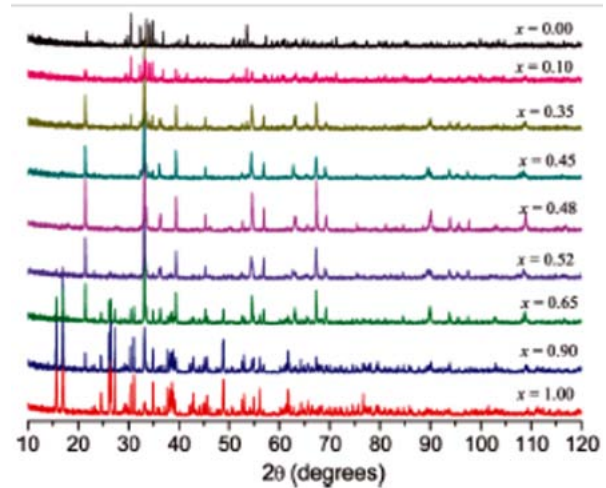


Fig 7. A few X-ray diffraction patterns obtained with samples from the system  $x\text{Li}_2\text{W}_2\text{O}_7 - (1-x)\text{La}_2\text{W}_2\text{O}_9$ . Pattern for  $x = 0$  corresponds to the phase  $\text{La}_2\text{W}_2\text{O}_9$  and for  $x = 1$  to  $\text{Li}_2\text{W}_2\text{O}_7$ .

## Neutron tomography

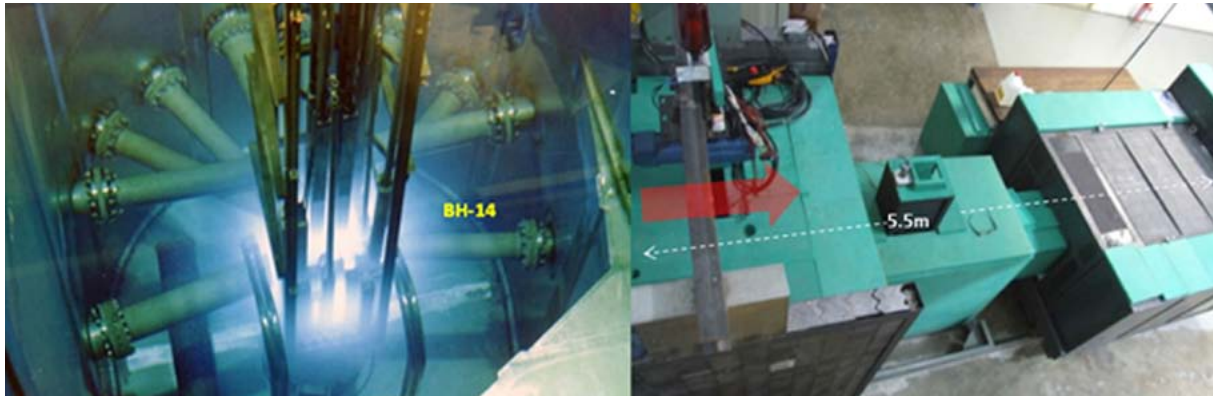


Fig. 10. Top view of the reactor under operation (left) and of the equipment for neutron tomography of IPEN-CNEN-SP

The neutron tomography (NT) is a non-destructive imaging technique to investigate the internal structure of objects, mainly the hydrogenous ones like oil, water, adhesives, plastics, etc., even wrapped by thick metal layers. Thus the information provided by NT are complementary to those provided by X-rays. The Brazilian Institute for Nuclear Technology IPEN-CNEN/SP has an equipment for NT showed in Figure 10, which is installed at the IEA-R1 Nuclear Research Reactor and operational since 2011. This equipment is able to provide high quality images, and a tomography is obtained as follows: the object to be inspected is positioned in a sample holder, to be irradiated in the neutron beam; the transmitted neutrons impinge a scintillator, forming a 2D (two dimensional) brilliant image of its internal structure; a plane mirror reflects this image to a high sensitivity video camera which is positioned at  $90^\circ$  with respect to the neutron beam and it is captured and stored in a computer; at the end of the capture, the object is rotated a small fraction of angle and another image is captured; after a complete rotation of  $360^\circ$ , 400 images are captured which are mathematically processed and the tomography is obtained; the time to obtain a tomography is about 400 sec. and the maximal size of the object is about 15 cm.

### Neutron tomography applications

**ARCHAEOLOGICAL SAMPLE.** Figure 11 (up) shows a small bone embedded into a pluvial rock basically consisting of quartz and sand. This sample was evaluated by the NT tech-

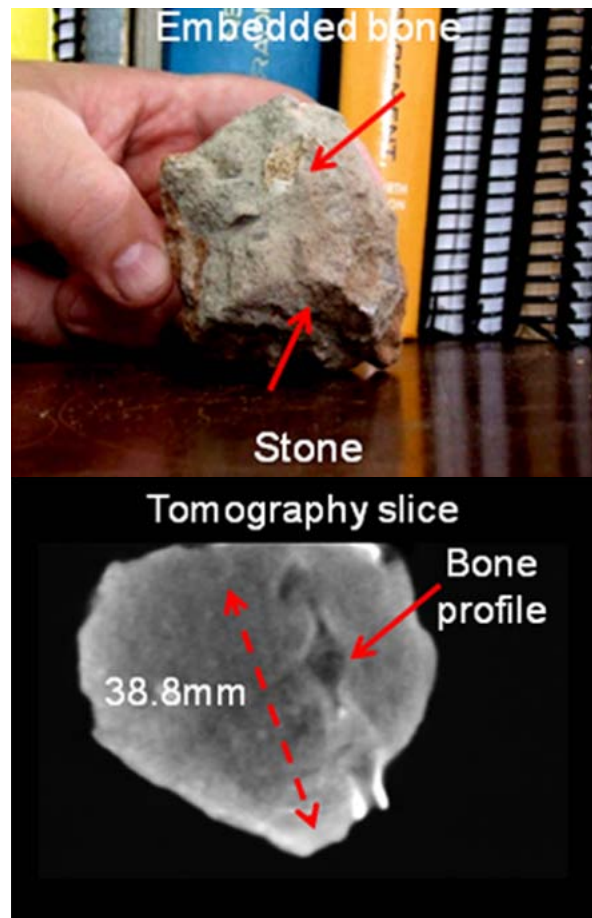


Fig.11. Archaeological sample photo (up) and tomography (down) showing the embedded bone.

nique and one of the obtained tomographies is shown in figure 11 (down). As it can be seen, the bone has 38.8mm in length and, though not shown in the figure, the bone is embedded at 47.25mm from its surface. According to an expert from the University of Brasília, this bone is part of a finger of a crocodylomorpha, from the cretaceous age (aprox. 70Ma) see figure 12.

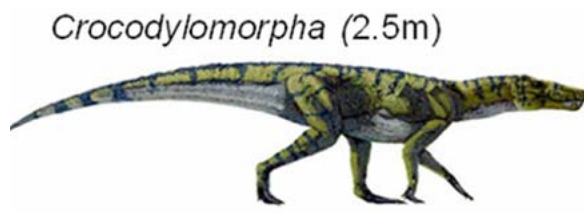


Fig. 12. Crocodylomorpha.

**CERAMIC PRESERVATION USING PARALOID B-72.** The Paraloid® B-72 is one of the most commonly consolidator used for ceramic restoration. A contemporary ceramic vessel was partially brushed with Paraloid® B-72 as shown in figure 13, and it was evaluated by the NT technique to verify the impregnation efficacy, the penetration depth, failures and homogeneity of Paraloid® B-72 distribution into the ceramic body.



Fig.13. Application of Paraloid® B-72 in a ceramic vessel.

Figure 14 shows some selected 3D (three dimensional) images through which the visualization of the Paraloid® B-72 impregnation is

possible, under a macroscopic point of view, helping in the evaluation and visualization of the ceramic - consolidator boundaries, changes in homogeneity of impregnation and depth reached by Paraloid® B-72. In figure 14, it is possible to verify regions with (brighter) and without (darker) Paraloid® B-72; in figure 14b a cut along the XY viewing plane shows some inhomogeneity in Paraloid® B-72 impregnation; in figure 14, a deeper cut along the same plane shows homogeneous impregnation regions with penetration depth of about 1.5mm.

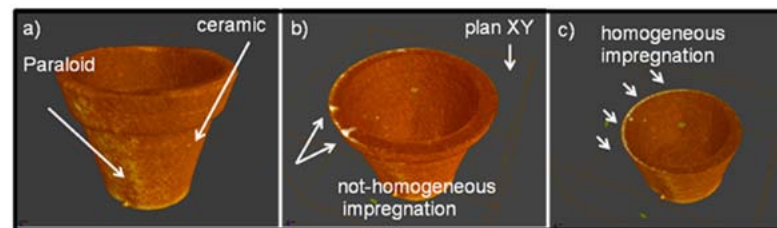


Fig. 14. 3D images showing the distribution of Paraloid® B-72 into the ceramic vessel.

The vessel was fragmented and as showed in figure 15, the impregnation with Paraloid® B-72, more specifically the boundary regions with the ceramic body and its depth, are not visible to the naked eye.



Fig.15. Vessel fragmented. The Paraloid® B-72 is not visible to the naked eye.

These presented results demonstrate the feasibility of the neutron tomography technique to support the archaeological sciences, and

the restorers of cultural heritage objects. The tomography along with the other important neutron imaging techniques such as the one of “real-time” to investigate dynamic processes of liquids, to evaluate water distribution into Hydrogen fuel cells (proton exchange membranes - P.E.M.), positioning of rubber o’rings into metal devices, evaluation of adhesive distribution in several kind of materials and others, demonstrate the wide application of the neutron imaging techniques in several research fields, which are available at IPEN-CNEN/SP.

## Radiation Spectroscopy and Spectrometry laboratory

The Radiation Spectroscopy and Spectrometry laboratory (LEER) at IPEN focuses its activities in measurement of radiations applied to health and environment areas. Analysis of biological materials in humans and animal models were performed to obtain reference values for use in diagnosis of different pathologies. These data are relevant to both veterinary medicine and to public health areas. These investigations are performed using Neutron Activation Analysis (NAA) and X-Ray Florescence (XRF) analytic techniques. In this period, several investigations in veterinary and sport medicine, immunology, genetic and nutritional fields were performed in collaboration with several Research Center: Instituto Butantan, UNISA, UNICAMP, IFUSP, UFF, FEI, I $\mu$ SC-USP, CEGH-IBC and HU/USP. The following studies were conducted:

### Whole blood differences of inorganic elements in dystrophic animal models

The use of alternative analytical techniques to investigate specific electrolytes in body fluids

has increased in past years with the goal of adding advantages and simplifications, compared to the procedures used in conventional clinical practice. Specifically, in this study, a portable X-ray spectrometer with Ag X-ray mini-tube has been employed for evaluation of inorganic elements in whole blood in mice species with Muscular Dystrophy. This disease is characterized by presenting an irreversible progressive degeneration of skeletal muscle. This happens because this disorder is caused by a mutation located in humans on the X chromosome, i.e., considering that the female has two X chromosomes and the male only one, males are affected while in females both chromosomes must be mutated to be affected, so the incidence is significantly lower. For this reason, most females are the DMD carriers. Currently, no effective treatment is available and the muscular dystrophy research progress depends on animal models. Usually the conventional procedures for clinical tests are performed in serum using samples of 0.5 to 1.0 mL. However, when the biological material is scarce (case of small size animal model, i.e. mice), the possibility to use whole blood became a fascinating alternative for clinical practice: the Energy Dispersive X-Ray Fluorescence (EDFRX) analyses can be done using 50  $\mu$ L (the total body blood in mice is around 1.0 mL). In this study, we investigated whole blood samples of three dystrophic mice strains: Dmd<sup>mdx</sup>/J, SJL/J and A/J. This alternative procedure was capable, in a few minutes, to determine inorganic elements of clinical relevance (such as: Ca, Cl, K, Fe, P) in whole blood without chemical digestion using direct and non-destructive analysis. The knowledge of the elemental composition in whole blood of these animal models may help to identify the physiologic difference among them. Moreover, these data can also be useful for biochemistry analyses contributing to studying in more details the anomalies caused by DMD.

### Blood elements concentration in cyclists investigated by instrumental neutron activation analysis

Cycling is one of the most efficient forms of human locomotion requiring low energy per unit mass per distance traveled. It is considered an aerobic activity that helps metabolic functions of the whole body, leading to health benefits. Cycling has been recognized as a means of promoting public health and some large population studies have shown the effects of commuting by bicycle on reducing mortality and cardiovascular risk and lower rates of obesity (in regions with high rates of cycling). Good athlete's performance is characterized by a combination of factors among which stand out physical training and proper nutritional intake. Although physical activities provide health benefits, cyclists impose considerable demands on their body during both training and competition period, which can result in muscle injury depending on the intensity and duration used in the efforts. Similarly, a balanced nutrition should provide nutrients to support growth, development and maintenance of several metabolic and physiological processes. A balanced nutrition reduces fatigue, increases the willingness and prevents the occurrence of injuries and infections, improving performance and recovery post-exercise. Several clinical analysis, mainly in serum and urine, are performed regularly in athletes to check their physical condition, such as, serum glucose, non-esterified fatty acids, thyroid hormones and insulin levels as well as plasma ions. The purpose of this study was to perform an investigation in blood of cyclists in constant training for the last 6 years. In this study, Br, Ca, Cl, Fe, K, Mg, Na, S and Zn levels in blood samples of cyclists were investigated using neutron activation analysis technique. The results were compared to individuals of the same age and gender, but not involved

with physical activities (control group), which showed considerable differences: a decrease mainly in Br (91 %) and Ca (78 %) and an increase in Fe (26 %), S (82 %) and Zn (22 %) levels were evidenced. These results emphasize the importance of blood monitoring for the maintenance of endurance athletes performance.

### Determination of Iron in blood using Portable X-Ray Fluorescence Spectrometer: an alternative for Sports Medicine

High aerobic activity and poor dietary habits may result in depletion of body iron stores, which could decrease aerobic performance and increase the risks of fatigue and immune disorders. Athletes, particularly those involved in endurance sports, are commonly diagnosed with iron deficiency, which leads to higher risks of fatigue, overtraining syndrome and vulnerability to infection. On the other hand, excess of iron is toxic: it can deposit in the form of aggregates in tissues such as liver, heart, pancreas and joints leading to irreversible organ dysfunction. Adequate iron intake recommended for adults are 8 mg/d for men and 18 mg/d for women and the tolerable upper intake levels for adults are 45 mg/d. As a result, the use of supplements by athletes must be strictly controlled. An alternate methodology based on a portable X-ray fluorescence spectrometry (PXRF) for determination of Fe in blood was applied. The iron concentrations was determined in whole blood of amateur athletes (runners) using this portable XRF spectrometer and compared with a control group (male donors at the same age, but not involved with physical activities). It was observed that Fe status in runners' blood was kept near upper limit and in some cases above the normal range, suggesting a slight tendency of iron overload. This increase may cause risk of infection, decreasing the athlete perfor-

mance and, in more severe cases, it can evolve to neurodegenerative disorders. Considering that the athletes did not report the intake of supplement, this increase suggests the need of nutritional reevaluation.

### Development of $^{177}\text{Lu}$ -DOTA-Dendrimer and determination of its effect on metal and ion levels in tumor tissue

Dendrimers are synthetic nanomolecules with well-defined chemical structures. Different strategies have been used for radiolabeling dendrimers with different radioisotopes. There is a variety of dendrimers, and each one has biological properties such as polyvalency, self-assembling, electrostatic interactions, chemical stability and low cytotoxicity. These varied characteristics make dendrimers a good choice in the medical field for several medical applications. In this study, the aim was to conjugate dendrimers with  $^{177}\text{Lu}$ , to observe the in vivo behavior of the labeled compound and to measure the elementary changes in tumor tissue that could be caused by ionizing radiation. PAMAM G4 dendrimers conjugated with DOTA were labeled with  $^{177}\text{Lu}$ . The radiolabeled compound was characterized and its stability was evaluated by reverse phase high performance liquid chromatography. Radiolabeling yield was 98% and stable for 24 hours. Biodistribution studies of  $^{177}\text{Lu}$ -DOTA-dendrimers in C57BL/6 melanoma-bearing mice showed blood clearance with hepatic and renal depuration and tumor uptake. The concentrations of Br, Ca, Cl, Fe, K, Mg, Na, Rb, S, and Zn were determined in tumor tissues of C57BL/6 mice treated with  $^{177}\text{Lu}$ -DOTA dendrimers and in untreated mice. The results showed decreased concentrations of Br (62%), Ca (24%), Cl (51%), K (12%), and Na (60%) and increased concentrations of Fe (8%), Mg (28%), Rb (100%), S (6%), and Zn (4%) in tumor tissues of mice treated with  $^{177}\text{Lu}$ -DOTA-dendrimers. These data may

be useful to evaluate changes in tumor tissues as indicators of damage that could be caused by ionizing radiation.

### Establishment of iron concentrations in whole blood of different mice strains: an alternative for pre-clinical tests of new drugs

Nowadays, Brazil's pharmaceutical companies are testing iron compounds to attend populations of low income. Drug development is complex and extensive (it usually takes years to be approved and marketed). It is a very expensive endeavor undertaken by scientists and pharmaceutical companies. Investment in new drugs requires several steps and it is mandatory to carry out various screening tests before starting the studies in human being. These tests are called pre-clinical and comprise the following fields of study: biopharmaceutical (formulation), in vitro pharmacological studies and in animals in vivo tests for the evaluation of potential clinical efficacy. While in vitro tests are used to identify the pharmacological properties (pharmacodynamics effects) of a new drug, in vivo tests are performed in order to evaluate the safety of new drugs prior to any clinical trial with humans. Considering the low cost, easy handling and simplicity related to the legal implications, the pre-clinical tests are usually performed in mice (small size animal model). There are several mice strains developed for the research of new drugs. The most used strains are C57BL/6J, A/J and BALB/c. Some of them are inbred for high and low antibody-producer ( $H_{III}$  and  $L_{III}$ ), some for maximum and minimum inflammatory response  $AIR_{MAX}$  and  $AIR_{MIN}$ , some for autoimmune diseases (B10.R $_{III}$ , NZW and NZB), others are mutants for muscular dystrophy (SJL/J and Dm(dmdx)/J). This study aims to determine the Fe concentration in whole blood of these distinct mice strains. The results will be cor-



related with human whole blood estimation for checking the similarities, a fundamental requirement to start the pre-clinical tests of new drugs. The Energy Dispersive X-Ray Fluorescence Technique (EDXRF) was applied to determine Fe concentrations in whole blood samples of twelve mice strains. This procedure has been chosen because it requires a small amount of blood for Fe analyses (ten times less comparatively to the conventional tests performed in serum), an important condition when the biological material is scarce (the mice weight is about 20 mg and total body blood is 1.2 mL). Fe concentration result for C57BL/6J mice strain (usually used for pre-clinical drug tests) shows that it is not in agreement with human Fe levels estimation. The present results suggest that A/J and BALB/c strains are more suitable. In addition, the possibility to select a similar strain as a reference facilitates and reduces the cost in pre-clinical tests of new drugs.

### **Analytic techniques to assist the anti-Bothrops serum production in Brazil**

According to the World Health Organization (WHO), the number of deaths by poisonous animals in developed countries is significant. The situation in Brazil has been monitored by SINAN (Sistema de Informação de Agravos e Notificação) and currently 400 accidents occur every month, of which 80% are due to venomous snakebites of the genus *Bothrops*. To meet the large number of incidences, Instituto Butantan (research center, SP city, Brazil) has produced various types of antivenomous including anti-*Bothrops* serum. However, due to the high diversity of snakes (380 species), a large portion of them being venomous, it can sometimes result in an inappropriate antivenom. In addition, recent investigation showed that the *Bothrops* venom of certain species can vary significantly according to the geographic

distribution (in the Northern region, the snake poison of jararaca is 30 times more potent than that found in the Southeast region). In this study, the inorganic elements concentration in blood of mice immunized with five different species of *Bothrops* snake venoms were investigated using NAA and XRF techniques. These results were compared to human estimates to prevent damage, due to toxicity of these elements in the immunological therapy.

### **Investigation of the antigen used for the production of antilonomic serum**

The caterpillar *Lonomia obliqua Walker (L. obliqua)* species is very poisonous and has the ability to cause serious and fatal hemorrhagic effects in humans after contact. In the absence of medical attention, which requires the administration of antilonomic serum (antidote), it can lead the patient to death in days.

These caterpillars live in forest regions, but can be found in rural areas and in existing vegetation in urban areas: mango, avocado, guava, peach, araticum, ipê, cedar and aroeira. They have nocturnal habits and live 200 days. During the day, they are grouped in the trunk, at rest. At night, these caterpillars feed on the leaves of the host plant. Since 1996, the Butantan Institute (IBu, Research Center, São Paulo city) produces antilonomic serum (antidote), to reverse such effects, using caterpillars mainly from Paraná (PR), where the prevalence of incidents is high. However, in recent years, the expansion and destruction of natural ecosystems provide their growth in other regions of the country (mainly Santa Catarina, São Paulo and Rio Grande do Sul). Nowadays, the number of accidents more than tripled in these regions. Considering that, the efficacy and safety of antivenom immunotherapy is closely related to process control, it is desirable to establish procedures that are

reproducible and traceable. Aiming to standardize the antigen obtained from different regions, its elemental composition was investigated using Neutron Activation Analyses technique (NAA). The measurements were performed in the IEA-R1 nuclear reactor (IPEN/CNEN-SP, Brazil). The elements Cl and Na were identified as majorities while the presence of As, Ca, Cr, Fe and S were also observed, but in small concentration ( $\mu\text{g/L}$ ). These data can be used to standardize a specific antilomic serum for caterpillars (*L. obliqua*) coming from different regions of Brazil.

### Characterization of inorganic elements in coxal fluid of *Ornithodoros brasiliensis* (Acari: Ixodidae)

*Ornithodoros brasiliensis* tick has distribution restricted to the State of Rio Grande do Sul (São Francisco de Paula). Due to its quick engorgement, hydrostatic balance is maintained through the secretion of excess body fluids and ions in the coxal liquid (CL) by coxal gland, during and after feeding. The biochemical and ionic compositions are unknown; moreover, recent investigations suggest that there are some molecules able to help the tick in anti-haemostatic strategies. The aim of this study was to determine the elemental composition of the coxal liquid of this tick using NAA. The liquid was collected during and after tick feeding; the ticks feed on rabbits (*Oryctolagus cuniculus*). The NAA measurements were performed in the IEA-R1 nuclear reactor at IPEN/CNEN-SP (3-4.5MW, pool type). These measurements revealed high concentrations of Na, Cl and S suggesting the association with osmotic pressure regulation mechanisms during tick feeding and the presence of Br, Mg, K, P and Ca as trace. The data are crucial for appropriate purification and characterization of the relevant proteins in this secretion.

### Quantitative analysis of light elements (Z<26) in serum and whole blood using compact XRF spectrometers

The use of analytical techniques to investigate specific ions in body fluids has increase in last year's presenting significant progress in clinical tests. This motivated us to check the performance of two compacts XRF spectrometers, consisting of Ag and Au X-ray mini-tubes associated with a Si Drift detector with Be window ( $12.5\mu\text{m}$ ) for this clinical finality. Using the Energy Dispersive X-Ray Fluorescence technique (EDXRF), specific ions of clinical relevance, such as, Ca, Cl, Fe and K were investigated using standards (certified solutions). The performance of these spectrometers were checked by evaluation of several parameter (linearity, reproducibility, accuracy, precision, sensitivity and detection limit) usually considered for validation procedures on analytical methods, according to ISO 17025 and EURACHEM/CITAC norms. The method was proved to give reliable results with limits of detection at levels of 0.23 to 0.58  $\text{mgL}^{-1}$ . Considering that the ranges of the body fluids, such as: blood, saliva, serum and urine, are in the order of hundreds of  $\text{mg L}^{-1}$ , this procedure is very promising for ions dosage requiring a small amount of sample ( $50\mu\text{L}$ , 10 times less comparatively to the conventional tests), simultaneous analysis, short time of analysis (minutes) and simple sample preparation. In addition, this procedure offers a non-destructive alternative for clinical usage.

These compact spectrometers have also potential use when the biological material is scarce, case of the pediatric practice in newborns and premature infants (blood collection is the main cause of transfusions) and in vivo tests, in small size animal model (mice and rats), in order to evaluate the safety of new drugs, vaccines and others medical supplies.

## Determination of iron supplementation in food fortification using X-ray fluorescence technique

Anemia, due to iron-deficiency in the World, is a public health problem that affects especially poor women and children ( 8.8 % of the population). If it occurs in early childhood and infancy, it causes impair cognitive performance in language skill, motor ability and coordination. Anemia in Brazil is a public health problem due to iron-deficiency. In the last decade, according to National Health Surveillance Agency (ANVISA), several strategies have been adopted for preventing iron deficiency in the Brazilian population, such as, the food fortification. However, this dysfunction is still a public health problem: the prevalence among children under 5 years' old and pregnant women is in a range of 20-40 %. Recent studies have shown that Fe supplementation is still inappropriately used: much iron fortified food does not reach the minimum amount (8mg/day) or exceed the recommended limit (44mg/day). Among the food highly consumed by the Brazilian population, wheat flour is a target of nutritional interest (fortified food with Fe). The application of a fast and precise methodology to iron evaluation becomes necessary. In this research, various brands commercially available were evaluated using X-ray fluorescence technique (EDFRX). The results were compared with the minimum amount recommended and with the tolerable intake limit. The results obtained show that in some cases it is in serious disagreement with the established limits.

## Elemental characterization of the extract of propolis produced by *Scaptotrigona Aff. postica* bee from Brazil

The *Scaptotrigona Aff Postica* bee (Tubi) species is an insect stingless belonging to Apidae family and subfamily Meliponinae. This ge-

nus occurs throughout Neotropics. In Brazil, it is found in the northeastern, mainly in the Barra do Corda County (Maranhão). A Tubi hive has around ten thousand bees; at least double the population found in hives of other Brazilian species. They are not large producers of honey, but they are very efficient producers of pollen (8 kg/year) and propolis (1.5 kg/year). Specifically, the propolis produced by this bee has several medical applications: it is used in the healing of wounds with an inflammatory process, in treatment of prostate tumors and has activity against herpes and rubella viruses. Considering its importance in medicinal use and the great variability in relation to botanical origin, its standardization in relation to the dosage of inorganic elements, it is important to meet the different medical applications. The objective of this investigation was to perform its multielemental characterization using Neutron Activation Analysis and X-ray fluorescence technique techniques. Several collections were performed after each flowering, because several factors influence the composition of propolis, such as: the collection site, the season, plants (trees and / or flowers) and if the bee makes use of the land. These data increase the knowledge of its inorganic components and can introduce improvements in the production of these extracts of propolis, mainly as regards to toxicity.

## Applied Nuclear Physics, Instrumentation and Scientific Computing

### Instrumentation

The measurement of short-lived isotopes often requires a compromise: either the source is placed close to the detector, implying in pile-up problems in the first half-lives, or farther, but then the count rates decrease quickly after

two or three half-lives. In an attempt to overcome these problems, a programmable sample positioning system was developed which accepts up to four different steps in the counting procedure, moving the source closer to the detector at pre-programmed intervals, and handling the data acquisition accordingly. The system, comprised of a step motor and an ABS plastic source holder and positioned, coupled to an Arduino Uno programmable board and to a PC, has an easy-to-use graphical interface (GUI) and interacts with Canberra's Genie-2000 data acquisition software. The prototype was thoroughly tested and the source positions were found to be accurately reproduced every time, showing that the system can be safely used in comparative measurements.

A low-noise charge-sensitive preamplifier built from low-cost commercially available components was developed, and its performance proved to be acceptable when compared to the reference ORTEC 142 preamplifier.

A neutron detector is under development which uses a commercial photodiode coupled to boron-deposited glass. The deposition is made by laser ablation, in collaboration with the Laser Center at IPEN (CLA).

A very extensive analysis of the long-term efficiency stability of HPGe detectors was performed using the daily verification data gathered for the Neutron Activation Laboratory's detectors over the last 25 years. Data from 11 detectors from the 2 major brands (Ortec and Canberra) were corrected for source decay and analyzed. The results showed that Ortec's Pop-Top detectors suffer from frequent vacuum degradation, requiring periodic annealing to restore the detectors to the nominal energy resolution. The Canberra detectors didn't require any annealing during these years, albeit suffering from a small, manageable, resolu-

tion decrease over time. The analysis of the detection efficiency, though, showed similar results for both brands, with detectors losing up to 1% of their detection efficiency per year.

In collaboration with the Advanced Studies Institute of the Aeronautic Technological Center (IEAv/CTA), a project aiming to the monitoring of ground neutron doses originated from cosmic rays is under development. The project also includes the development of a specifically-designed neutron monitor.

In collaboration with the Relativistic Heavy Ion Group of the Physics Institute of the University of São Paulo, we are developing a neutron detector based on the Gas Electron Multiplier concept (GEM). In this detector, the radiation ionizes gas molecules generating free electrons that are accelerated by strong electric fields present in small holes bored on thin plates (typical 50  $\mu\text{m}$ ), subject to high voltage between their surfaces. Due to the high field, these electrons produce secondary free electrons (multiplication process), which are collected in the anode. Since neutrons do not produce ionizations, we use enriched  $^{10}\text{B}$  or natural B films deposited on the cathode and on the GEM plates to work as neutron converters by the  $^{10}\text{B} + n \rightarrow ^7\text{Li} + ^4\text{He}$  reaction. The  $^7\text{Li}$  and  $^4\text{He}$  ions are the particles that produce the primary free electrons. In this project, the thin GEM plates were changed by thick plates of FR4 (0.5 mm), which are common circuit boards used in electronics. As, for this detector called thick-GEM (TGEM) the materials are found in the electronics market, it has a low cost compared to the previous GEM plates.

### Enhancements in NAA procedures and analyses

The Neutron Activation Analysis technique is a very well-established and largely used

analytical technique in IPEN at the Neutron Activation Laboratory (LAN). Nevertheless, several tasks have been undertaken in the last years aiming to improve IPEN's NAA results, either by focusing in the technique itself or in the data analysis.

In this sense, Sm determination in uranium-rich samples was studied, focusing not only in the interference of fission-produced Sm, but also in the spectral interference in the 103keV gamma-ray line that arises from the x-rays of Pu, which is produced by sequential neutron captures on  $^{238}\text{U}$  and  $^{239}\text{Np}$ . The resulting time-depending correction factor, a novel concept that arose from this work, proved to properly address the problem, rendering reliable results for Sm even in the presence of high amounts of uranium.

A thorough investigation on sources of uncertainty in comparative NAA measurements has also been made, focusing not only in the explicit uncertainty factors, but also in factors that are hidden in the simplification made in the comparative method. In this work, the possible variation in the HPGe detector efficiency between measurements was studied in great detail, and it was shown that for dead-times below 10%, the efficiency variation won't contribute with more than 0.05% to the final uncertainty. A study on the explicit sources of uncertainty has shown that, for long-lived isotopes (half-lives greater than one day), the time-related parameters (decay constant and time) contribute with no more than 0.5% of the final uncertainty; the counting statistics and comparator concentration contribute with most of the uncertainty (usually around 80-90% of the total), while the uncertainties in the masses typically contribute with less than 20% of the final uncertainty value.

In an attempt to promote automation of the

NAA data analysis procedures, a simple software that automatically analyses spectra in different formats (CHN, CNF and MCA) and exports the results to an Excel-compatible spreadsheet was developed. The software, written in the Pascal computer language, makes use of several tools shipped with Canberra's Genie-2000 to import all the spectra found in a given folder, import energy and FWHM calibrations from a saved reference spectrum (chosen by the operator according to the detector system from which the spectra came) and analyze the resulting spectra; an in-house procedure then reads Genie's output file and produces a Comma-Separated Values (CSV) file converted to the Brazilian language standards (commas as decimal separators and semicolons separating fields) that can be opened in a typical installation of Microsoft Excel.

Preliminary studies aiming to implement coincidence comparative NAA in IPEN were started, in collaboration with NIST and UTexas-Austin (USA), and a fully-digital gamma-gamma coincidence system is under development at IPEN's Applied Nuclear Physics Laboratory. This technique aims to provide an extra tool for NAA analyses when regular NAA can't give good results because of strong spectral interferences, either from very similar gamma-ray peaks or from strong Compton or bremsstrahlung continua.

### Basic Nuclear Physics

The half-life of short-lived  $^{27}\text{Mg}$  was studied by following the activity of samples after they were irradiated in the IEA-R1 reactor. The resulting value of 564.5(7) s is compatible with most of the literature values, but not with the ENSDF compilation value, accepted as a reference value for most experiments, suggesting that further precise measurements of this half-life should be made, and that the ENSDF

value should probably be reassessed.

In a collaboration with the Pelletron laboratory in USP's Physics Institute, the possibility to use gamma-gamma-particle coincidence measurements to determine nuclear reactor cross sections was studied, and the results proved that this can indeed be a very useful technique in these measurements.

In another collaboration with the Pelletron laboratory, together with the Advanced Studies Institute of the Aeronautic Technological Center (IEAv/CTA) and CERN, damage induced by irradiation with electrons, heavy particles and fast neutrons in both regular and aerospace-specific electronic devices is under study.

## Scientific Computing

The efficiency of TGEM detectors for neutrons increases with the number of boron coated plates. The boron layers absorb neutrons and the produced particles ( ${}^7\text{Li}$  and  ${}^4\text{He}$  ions) must have enough energy to leave the boron layer and enter the gas region, which is the sensitive part of the detector. If the boron layer is very thick, most of the  ${}^7\text{Li}$  and  ${}^4\text{He}$  ions are absorbed in the layer and will not enter the gas to produce a signal. There is a maximum thickness for the layer, for which the  ${}^7\text{Li}$  and  ${}^4\text{He}$  ions can cross and enter the gas region. Besides that, when several layers are placed in series, there is an optimal thickness, which depends on the number of layers. Calculations were performed with the GEANT4 Monte Carlo toolkit in order to obtain the optimal thickness for several configurations. The simulated energy spectra of the ions that enter the gas are presented in Figure 16 for several values of boron thickness. Figure 17 shows the dependence of the efficiency on the boron thickness for several layers and Figure 18 shows the efficiency and optimal thickness depending on the number

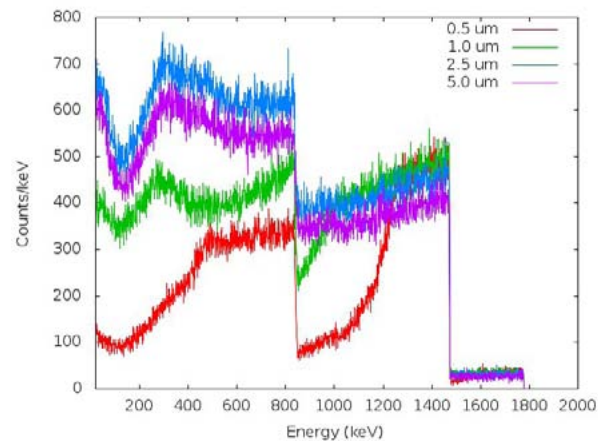


Fig 16. Energy spectra of  ${}^7\text{Li}$  and  ${}^4\text{He}$  ions produced by neutron capture in  ${}^{10}\text{B}$  layers in a gas detector for layer thicknesses of 0.5, 1.0, 2.5 and 5.0  $\mu\text{m}$ .

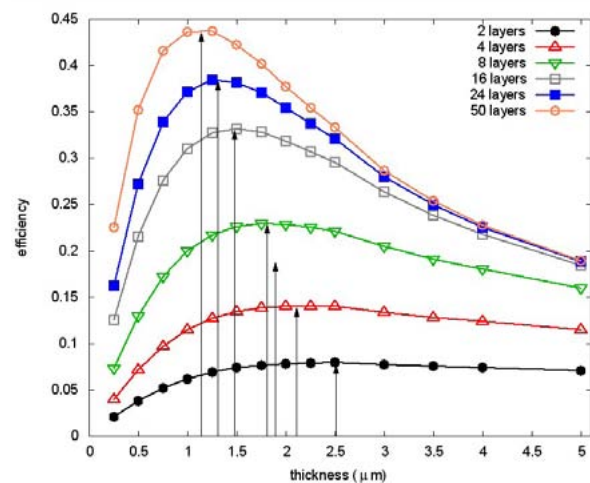


Fig 17. Dependence of the efficiency on the thickness of layers for neutron detectors mounted with several layers of boron deposited on thick-GEM plates.

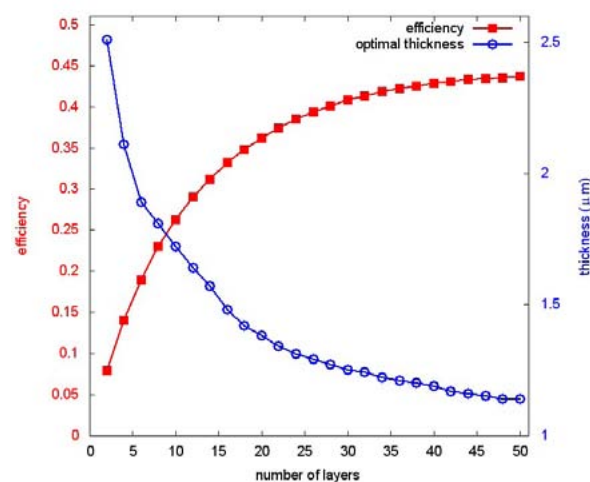


Fig 18. Efficiency and optimal thickness for boron layers of thick-GEM detectors mounted with several plates coated with boron.

of layers used to build the detector. The results of these calculations will give support for the building of real detectors.

## e-Science

At the heart of the scientific development is the finding of new knowledge; generation, support and knowledge maintenance form the basis of the scientific challenge.

One of the pillars of science is the ability of reproduction of the results of scientific research by independent researchers, making possible the validation of methods, results and their conclusions.

In order to enable this in the current scenario, where the scientific data production became so intense (“big data”), systematic storing and curation methods, together with mechanisms for making this data available in a secure way, must be implemented.

With this data deluge, the whole scientific process is impacted, giving rise to a new science paradigm, the e-Science, known as “The Fourth Paradigm of scientific exploration”; it’s related to the data intensive science as distinguished from the traditional computational science.

e-Science is related to finding and sharing knowledge in the form of experimental data, rich theoretical vocabularies, papers and reusable services, useful to scientific community.

To deal with all challenges of this new scenario, a complex and large set of knowledge, systems, methods and technologies is involved. Mathematical models, digital repositories and data management, new hardware, software, protocols, tools and services are some of the necessary items to support the demands of

this new science paradigm.

IPEN has a large number of different researches, such as the Lidar applications in environmental measurements or the neutron activation analysis and its applications in environmental studies, archaeology, forensics, nutrition and health, all generating a large volume of data that must be stored, curated, processed and made available to the scientific community as well as to the society.

The e-Science project at IPEN aims to create a technological infrastructure that can embrace this new methodology and that would allow new workflows of scientific discovery, solving what has become an important problem for the scientific research - the organization, classification, selection and sharing of the giant amount of data produced in recent years by all research areas of IPEN.

The first project, under the scope of the e-Science umbrella, is the creation of a Data Ontology for Neutron Activation Analysis (NAA) laboratory. A semantic layer is being built atop of the traditional data layer to allow more intelligent exploration of all data produced by the NAA technique.

## Activities at the Nuclear Metrology Laboratory

For many years, the Nuclear Metrology Laboratory (LMN) has been involved in developing procedures for the standardization of important radionuclides applied in nuclear medicine or reference standards for semiconductor detectors. The primary systems used by the LMN for this purpose are two  $4\pi\beta\text{-}\gamma$  coincidence systems: one consisting of a proportional counter, coupled to one or two 3”x 3” NaI(Tl) crystals, and a triple coincidence system, consisting

of a proportional counter, coupled to a 2" x 2" NaI(Tl) crystal and to a HPGe crystal. An additional coincidence system has been established, employing a plastic scintillator detector in 4 $\pi$  geometry, called 4 $\pi$ (PS) $\beta$ - $\gamma$ . The disintegration rate is obtained by the application of the efficiency extrapolation technique.

These systems can run by means of conventional electronics for data acquisition or by applying a Software Coincidence System (SCS) capable of registering both amplitude and time of occurrence of all pulses produced in the beta and gamma detection channels. The SCS allows selection of parameters such as beta and gamma discrimination windows or dead time and resolving time after the measurement has been completed. As a result, several extrapolation curves, each one obtained in a different experimental condition, can be determined from a single measurement.

Liquid scintillation counting is another primary standardization technique recently adopted by the LMN. In this case, the CIEMAT/NIST and TDCR methodologies have been applied.

During the period from 2014 to 2016, the following radionuclides have been standardized by these primary techniques:  $^{14}\text{C}$ ,  $^{32}\text{P}$ ,  $^{64}\text{Cu}$ ,  $^{90}\text{Y}$  and  $^{111}\text{In}$ .

As a complementary activity related to radionuclide standardization, the LMN has been heavily involved in Monte Carlo simulation of the extrapolation curves obtained by the 4 $\pi$  $\beta$ - $\gamma$  coincidence technique. For this purpose, the response functions of beta and gamma detectors have been calculated by means of the transport code MCNP, version 6. These response functions are used as input data for another code developed at the LMN, called ES $\mu$ UEMA. This code makes use of the Monte Carlo method

for simulating all detection processes involved during radionuclide decay, being able to predict the beta and gamma detection spectra, including coincidence events and secondary radiation emission such as conversion electrons, X-rays and Auger electrons. A new code has been started to calculate the cascade summing correction based on MCNP6 calculations.

The LMN has also been involved in the determination of gamma ray emission probability per decay of  $^{64}\text{Cu}$ . The measurement of gamma ray emission probability per decay was carried out by means of a REGe spectrometer with a Be window. As a by-product of this technique, gamma emitting radionuclide impurities from the radiopharmaceuticals produced by IPEN have been determined by the LMN for quality assurance as required by the Brazilian authorities.

Another field where the LMN has been involved is neutron measurements. Since 2007, research is being developed on covariance analysis of  $k_0$  Nuclear Activation Analysis (NAA) methodology. During the period from 2014 to 2016, the neutron spectral parameter  $\alpha$  and the neutron flux ratio  $f$  were determined at the 24A irradiation position near the IEA-R1 research reactor core. In addition, parameters  $k_0$  and  $\mu_0$  were determined experimentally for reactions  $^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$ ,  $^{74}\text{Se}(n,\gamma)^{75}\text{Se}$ ,  $^{94}\text{Zr}(n,\gamma)^{95}\text{Zr}$ ,  $^{96}\text{Zr}(n,\gamma)^{97}\text{Zr}$ ,  $^{113}\text{In}(n,\gamma)^{114}\text{In}$ ,  $^{186}\text{W}(n,\gamma)^{187}\text{W}$  and  $^{191}\text{Ir}(n,\gamma)^{192}\text{Ir}$ .

The LMN also supplied standard sources of  $^{152}\text{Eu}$ ,  $^{133}\text{Ba}$  and  $^{57}\text{Co}$  for the calibration of detection systems as part of the FAPESP-approved project "Ionization of internal atomic layers by impact of electrons with energies of 10 keV to 5 MeV in the Microtron of São Paulo" coordinated by Prof. Vito R. Vanin from the Institute of Physics of the University of São Paulo (IFUSP).



# Neutron Activation Analysis

## Environmental applications of neutron activation analysis

### Trace elements status in the terrain of an impounded vehicle scrapyard

Urban soil contamination varies considerably depending on different anthropogenic activities within city perimeters. However, one of the most common sources of pollution present in most cities is vehicular. Over the past decade, worldwide vehicle production has increased rapidly and tends to continue to rise due to demand. In Brazil, the number of licensed vehicles has increased by 118% over the last decade, totaling a fleet of 89 million vehicles in 2015. Impounded vehicle scrapyard (IVS) overcrowding has become a problem in many Brazilian cities. Brazilian law states that apprehended vehicles must not remain longer than 90 days in an impound yard. However, in spite of this, they remain longer than that and suffer from weathering action. Mostly, the ground of these areas is not impermeable. The main sources of pollution are liquid residue spills, leachates produced by rainwater leaching and particulate material resulting from vehicle decomposition.

Metals and some metalloids are important pollution sources in different parking areas. Many metals are present at different levels in leaded and unleaded gasoline, diesel oil, anti-wear substances added to lubricants, brake pads, and tires, as well as emitted by vehicle exhausts. The main components of automobiles are steel materials, including those that contain alloys and are composed by elements such as Al, Co, Cr, Cu, Fe, Mn, Mo and Ni. Metals are non-degradable in soil, and their high toxicity and persistent nature in the environment, even at low levels, may

result in long-term cumulative health effects, making them priority pollutants. Several authors studied metal contamination in soils under and in the vicinity of discarded vehicle scrapyards, mechanic workshops and vehicle dismantlers. Most of them observed moderate to high contamination by Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn in the top layer of soil (0-10 cm), decreasing with depth.

In Brazil, in spite of the increasing number of IVS, the consequent soil metal contamination has still received little attention. Therefore, studies on metal contamination in soils of Brazilian vehicle impound scrapyards may provide valuable information to support remediation procedures, as well as encourage improvements in the management practices of these areas.

The aim of this study was to evaluate topsoil samples from an IVS located in Ribeirão Pires, São Paulo, for potentially toxic elements (PTEs), such as As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V and Zn, and rare earth elements. Mass fractions of all elements, except for Co, Cu, Mo and Zn, were higher than reference values. Hot spots were observed for most elements suggesting vehicular source. The geoaccumulation index showed moderate pollution of As. The enrichment factor pointed to a significant enrichment of As, Mo and Pb. The normalization of REEs to Earth's crust values indicated a positive anomaly of Ce. The results indicate a potential risk to the soil quality of the scrapyard. (Partnership: Instituto de Geociências da UNICAMP; Financial support: CNEN, CNPq).

### Potentially toxic elements in tunnel dusts from São Paulo city

The vehicle traffic is the major source of air pollution in São Paulo, one of the largest megacities in the world (20 million inhabitants in

an area of 8,511 km<sup>2</sup>). Vehicle emissions are one of the main contributions to atmospheric particle concentrations, including their exhaust, the mechanical wear of tires and brakes and the ejection of particles from the pavement by re-suspension processes. Several studies of metal flows in the anthroposphere point to the traffic sector as a major contributor of diffuse metal emissions. Tunnel dusts have been the subject of several environmental studies worldwide, since measurements inside traffic tunnels can provide an evaluation of emission factors of vehicles in real conditions. In this study, the results of metals and metalloids concentrations of tunnel dusts of the Jânio Quadros tunnel, in São Paulo city, were determined by Neutron Activation Analysis. The results showed higher concentration levels of Ba, Cr, Fe, Sb e Zn in relation to similar studies, mainly in the finer fractions (< 63 μm). Principal component analysis (PCA) indicate that the elements As, Ba, Co, Sb e Zn are originated from vehicular sources. (Financial support: CAPES, CNPq).

### **Bioaccumulation of potentially toxic elements in floating aquatic macrophytes of Guarapiranga reservoir, São Paulo**

The Guarapiranga reservoir is one of the main water supply reservoirs in the São Paulo Metropolitan Region, providing water for about 4 million inhabitants. The contamination of aquatic ecosystems by trace elements originating from anthropogenic activities is of great concern. Besides the increase of metallic elements, the eutrophication of aquatic systems is a serious problem, since it can affect aquatic community dynamics. In Brazil, domestic sewage is the main input of nutrients, which in turn aggravates the process of eutrophication. This results in excessive growth of aquatic macrophytes. Macrophytes are defined as macroscopic size higher plants, which are present in aquatic environments. They are classified as rooted and

emerged plants, with floating or submerged leaves and submerged or free floating plants. Macrophytes are used for monitoring aquatic environments by changes in the composition of the communities as impact indicators and by chemical essays to evaluate contaminant bioaccumulation. Nowadays, there is not sufficient information about trace elements contamination in sediments, water and macrophytes in the Guarapiranga reservoir. The present study aims to assess the contamination of metallic elements in water, sediment and macrophytes in the Guarapiranga reservoir, to provide a more current diagnosis of this important and strategic environment.

Sediment and macrophytes sampling was made with the support of the Environmental Agency of the state of São Paulo (CETESB), following the CETESB guidelines of sampling and sample preparation. The samples were analyzed by Instrumental Neutron Activation Analysis (INAA), ICP OES e CV AAS in order to determine the following elements: As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. The results obtained for the sediments were compared to the limit values reported by The Canadian Council of Ministers of the Environment. These values, TEL (Threshold Effect Level) and PEL (Probable Effect Level) indicate the concentrations limits which can cause adverse effects to the biota. The Cu levels exceeded TEL values in all sites. It should be noticed that Cu is frequently used as algicide in the reservoir, as CuSO<sub>4</sub>.

The results obtained for the macrophytes were compared to reference values for aquatic plants, and most of the analyzed elements presented concentration levels above reference values. There was no statistical difference of the analyzed metals among the studied species of macrophytes: *Eichhornia crassipes* (Mart.) Solms. (Aguapé), *Pistia stratiotes* L. (Alface d'água), *Salvinia herzogii* de la Sota (Salvinia,

Orelha-de-rato) e *Salvinia cf molesta* D. S. Mitch (Salvinia, Orelha-de-rato). Multivariate statistical analysis suggested that the elements As, Co, Cr, Hg, Ni, Pb e Se may have a common source. (Partnership: Companhia Ambiental do Estado de São Paulo - CETESB; Financial support: CNEN, CNPq).

## Sediments

The study of the metal distribution in sediments is very important from the point of view of environmental pollution. The sediment concentrates metals in aquatic systems, and represents a relevant contamination monitor. Studies of sediments from estuaries, lakes and rivers, which have been polluted by heavy metals, represent the comprehension of transportation phenomena in these complex ecosystems and the discovery of the pollution history. Two projects were developed within this important subject: "Toxic Metal, Trace and Rare Earth Element assessment in sediments from water supply reservoirs from São Paulo State". Five important reservoirs, Rio Grande, Guarapiranga, Billings, Itupararanga and Graminha (Caconde) were and are still being studied. The other important project is "Evaluation of the Extension and Pollution History by Metals and Trace Elements in River Sediments - Case Study, Tietê River, State of Sao Paulo". The Tiete River drains an area composed of six sub-basins (Alto Tiete, Sorocaba/Médio Tiete, Piracicaba-Capivari -Jundiai, Tiete/Batalha, Tiete/Jacaré and Baixo Tiete). Along its extension (1,100 km), its margins bathe 62 municipalities. In spite of all its historical contribution, hydroelectric potential and being one of the most economically important rivers in the state of São Paulo, the Tiete River is also one of the world's most polluted rivers, especially in the municipality of the city of São Paulo. As a result of pollution problems observed in the last few decades, the aim of this study was to

evaluate the concentration of metals, major and trace elements in surface and core sediment samples, in 34 points from its source in Salesópolis until the end, on Parana River. In all these studies, the toxic metal, some trace and rare earth element concentrations using three analytical techniques (INAA, AAS and ICP OES) were assessed in bottom and core sediment samples. The distribution of some major (Fe, K and Na), trace (As, Ba, Br, Co, Cr, Cs, Hf, Hg, Rb, Sb, Sc, Ta, Tb, Th, U and Zn) and rare earth (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) elements in sediment samples was done by using INAA. ICP OES was used to determine metals Al, As, Ba, Cu, Cr, Fe, Mn, Ni, Se and Zn. For the toxic metals Cd, Hg and Pb, the AAS (GF and CV) technique was applied. The concentration values obtained for the metals As, Cd, Cu, Cr, Hg, Ni, Pb and Zn were compared to the Canadian Council of Minister of the Environment (CCME) oriented values (TEL and PEL values), adopted by CETESB. The Enrichment Factor (EF) and Geoaccumulation index (IGeo) were also used for sediment contamination assessment. From these data, an evaluation of metal and trace elements accumulation in sediments was done as well as the assessment of possible adverse interference of these elements in the biota and water quality of these environments.

Another study was related to the contamination of an estuarine system, a lagoon-estuary complex area of Iguape-Cananéia, located in the coast of São Paulo State. Cananéia is considered as part of Biosphere Natural Reserve due to its environmental and cultural importance and is considered unpolluted. The region encloses the Valo Grande channel, built more than 160 years ago, which favors the introduction of fresh water from Ribeira de Iguape River directly into the estuarine system, contributing to important biogeochemical changes in the region. Through this channel, many nutrients arrive at the estuary, as well as, metals and

other slightly soluble elements, which end up as sediments. The purpose was to undertake a comparative study of biogeochemical impacts in this area, with emphasis to the Valo Grande influence, analyzing sediment samples collected along the region. The sediment samples (superficial and cores) were analyzed by INAA technique. The focus was on the Rare Earth Elements (REE) behavior and distribution in this estuarine system and surroundings. These findings are very important, considering the different scenarios of impact and environmental preservation contained in the various sectors of a single system, seeking to highlight processes of transportation and distribution of materials, as well as the recording of preterit processes. Finally, this work allows the verification of the potential of this tool in the evaluation of natural and anthropogenic environmental contributions in coastal water systems. (Partnership: Environmental Company of the São Paulo State - CETESB, Instituto Oceanográfico - IOUSP, Instituto de Geociências da USP; Financial support: FAPESP).

### Biomonitoring of marine pollution

Sea urchins are marine and benthic invertebrates, many of which sessile or with reduced mobility. The species *Lytechinus variegatus* (Lamarck, 1816) is geographically widely distributed, from North Carolina, in the United States, to the South of Brazil (Figure 19). The species *Sterechinus neumayeri* (Meissner, 1900) is most abundant in shallow Antarctic seawater, from the coast until 400 m depth (Figure 20). The purpose of the present study was to verify if these sea urchin species can be used as biomonitor for metal contamination studies in two regions. In each region, two different places were selected for study: The north coast of São Paulo, the São Sebastião Channel (contaminated region) (23.058' – 23.053'S) and Ilhabela (control place) (45.230' – 45.589'W)



Fig 19. Sea urchin, *Lytechinus variegatus* (Lamarck, 1816).



Fig 20. Sea urchin, *Sterechinus Neumayeri* (Meissner, 1900).

by using the *Lytechinus variegatus* species and Comandante Ferraz Brazilian Antarctic Station (EACF), part of the Brazilian Antarctic Base, King George Island, Admiralty Bay, Antarctica, by using *Sterechinus neumayeri* species. In this last region, two places were chosen: the “control” place known as Botany (62 05. 400' - 62 05. 556' S; 058 18,127' - 058 18. 612' W) and the other, the “contaminated” one, an area near the station where a fire occurred in 2012, consuming about 70% of the facilities. After collection, a mixture of gonads and gut of the sea urchins (20 individuals of each site) were prepared for analyses. Two analytical techniques were applied and the concentrations of the following elements were determined: some trace elements (As, Ba, Br, Ca, Co, Cr, Rb, Sb and Sc) and micronutrients (Ca, Fe, K, Na, Se and Zn) by instrumental neutron activation

analysis technique (INAA) and toxic metals (Cd, Hg, Ni and Pb) by Atomic Absorption Spectrometry (CV AAS and GF AAS). In order to verify if they can be used as a biomonitor for metal contamination in the regions studied and others, the concentration results for the toxic metals and trace elements in the sea urchin species tissues are being investigated. This project also aims to contribute with values for micro and macronutrient concentrations for these organisms, due to the lack of information in the literature. (Partnership: Instituto de Ciências Biomédicas da Universidade de São Paulo; Universidade Estadual Paulista JÁlio de Mesquita Filho, Campus do Litoral Paulista; Financial support: CNPq - PROANTAR)

### Biomonitoring of chemical element pollutants in Tree barks

Investigations on aerial pollution and its effects on public health have become important in programs related to the reduction of pollutant levels in many cities of the world. São Paulo city is no exception. The use of a biomonitor to evaluate pollution levels should be considered as an additional support to conventional instrumentation currently in use by the governmental agency, the Environmental Company of São Paulo State (CETESB) due to the extension of São Paulo city, as well as, to serious pollution problems. Thus, in order to develop a biomonitoring program, it is very relevant to choose a suitable monitor.

The applicability of tree barks for air monitoring purposes is increasing due to its simplicity of sampling without causing damage to the tree, easier sample treatment and tree species identification when compared with other species such as lichens or mosses that often require a specialist in taxonomy.

This study focused on the evaluation of ele-

ment pollutants in two arboreal species, *Sibipiruna* (*Poincianella pluviosa*) and *Tipuana* (*Tipuana tipu*, Kuntze) abundant and dominant in urban areas of São Paulo city, using the instrumental neutron activation analysis (INAA) and graphite furnace atomic absorption spectrometry (GF AAS) methods.

Results obtained indicated that element concentrations in the barks depend on the tree species. Higher element concentrations obtained for *Tipuana* rather than those for *Sibipiruna* can be attributed to the characteristics of the bark surface. The *Tipuana* bark surface is porous, roughened and fissured while *Sibipiruna* presents barks in squamous form. Fig 21 shows trunk bark images of the *Sibipiruna* and *Tipuana* tree species. The entrapment and accumulation of elements in tree barks depends on structure porosity.



Fig 21. Bark surfaces of the *Sibipiruna* and *Tipuana* trunks..

Besides, to obtain a representative sample, it is relevant to collect barks around the trunk as well as to take the same thickness of outer layer for the analysis since there are differences between outer and inner layer element concentrations. Different layers of tree bark indicated that most of the element concentrations in the outer layer are higher than those found in the inner layer (Fig 22). Results of bark analyses collected in different sampling sites of São Paulo Metropolitan

Region indicated variability in the elements concentrations with the proximity and intensity of the different emission sources and these results indicated four possible emission origins, such as vehicular plus soil resuspension, industrial, marine aerosol and tree bark composition itself.

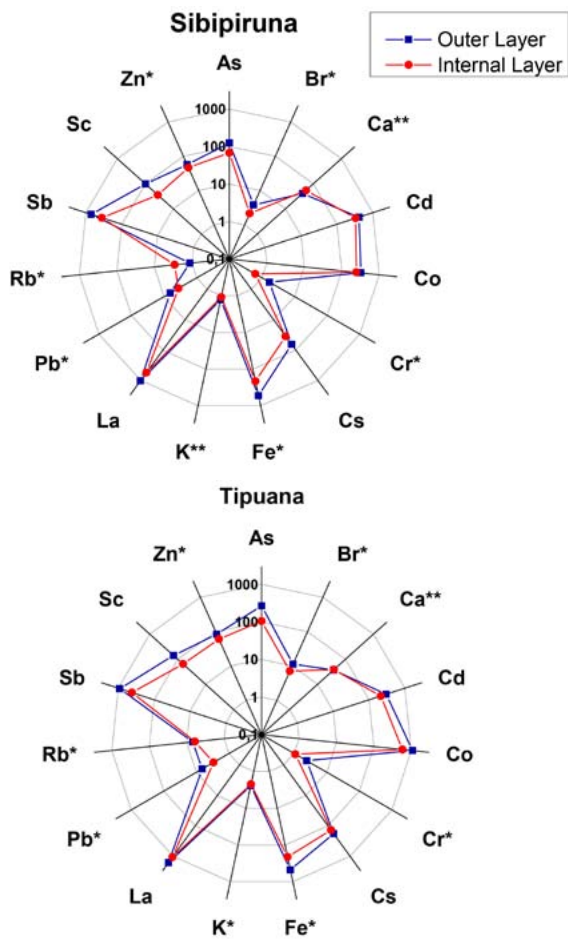


Fig 22. Radar chart of element concentrations in different bark layers of Sibipiruna and Tipuana trees. Concentrations are given in  $\text{g kg}^{-1}$  unless indicated with asterisks (\* - indicates concentration in  $\text{mg kg}^{-1}$  and \*\* - in  $\text{g kg}^{-1}$ ).

### Biomonitoring of chemical element pollutants using Epiphytic lichen

In this study, for passive biomonitoring of air pollution levels at the Cidade Universitária Armando Salles de Oliveira (CUASO), University of São Paulo campus, epiphytic lichens of *Canoparmelia texana* species were used. The

lichens collected from tree barks at different sampling sites in the CUASO were cleaned, freeze-dried and ground for analyses. The analytical methods of X-ray fluorescence spectrometry (XRFs) and neutron activation analysis (NAA) were applied to these analyses. Replicate analyses of a lichen sample by XRFs and NAA, indicated good homogeneity of the sample for the elements determined. The lichen results showed that the mean concentrations of As, Br, Ca, Cd, Co, Cr, Cs, Rb, Sb, Se and U were higher in samples from CUASO than those from regions considered unpolluted. For Fe, K, La, S, V and Zn, they were of the same order of magnitude. For some elements, the hot spots of their concentrations were probably verified due to the dispersion of particulate material from laboratory or incinerator emissions and building constructions.

### Production and characterization of biological reference materials

A certified reference material (CRM) is a reference material accompanied by a certificate, whose values are certified by a procedure which establishes its traceability to an accurate realization, in which the value is expressed and each certified value is accompanied by an uncertainty at a given level of confidence. Certified reference materials are still not widely used in Brazil and other Latin American countries. The main reason is the high cost of these materials, since most of them are imported. Reference materials are important tools in the quality assurance of analytical results as they are used in method validation, calibration of instruments and in the realization of the traceability of analytical results to stated references. The Neutron Activation Laboratory has been involved in the development of Brazilian biological reference materials, such as mussel and fish with support of the International Atomic Energy Agency (IAEA).



Fig 23. Bottles of the bovine kidney reference material.

All the steps for the production of a bovine kidney reference material were developed, including sampling, sample pretreatments, freeze-drying, grinding, sieving, homogenization and gamma ray sterilization (Fig. 23). Physical and chemical characterization following internationally agreed recommendations were performed, with emphasis on the assessment of the stability of the material, its homogeneity status, residual water content and granulometric characterization. An international interlaboratory program was performed for assignment of As, Cd, Cu, Cl, Co, Cr, Fe, Hg, K, Mg, Mn, Na, Pb, Se and Zn values and associated expanded uncertainties for the kidney tissue.

In the case of the previously prepared mussel reference material, its particle size distribution was characterized by Laser Diffraction Particle Analysis and compared with other reference materials as the distribution may interfere with the homogeneity properties of the material. It was observed that the mussel candidate reference material presents mean particle size of  $94.6 \pm 0.8 \mu\text{m}$ , with Gaussian distribution. The comparison with the results obtained for certified reference materials with similar matrix

showed that the mussel candidate reference material presents particle size distribution similar to the IAEA-407 fish homogenate, prepared with similar technique (Fig. 24). (Partnership: C $\mu$ MA – IPEN; Funding: IAEA, FAPESP, CNPq, CNEN, CAPES).

### NAA studies in *Crassostrea* oyster shells

In this study, the neutron activation is used in

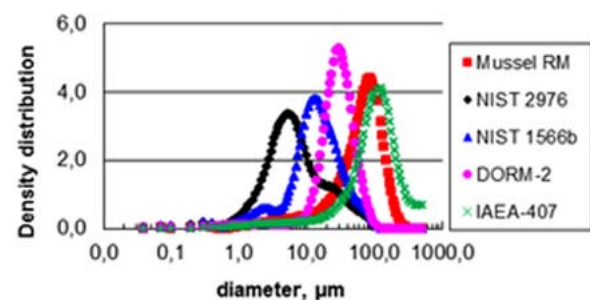


Fig 24. Particle size distribution for various reference materials.

the *Crassostrea* genus oyster shells (Fig. 25) to verify the feasibility of using trace elements as paleo-environmental markers. Samples of oyster shells were collected covering the South, Southeast and Northeast regions of Brazil. To determine the crystalline structure of the





Fig 25. *Crassostrea* genus oyster shells.

samples, X-ray diffraction spectroscopy analysis was used. Differences between origins, elemental composition and mineralogical parameters were used to correlate the results obtained. The normalization factor was calculated using sea water and La as normalizer. Samples were analyzed by chemometric statistical methods: Pearson correlation coefficient and cluster analysis. The results obtained by this normalization indicated a good separation between samples from mangrove regions and samples from the region of higher salinity corroborating the hypothesis that the elemental composition of the oyster shells is indicative of the environment in which they formed. Therefore, the application to environmental and paleo-environmental studies can be an important application of these results.

## Nutritional studies in foodstuffs and diets

Food being the main source of intake of elements, it becomes imperative to monitor the concentration of toxic and essential elements in various food items and products of daily consumption. Trace element concentrations have been measured extensively in Brazilian food and diets of different regions. Neutron Activation Analysis, NAA, has become an important and useful research tool due to the methodology's advantages. These include high accuracy, small quantities of samples and no chemical treatment has been successfully used

on a regular basis in several areas of nutrition and foodstuffs.

### Total Diet Studies: Determination of essential and toxic elements in foodstuffs from São Paulo city.

The techniques of Neutron Activation Analysis and Atomic Absorption Spectrometry have been applied to determine the content of essential and toxic elements in diets from different Brazilian regions. During this period, a Total Diet Study (TDS) was carried out using data of food consumption of the Southeast region of Brazil based in the POF 2008-2009 National Household Food Budget Survey of the Brazilian Institute for Geography and Statistics (IBGE), to evaluate essential (Ca, Cu, Cr, Fe, Mg, Mn, K, Na, Se and Zn) and toxic element (As, Cd, Hg) dietary intakes. This study is on the context of the Fapesp Project 2013/08869-6 about Brazilian Total Diet Study that was approved for the 2013-2015 period. This study is the 2nd TDS, carried out by our laboratory, and included daily individual food consumed both inside and outside of the household, resulting in a total daily individual consumption of the population. The food group approach was chosen over the individual approach so as to provide a smaller number of food samples to the kitchen preparation and analysis. The Food List included 82 food items reported consumed foods, according to the survey. Since it is unavailable

for individual laboratory analyses, food with similar nutritional composition are grouped together, resulting in 19 food groups. The nineteen resulting food groups are as follows: Beans; Beverages; Cakes and biscuits; Cattle meat; Cereals; Dairy products; Eggs; Fish; Flours, pasta and bread; Fruits; Industrialized meat and offal; Nuts and seeds; Oils and fats; Pizza, snacks, sandwiches, soups, sauces, and mixtures; Pork; Poultry; Salt; Sweets; Vegetables. All food samples were acquired in food stores of São Paulo city. The concentration and the dietary intakes of As, Cd, Ca, Co, Cr, Fe, K, Na, Se and Zn in the 19 food groups from the Food List of the 2nd Brazilian TDS were evaluated. This TDS showed that the São Paulo diet was adequate for Cr, Mg, Mn, Se and Zn and deficient for Ca and K. The Cu, Fe, Mg and Mn dietary intakes were higher than the recommended daily intake values and the Na daily intake was higher than the tolerable limit value, confirming the results obtained by the other Brazilian diet studies.

#### **Determination of $^{234}\text{U}$ , $^{235}\text{U}$ , $^{238}\text{U}$ , $^{228}\text{Th}$ , $^{230}\text{Th}$ , $^{232}\text{Th}$ , $^{226}\text{Ra}$ , $^{228}\text{Ra}$ and $^{210}\text{Pb}$ levels and other elements in rural and urban diets from a high natural radiation region of Brazil**

The presence of radioactivity has been detected in food and water in several parts of the world. The natural radionuclide concentrations vary according to several factors, such as local geology, climate and agricultural practices. The degree of damage to human health depends on the type of radionuclide and the period of time that people are exposed to it. It is known that food and water contain radioactive elements, which contribute to an effective internal dose after ingestion. Natural radionuclides from the uranium and thorium series occur widely distributed in the earth's crust. The radioactivity measurement

in food and the environment is extremely important to monitor the radiation levels to which man can be directly or indirectly exposed. Some foods have the ability to retain radionuclides, such as natural radioisotopes and other contaminants. The determination of low concentrations of these elements in food samples is time consuming and requires tedious chemical procedures. An essential feature of these methods is the pre-concentration and purification of the radionuclides of interest. This is important to isolate them from the large amounts of inactive substances present in the sample and also to separate them from radioisotopes that may interfere in these determinations. In this TDS, the activity concentrations of the radionuclides of U and Th series are being determined in rural and urban food from Poços de Caldas Plateau, region that present high natural radiation.

#### **Determination of Cl, K, Mg, Mn, Na and V in Brazilian Red Wine by Neutron Activation Analysis**

Wine contains over 600 different substances known and its moderate consumption has health benefits in the prevention of numerous diseases and longer life expectancy, related in particular to the intake of antioxidants such as polyphenolic compounds. Studies have shown that its inorganic composition depends on various factors which are specific for each production area such as grape variety, the potential of the grapes to absorb soil substances, climatic conditions, vineyard soil, vinification practices and storage conditions. The wine inorganic composition can originate from external factors, such as environmental pollution and absorption of the elements in vineyard soil during grape growth (geogenic); or from the application of fertilizers, pesticides and fungicides to protect the plants. The inorganic components in

wine are important for: organoleptic features that consequently affect the sensor quality, including flavor, freshness, aroma, color, taste and so on. The trace elements are also good indicators of the origin of the wine, due to its direct relationship with soil composition and their concentrations can be used as criteria to ensure authenticity. There are virtually no studies that apply Instrumental Neutron Activation Analyses (INAA) specifically in wines. Among its advantages, the analysis does not require large amounts or chemical treatment of the samples and the ability to determine various elements with high sensitivity. In this study, the concentrations of Cl, K, Mg, Mn, Na and V in seven Brazilian red wine freeze-dried samples from Rio Grande do Sul were determined by Instrumental Neutron Activation Analysis (INAA).

### Determination of essential and toxic elements in marine algae by Neutron Activation Analysis

Overtime, seaweeds have been used as food mainly due to their high nutritional value. This type of food is considered as functional food and contributes to the nutritional human requirements, being beneficial to human health. In this study, 13 edible seaweed samples, acquired in the marked of São Paulo city, were analyzed and the concentrations of elements As, Br, Ca, K, Fe, Mg, Mn and Na were determined by Instrumental Neutron Activation Analysis (INAA). Cu, Cd and Pb will be determined by Graphite Furnace Atomic Absorption Spectrometry (GF AAS). The following edible seaweeds were analyzed: Nori (*Porphyra umbilicates*); Hijiki (*Hijikia fusiforme*); Kombu (*Laminaria sp.*) and Wakame (*Undaria pinnatifida*) species from China, USA, Japan and South Korea. Hijiki specie showed to be source of Ca and Fe while Kombu specie for K.

### Contribution to food safety assurance of fish consumed at São Paulo city

Controlling seafood quality is essential to ensure its safety for human consumption. However, scarce information is available about seafood contaminant status in complex metropolitan markets in Latin America. By the Brazilian law enforcement, the presence of toxic elements such as As, Cd, Hg, Pb, Se and Zn in fish must be monitored and be below stated values prior to human consumption. But little is known about the actual dietary fish intake in Brazil as it may be a regionalized issue. Toxic and essential elements were determined in some of the most consumed fish species in São Paulo city, Brazil: whitemouth croaker (*Micropogonias furnieri*), smooth weakfish (*Cynoscion leiarchus*), common snook (*Centropomus undecimalis*) and Brazilian sardine (*Sardinella brasiliensis*). These fish species are locally known in Portuguese as “corvina”, “pescada” “robalo”, and “sardinha”, respectively. INAA was applied for the determination of As, Br, Co, Cs, Fe, K, Na, Rb, Se and Zn while Cd, Pb and Hg were determined by Atomic Absorption Spectrometry. *Centropomus undecimalis* was the only species to present element mass fractions under the limits of national and international legislations for all elements, with the exception of As results that surpassed the Codex Alimentarius limits. Results for As for all the other species were above those permitted by the Brazilian legislation. Nevertheless, it cannot be affirmed that these species are toxic for humans and should be avoided as most of the As in fish is in the organic form arsenobetaine that is assumed to be of no toxicological concern.

### Activity levels of gamma-emitters and barium concentrations in Brazil nuts

In recent years, nutritionists have suggested daily intake of a certain portion of Brazil nuts

due to its high selenium concentration. Some studies have shown that the daily consumption of one unit of Brazil nuts is sufficient to restore the status of selenium in obese women and the elderly. Selenium is an important part of antioxidant enzymes that act in the prevention of age-related illnesses such as cancer and cardiovascular diseases. In addition to selenium, it is known that Brazil nuts also accumulate barium and radium. Due to the presence of radium in these nuts, the level of radioactivity is 2-4 times higher than that of other vegetable foodstuffs, of the same region. This accumulation of Ba and Ra has been explained as a possible formation of organic complexes that increases the mobility of alkaline earth ions, particularly for these elements, favoring their redistribution during fruit development. Barium is not considered essential and can be toxic depending on its chemical form. The  $Ba^{2+}$  ion and the soluble compounds of barium (notably chloride, sulfide, nitrate and hydroxide) are toxic to animals and humans. Several radioactive substances are considered carcinogens (Group 1 agents), according to the International Agency for Research on Cancer. The carcinogenic activity is attributed to radiation, such as the radiation emitted by  $^{224}Ra$  or  $^{226}Ra$  or  $^{228}Ra$  and their decay products.

In this project, it was proposed to evaluate the concentrations of natural ( $^{226}Ra$ ,  $^{228}Ra$ , and  $^{40}K$ ) and artificial ( $^{137}Cs$ ) radionuclides and Barium concentration in samples of Brazil nuts acquired at final points of sale, in various Brazilian regions. Gamma-ray spectrometry measurements were used to determine the radionuclide activity concentrations and Instrumental neutron activation analysis (INAA) was the analytical method used to determine barium concentration.

Among the radionuclides determined in samples of Brazil nuts  $^{137}Cs$ ,  $^{40}K$ ,  $^{226}Ra$  and  $^{228}Ra$ , the

$^{228}Ra$  was the main contributor to the dose estimated annual intake of 0.27 mSv, with a contribution of 0.24 mSv. Contribution from radioactive fallout, fission product  $^{137}Cs$ , was negligible. Based on the data obtained, it can be said that the radioactivity present in Brazil nuts does not offer health risks for a daily ingestion of one unit. The concentration of Barium in the analyzed samples ranged from 22 to 3700  $\mu g g^{-1}$ . As high concentrations of Ba were found in some samples, the project is still in progress for determination of Selenium in these same samples with the objective of verifying the correlation between the concentrations of Ba and Se present in the Brazil nuts.

### Neutron activation analysis applied to the characterization of different materials

Neutron activation analysis is the elemental analysis method usually chosen for the characterization of different matrices because of some features such as: small amount of sample available, minimal sample handling and high sensitivity for many elements.

### Neutron activation analysis applied in the evaluation of bismuth iodide purification methodology

Bismuth tri-iodide ( $BiI_3$ ) is an attractive material for using as a semiconductor. However, the behavior of semiconductor devices is strongly influenced by the presence of impurities or contaminants remaining due to incomplete purification of the semiconductor material. Small quantities of impurities present at concentrations below 1 ppb can have a significant effect on quality of semiconductor devices. In this project,  $BiI_3$  crystals have been grown by the vertical Bridgman technique using commercially available powder. Efforts have been concentrated on the purification of the  $BiI_3$  and, the purification efficiency was assessed by

analyzing the crystals, through instrumental neutron activation analysis (INAA).

The samples were provided by the Laboratory of the Radiation Detector at IPEN that was developing the BiI<sub>3</sub> crystals growth to be used as radiation semiconductor detector. For purification, BiI<sub>3</sub> crystals have been grown by the vertical Bridgman technique, based on the melting and nucleation phenomena. After completion of the growth step, some crystals were selected from the bottom, middle and top of the system, for analysis of impurities. Another part was reprocessed, i.e. the entire process was repeated. Several repetitions were made in order to obtain the crystal with a high degree of purity.

In this case, INAA demonstrated to be a sensitive analytical technique useful to identify and quantify the impurities: Ag, As, Br, Cr, K, Mo, Na and Sb in BiI<sub>3</sub> crystals in order to distinguish the segregation of the impurities along the crystal and, to evaluate the reduction of the trace impurities, after each purification number.

### Characterization of Brazil Nut Fibers

The agro-industry generates innumerable sources of biomass that are neither sufficiently nor adequately utilized. The use of lignocelluloses fibers and their constituents as raw materials in the production of polymeric and composite materials represent an exceptional opportunity for sustainable technological development. In order to think about potential and future exploitation and applications of lignocellulosics, properties and performance of fibers under environmental or other conditions must be known.

Brazil nuts (*Bertholletia excelsa*, family Lecythidaceae) grow on wild trees with some

of them reaching up to 50 meters in height. These trees can be found scattered throughout the Amazon region. The fruits, known to Brazilians as Castanha do Pará, are characteristically a spherical capsule, with a thick, hard, dark brown surface. From the capsules are extracted the edible seeds, the Brazil nut, considered as one of the most valuable products harvested from a tropical forest. In the extraction process, large amounts of residues formed from Brazil nut shell and bur fibers are generated. In this case, the project consisted in making the physical and chemical characterization of these residues. Instrumental neutron activation analysis (INAA) was used to make the mineral characterization of the extraction by-product. The inorganic composition found in Brazil nut shell and bur fibers were Br, Cl, Cs, Na, Rb (at  $\mu\text{g g}^{-1}$ ) and Co, Sb, Sc, Se and Th (at  $\mu\text{g kg}^{-1}$ ).

## Applications of neutron activation analysis in the study of human health

### Analysis of medicinal clays

In order to meet the demands of the National Policy on Integrative and Complementary Practices of the Ministry of Health that advocates encouraging research in these field, including the social thermalism and medicinal plants, with a view to evaluating the efficiency, effectiveness and safety of care, the nuclear analytical techniques are used in the characterization of the chemical, mineralogical and radiological composition of clays with therapeutic and cosmetic application, elemental composition determination of medicinal plants, studies of the soil elemental composition influence on the production of secondary metabolites, verification of the adequacy on the trace elements contents to the ingestion

limits and evaluation of the potentially toxic elements content in medicinal plants. For such, the techniques of Neutron Activation Analysis, Atomic Absorption Spectrometry, Gamma Spectrometry and X-ray Diffraction have been used.

In the study of the clays' medicinal use, it is important to characterize the raw material and water used in its maturation process (Fig. 26). Although the peloid mechanisms of action are still not well understood, some studies indicate that these may be related to the topical absorption of both inorganic and organic components present in the water and clay mature mixture. In this study, the Peruíbe Black Mud (PBM) was used to treat cutaneous conditions and osteoarthritis. It was verified that the PBM is mainly composed of quartz and presents lower concentrations of Ca, Mg and Mn and higher concentrations of  $SO_3$ , that the maturation process makes the mud enriched in Cl and Mg, that the PBM is also enriched in the elements As, Br, Cr Sb, Se and Zn and depleted in the elements Ca, Rb and Ta in relation to other peloids reported in the literature and that the elements Ca, Mg, Mn and Na are the most available for skin absorption. From the radiological point of view, it was determined that the effective dose resulting from the topical mud applications is three times lower than the allowed dose increment of 1 mSv per year. Clinical evaluation of the use of PBM for the knees osteoarthritis treatment indicated a perception of improvement in 100% of the patients who received this treatment.

Another ongoing project on the medicinal use of clays is the production of artificial peloids. In this project, commercial clays are matured in mineral-medicinal waters of Águas de Lindia, Poços de Caldas and Peruíbe sea water. This study intends to evaluate the influence of water used in the maturation process on the obtained peloid.

## Investigation on elemental composition of pharmaceutical products

Medicinal plants, phototherapies and dietary supplements (multivitamins and proteins) are among the most rapidly growing pharmaceuticals not only in developing countries, but also in industrialized countries. These products are generally commercialized without medical prescription and they may not always present the reliable composition on their labels. Consequently, it becomes of great importance to evaluate the risks arising from the use of these products by means of the determination of toxic elements as well as the essential ones present in excessive doses. At the current stage in which the Ministry of Health and the National Sanitary Surveillance Agency (ANVISA) are investing greater efforts to control all products related to human consumption, it is necessary the development and application of reliable methodologies to analyze pharmaceutical products. These determinations are of great interest not only to the population and medical professionals, but also to industries for quality control of their production

The objective of this project is to evaluate chemical elements in pharmaceutical products for identification of their health risks due to the presence of toxic elements or essential elements in concentrations that could cause adverse effect to human health.

## Phytotherapies and medicinal plants

In Brazil, our tropical forests constitute a rich source of biodiversity for the pharmaceutical industry. Therefore, this type of study has aroused great interest in chemical and pharmacological research for scientific verification of the therapeutic properties from national flora specie. Existing research is still incipient and there is no effective control of the official

bodies for its commercialization in fairs, public markets or natural product stores.

The analyzed phytotherapics were coded with letter F followed by a number. The phytotherapics with their respective content of medicinal plants (in parenthesis) were the following: F1 (*Paullinia cupana* Mart, *Sapindaceae*), F2 (*Peumus boldus*, *Rhamnus purshiana* and *Rheum palmatum*, F3 *Camellia sinesis*), F4 (*Passiflora alata*, *Erythrina mulungu* and *Crataegus oxyacantha*, F5 (*Peumus boldus*, *Rhamnus purshiana* and *Rheum palmatum*). Besides these phytotherapics, the medicinal plants Babosa (*Aloe vera*) and Amoreira (*Morus spp.*), both from the national list of medicinal plants of the Sistema Único de Saúde (SUS) (<http://www.plantas-medicinasefitoterapia.com/plantas-medicinaiis-do-sus>), were also analyzed.

Concentrations of the elements As, Br, Ca, Co, Cr, Cs, Fe, K, La, Na, Rb, Sb, Sc and Zn were determined in these phytotherapics and medicinal plants by applying neutron activation analysis. The high concentration of Ca found in these samples can be associated to the absence of side effects of stomach lesions. The element K was also found in high concentration and the presence of this element has been related to diuretic actions. Potassium is present in natural diuretics, as well as, in drugs used for eliminate phlegm and to invigorate the stomach. In addition, K can regulate body fluids and participate in cardiac muscle contraction. Elements such as Ca, Co, K, Fe, and Zn found in herbal medicines are essential to humans. Zinc is an element present in drugs used in the treatment and prevention of ulcers and to heal wounds. High concentrations of Zn were found in leaves of *Aloe vera* medicinal plant.

The determinations of chemical elements in phytotherapics and medicinal plants are used to verify if they are present at high levels, above

the permissible limit values.

In the study of the influence of elemental soil composition on the production of secondary metabolites in medicinal plants, the elemental concentration was determined by instrumental neutron activation analysis (INAA), graphite furnace atomic absorption spectrometry (AAS GF) and optical emission spectrometry with source of inductively coupled plasma (ICP-OES) in the leaves of *Melissa officinalis* and in cultivated soils. *Melissa officinalis* volatile oils were extracted by the hydrodistillation technique using the Clevenger apparatus and the main secondary metabolites, citronellal, neral, geranial, citronellol, nerol and geraniol were determined by gas chromatography coupled to the mass spectrometer (GC-MS). Spring and summer presented the best quality oils because they had lower contents of citronellol, nerol and geraniol. Neral and geranial formation was favored in the conventional management correlated with the presence of Co, Cr, Mg and Ni elements, while citronellal formation was favored in organic management correlated with Mn.



Fig 26. Medicinal clays.

### Dietary supplements (Multivitamins and proteins for athletes)

The consumption of dietary supplements has become of increasing importance not only to supply nutritional deficiencies, but also to

optimize the metabolic pathways that these minerals are involved in. Besides, dietary element supplementation can result in an improvement in athletic performance. These facts have resulted in an increase in the number of brands and types of multivitamins or mineral supplements as well as dietary proteins available in the market, which makes quality control of these products a subject of great concern to government entities responsible for the general health of the population.

In this study, dietary supplements acquired in pharmacies and drugstores in São Paulo city were analyzed by neutron activation analysis. Concentrations of As, Br, Ca, Co, Cr, Cu, Fe, K, La, Na, Sb, Sc Se and Zn were determined. From these results of element concentrations, it was possible to calculate the data to be used to compare with product label values. These comparisons indicated, in general, a good agreement of the data obtained and the values of the product label depending on the supplement. Daily intake of these supplements was calculated as per consumption instructions stated on the product labels. According to the technical regulation of nutritional labeling of foods and dietary supplements in Brazil, there is a legal tolerance of  $\pm 20\%$  of the declared nutrient quantities on the label. Multivitamin supplements showed amounts of elements within the legislation, unlike dietary supplement proteins for athletes that presented several elements with quantities outside the tolerable level.

The findings of this study suggest a careful evaluation of nutritional supplements available in the market. The study also showed that NAA can provide important information about the composition of minerals present in supplements and, this technique can be used as a control of supplement composition.

### Evaluation Of Mercury Levels In Hair Of Children Residents In Garimpo Area On The City Of Chapada de Natividade – Tocantins

The objective of the work is to evaluate the mercury exposure of children living in the artisanal gold mining area and in a control area, without mining. A cross-sectional study was conducted with children living in the municipalities of Chapada de Natividade and Porto Nacional, in the State of Tocantins, where hair samples were collected for laboratorial analysis of mercury concentrations, comparing between municipalities, gender, monthly fish consumption, profession of parents and the presence of amalgam in dental restorations (Fig. 27 and 28). The participating children were selected from information registered in the cadastre of the service of basic health assistance of Brazil (SUS). The chosen age range was of children from 5 to 6 years, with the aim of not including older children, which might be already submitted to work in the artisanal gold mining activities. The hair samples were analyzed by the methods of neutron activation analysis and also by means of the DMA (Direct Mercury Analyzer) equipment, in the last case in partnership with CETESB. There was no evidence of mercury-related diseases in the



Fig 27. Preparation of fish samples from Natividade, in the state of Tocantins, for mercury analysis.





Fig 28. Collection of hair samples of children living in the state of Tocantins, for mercury analysis.

studied children. The mean concentration of mercury in children in Chapada de Natividade was significantly higher than in Porto Nacional. Children exposed to artisanal gold mining areas had higher concentrations of mercury than children living in non-artisanal gold mining areas. There was no significant relationship between mercury concentrations and gender, monthly fish consumption, parental profession and amalgam presence in dental restorations. The results suggest that the children living in an area exposed to mining experience greater environmental exposure to mercury, regardless of their eating habits or gender. Since it is known from many studies in the literature that hair mercury concentrations may be related to fish consumption, it was considered as relevant to analyze some of the fish most consumed by the studied populations. The fish species chosen were: *Lutjanus cyanopterus* (Caranha), *Leporinus fasciatus* (Piau), *Piaractus mesopotamicus* (PacÁ) and *Colossoma macropomum* (Tambaqui). The concentrations obtained for

the fish ranged from  $29,56 \pm 0,26 \text{ ng g}^{-1}$  to  $44,54 \pm 0,67 \text{ ng g}^{-1}$ , which can be considered as low, if compared to the standards established by the Brazilian legislation (ANVISA).

## Nuclear and non-nuclear analytical techniques applied to archaeological studies

Classification of archaeological ceramics by multi-elemental analysis generally consists of two steps: sampling and measurement of many chemical elements with multi-elemental techniques, such as instrumental neutron activation analysis. The first significant application of activation analysis in archaeology occurred in 1954, when Robert Oppenheimer suggested to a colleague R.W. Dodson the possibility of using trace elements analysis via NAA to establish the provenance of archeological ceramics. The samples were irradiated in a nuclear reactor and measured with a sodium iodide detector coupled to a 100-channel analyzer. The elements Mn and Na were determined, and the results were expressed as ratios of  $^{56}\text{Mn}/^{24}\text{Na}$  showing distinct differences between ceramics from different regions, but similar for samples from the same region. The next major advancement occurred with the modern detectors that greatly increased the energy resolution of gamma rays relative to the sodium iodide detector.

The more abundant and important artifacts found in many areas worldwide are ceramics which combine, in the most part, durability with ubiquity. Today several analytical methods including the nuclear and non-nuclear analytical methods are used for the study of the characterization and the manufacturing of the artifacts. From the chemical and physical analyses, it is possible to infer information about

production centers, trade route identification, raw material, object exchange, time scale, and prehistoric people mobility patterns. This information is possible because differences in chemical composition are typically interpreted as evidence for different production locations.

In our laboratory, the Archaeometric Studies Group of the IPEN-CNEN/SP is working with a research program as a means of physical and chemical characterization of ceramic from several regions of the country. The researchers are inserted in an archaeometric program at Activation Analysis Laboratory – LAN – and are focused on identifying the behavioural factors that affect chemical variability. The group use several analytical techniques, like instrumental neutron activation analysis, INAA, X-ray diffraction, XRD, thermoluminescence dating, electron paramagnetic resonance, among other answering questions like “why”, “where” and “when” in studies of the natural and man-made objects. There is no doubt that if an artifact is held in hand, its age and authenticity is of utmost interest. The most classical dating methodology is based on seriation, stylistic technique, clay and pigment. However, these approaches may reveal which objects belong together, but not their age in a quantitative manner.

A typical procedure used in our laboratory consist in cleaning the ceramics outer surface and drilling using a tungsten carbide rotary file attached to the end of a flexible shaft, variable speed drill. After that, this material is dried in an oven at 105°C for 24h and stored in a desiccator.

For INAA, approximately 100 mg of ceramic samples, the standard reference materials NIST-SRM-1633b and IAEA-Soil-7, are weighed in polyethylene bags and wrapped in aluminum foil. Groups of 8 to 10 samples

and one of each reference material are packed in aluminum foil and irradiated in the research reactor swimming pool, IEA-R1, from IPEN-CNEN/SP at a thermal neutron flux of about  $8.92 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$  for 8 h. Arsenic, Ba, K, La, Lu, Na, Nd, Sm, and Yb are measured after a 7-day cooling time and Ce, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Tb, Th, Zn and U after 3 or 4 weeks' time.

By means of XRD, it is possible to determine the mineralogical composition in the ceramics, i.e., it indicates the relative proportions of minerals in the sample. The chemical and the mineralogical compositions of the ceramics are both complementary and equally important in determining its properties. Both are necessary to understand the history and properties of the material being investigated.

The firing temperature and dating is being used in our Group by means of electron paramagnetic resonance and thermoluminescence to found the firing and the age of ceramic materials found at archaeological sites.

The quartz and feldspar grains found in pieces of pottery or other types of fired clay acted as dosimeters, i.e., they were able to record the amount of radiation to which they had been exposed. In the case of pottery, this radiation dose was that received by the grains since the time when they had been heated. The heating erased the previous TL signal and with it the information on the previous radiation exposure, i.e., that related to the time elapsed since the minerals had been formed. The age calculation in luminescence requires the estimation of two factors: the equivalent dose (De) which is the absorbed dose, generally expressed in Gy (1Gy = 1J) and measured in a luminescence reader, and the annual dose (Dan), which is the received dose of ionizing radiation rate, expressed in mGy/year or Gy/ka. The ratio between both doses, De / Dan,

provides the age.

A typical vessel from Amazon is presented in the Fig. 29.

Fig 29 shows the Marajoara ceramic from Maraj Island on the Amazon river delta area, highly elaborated by means of a process of cultural change that occurred within communities that inhabited the area 3500 years ago.

Radiocarbon dates place the period of major growth and expansion of Marajoara culture between the 5th and 14th centuries. The Marajoara style seems to be related to different regions within the Marajoara domain, as well as to different chronological periods. The designs have a symbolic significance of a social or religious character with highly complex ceremonial wares in form and decoration.

In order to test the archaeological hypothesis, with the elements determined by INAA, special attention is paid in establishing inter-sample similarity by means of advanced statistical methods. The dataset obtained are studied using several multivariate analyses, such as Mahalanobis distance, cluster analysis, principal components analysis, kernel density, discriminant analysis, Procrustes analysis, self-organizing maps, etc. Mahalanobis distance is used to determine outliers in multivariate data. Cluster analysis using the squared-mean Euclidean distance represented in a dendrogram as an initial step in the identification of groups. In principal components analysis, the transfor-



Fig 29. Funerary urn.

mation of the dataset is based on eigenvector methods to determine the direction and the magnitude of maximum variance in hyperspace. However, canonical discriminant analysis extracts a new set of variables that maximize the differences between two or more groups rather than maximizing the total variance of the dataset. It is based on the assumption that the pooled variance-

covariance matrix is an accurate representation of the total variance and covariance. It is assumed that all elements in the data necessarily belong to one of the known groups. Procrustes analysis with stopping rule is used for selection of subsets of variables preserving multivariate data structure.

## Neutron Activation Analysis and Electron Spin Resonance for Fossil Samples Dating

The Electron Spin Resonance (ESR) dating is based on the fact that ionizing radiation can create stable free radicals in insulating materials, like tooth enamel and bones. The concentration of these radicals - determined by ESR - is a function of the dose deposited in the sample along the years. The accumulated dose of radiation, called Archeological Dose (AD), is produced by the exposition to environmental radiation provided by U, Th, K and cosmic rays. If the environmental dose rate (Dan) in the site

where the fossil sample is found is known, it is possible to convert this dose into the age of the sample by the equation:  $\text{age} = AD/D_{an}$ . The annual dose rate coming from the radioactive elements present in the soil and in the sample itself can be calculated by determining the U, Th and K concentration. Therefore, the determination of the dose rate depends on the concentration of these main radioactive elements.

Neutron Activation Analysis has the sensitivity and the accuracy necessary to determine U and Th with this objective. Depending on the composition of the sample, the determination of U and Th can be improved irradiating the sample inside a Cd capsule, reducing the thermal neutron incidence on the sample and, therefore, diminishing the activation of possible interfering nuclides.

Electron spin resonance (ESR) dating was applied to a *Smilodon* populator tooth found in “Toca de Cima dos Pilão”, located in the surroundings of the Serra da Capivara National Park. Neutron Activation Analysis was used to determine the concentration of radioisotopes present in the sample and in the sediment to calculate the internal and external dose rates. The result of age found is  $93 \pm 9$  ka, which confirmed the presence of this species in Serra da Capivara National Park in the late Pleistocene.

Electron spin resonance (ESR) dating was applied to a fossil human tooth and shell found at the archaeological site Toca do Enoque located in Serra das Confusões National Park (Piauí, Brazil). The ages for the tooth and the shell ( $4.8$  kyBP) agreed with C-14 dating of the shell and other samples (charcoal) collected at the same study site, showing the validity of ESR dating for this range of ages.

Electron spin resonance (ESR) dating was applied to date a sample of fossil tooth found in Ribeira Valley, São Paulo, Brazil. This region is characterized by abundant fossil records of Pleistocene–Holocene South American megafauna belonging to different faunistic moments related to climate changes during the quaternary. The equivalent dose ( $D_e$ ) was determined using single exponential fitting resulting in  $(24 \pm 1)$  Gy. The  $D_e$  was converted to age using ROSY ESR Dating program and the concentration of radioisotopes present in the sample and soil determined through neutron activation analysis. The ages cover the range of 25–34 ka. This information is important to contextualize other findings in the region from different sites and to help obtain better information about the climate changes in this region. (Partnership: Universidade Sagrado Coração, Bauru, SP, Brazil; Departamento de Física, Faculdade de Filosofia Ciências e Letras, USP, Ribeirão Preto, SP, Brazil).

### Relative INAA and $k_0$ -INAA at IPEN: a Comparative Study

The Neutron Activation Analysis Laboratory at IPEN (LAN-IPEN) has been analyzing different kinds of samples for decades, using the relative method of instrumental neutron activation analysis (INAA) at the IEA-R1 nuclear research reactor of IPEN. In this method, samples and standards are irradiated simultaneously with neutrons under the same conditions. Elemental concentrations are calculated by comparison of the activities of the gamma-rays from the sample and standard. This procedure requires the preparation of element standards, which is very laborious and time consuming. Furthermore, some elements present in the sample cannot be analyzed due to the absence of a corresponding element standard. The  $k_0$ -INAA method, developed by the Institute of Nuclear

Sciences, Gent, Belgium, has been increasingly used, as it requires only a single comparator such as  $^{197}\text{Au}$  for multielemental determination instead of multielemental standards required in the relative method.

The INAA relative method is considered one of the most accurate analytical methods, but more and more neutron activation laboratories in Brazil and in other countries all over the world are using the  $k_0$ -INAA method, due to the quite accurate results obtained and the improvement of the analysis procedure and time.

The objective of this study was to compare the results obtained by relative INAA and  $k_0$ -INAA methods at the IEA-R1 reactor of IPEN. The same input parameters (sample mass, nuclear data, net peak area for the same gamma line and the same measurement and same cooling and measurement times) were employed in the analysis of reference materials of different matrices: basalt BE-N (IWG-GIT), SOIL-5 (IAEA), Buffalo River Sediment (NIST-BRS-8704), INCT-MPH-2 Mixed Polish Herbs, Oyster Tissue (NIST-SRM-1566b) and Bovine Liver (NIST-SRM-1577c). The  $k_0$ -standardization method has been applied by using the  $k_0$ -IAEA software. To evaluate the accuracy of the results, bias (%) and En-number test were applied to the results obtained for more than 20 elements in the analysis of the reference materials. The results pointed to the possibility of using the  $k_0$ -INAA method with good accuracy. (Financial Support: CNEN, CNPq).



# **Radiation Metrology**

# Naturally Occurring Radioactive Materials and Environmental Radiological Impact

## Lixiviation of natural radionuclides and heavy metals in tropical soils amended with phosphogypsum

The Brazilian phosphate fertilizer is obtained by wet reaction of the igneous phosphate rock with concentrated sulphuric acid, giving as final product, phosphoric acid, and dehydrated calcium sulphate as a by-product, aka phosphogypsum (PG). PG is stored in stacks at open air. Part of this PG has been used in agriculture as soil amendment, mainly due to the characteristics of  $\text{CaSO}_4$ , which improves the root penetration in soil. It provides calcium in the soil depth, reduces the aluminium saturation, contributes to the deepening of the plant root system and favours the absorption of water and nutrients. However, the presence of radionuclides and metals put restrictions on the use of PG in agriculture. To assure a safe application of PG, it is important to estimate the lixiviation of radionuclides and metals present in it. The main objective is to study the availability of natural radionuclides, important in terms of radiological protection ( $^{238}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ ), and metals (As, Cd, Cr, Ni, Se, Hg and Pb), present in the Brazilian PG used in agriculture. For this purpose, an experimental protocol was conducted in the laboratory, in which columns filled with Brazilian typical sandy and clay soils and PG were percolated with water, to achieve a mild extraction of these elements. The availability of the radionuclides and metals was evaluated by measuring the total concentration in the soil amended with PG and the concentration in the leachate, to establish the ratio between the available fraction and the total one. An

experimental procedure was established for the sequential determination of the radionuclides in the leachate. The concentration of the radionuclides  $^{238}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in PG from the two provenances varied from  $86 \text{ Bq} \cdot \text{kg}^{-1}$  to  $352 \text{ Bq} \cdot \text{kg}^{-1}$ . The concentration of the radionuclides  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  showed compliance with the limits adopted by CNEN, for the safe use of phosphogypsum in agriculture. The concentration of As, Cd, Cr, Ni, Se, Hg and Pb in phosphogypsum were below the limits adopted by Brazilian Ministry of Agriculture, Livestock, and Supply (MAPA), for the safe use of PG in agriculture. The available fractions of the radionuclides  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$ ,  $^{210}\text{Po}$  and  $^{228}\text{Ra}$  in soils and soil amended with PG varied from 0.05% to 1.2%. For  $^{238}\text{U}$  and  $^{232}\text{Th}$ , the available fractions were lower than 0.05%. The metals showed available fractions in soils and soil amended with PG from 0.05% to 1.07%. The results obtained for the concentration of the radionuclides and metals in the available fractions were low, giving evidence that, even when these elements are present in the PG, they do not contribute to an enhancement of their content in water. It can be concluded that the utilization of Brazilian phosphogypsum as soil amendment is viable, concerning the availability of the metals and radionuclides studied (Figure 30).



Figure 30. Phosphogypsum stack outdoors at Vale Fertilizantes in Uberaba, MG, in 2016.



### Availability of $^{210}\text{Po}$ present in phosphogypsum used in agriculture

The main phosphate industries in Brazil are responsible for the production of  $5.5 \times 10^6$  metric tons of a TENORM residue, phosphogypsum (PG) annually, which is stored in stacks. The presence of radionuclides puts restrictions on the use of PG in building materials and in soil amendments. The Brazilian regulatory body, CNEN, ruled that PG would only be permitted for use in agriculture or in the cement industry if the concentration of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  does not exceed  $1 \text{ Bq} \cdot \text{g}^{-1}$ . In Brazil, PG has been widely used as soil amendment, to improve soil fertility. To assure a safe utilization in agriculture, it is important to estimate the lixiviation of the radionuclides in PG. The main objective is to evaluate the availability of  $^{210}\text{Po}$  in the utilization of PG in agriculture as soil amendment. An experiment was carried out, in which columns filled with sandy and clay Brazilian typical soils and PG were percolated with water, to achieve a mild extraction of determination of  $^{210}\text{Po}$ . The technique used for the  $^{210}\text{Po}$  in the samples of soil, soil + PG and PG was alpha spectrometry which is suitable for the measurement of low activity of  $^{210}\text{Po}$  in environmental samples, since it presents high efficiency and sensibility. The concentration present in the leachate was compared with the total concentration of  $^{210}\text{Po}$  in soil, in the mixture soil + PG and sole PG, in order to evaluate the availability of the activity concentrations of  $^{210}\text{Po}$ . The results obtained for  $^{210}\text{Po}$  in the clay soil were approximately 2.5 times higher than the sandy soil. The results obtained for the radionuclides concentration in the PG varied from  $155 \pm 11$  to  $346 \pm 7 \text{ Bq} \cdot \text{kg}^{-1}$  for  $^{210}\text{Po}$ . However, the addition of PG to the soils studied did not represent any increase in the final activity concentration. The results obtained for the activity concentration of  $^{210}\text{Po}$  in the leachate were close to the detection limits of

the methodologies adopted, giving evidence that, although the radionuclides are present in the PG, they are not available in the leachate.

### Availability of $^{238}\text{U}$ and $^{232}\text{Th}$ in the utilization of phosphogypsum in agriculture

Phosphogypsum (PG), a byproduct of the phosphate industry, is classified as Technologically Enhanced Naturally Occurring Radioactive Material (TENORM) or as a NORM waste. It is obtained during the attack of the phosphate rock with sulfuric acid for the production of phosphoric acid. PG presents in its composition radionuclides of the natural U and Th decay series: mainly  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{232}\text{Th}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ . The Brazilian producers stock the PG in dry stacks, posing risks to the surrounding environment. Therefore, several studies were undertaken to evaluate viable ways of its reuse. One possible solution to this problem is to reuse PG in agriculture as a soil conditioner. The Brazilian regulatory body, CNEN, established exemption limits for the use of PG in agriculture or cement industry: the  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  activity concentration should be below  $1.0 \text{ Bq} \cdot \text{g}^{-1}$ . However, for its safe application, it is still necessary to ensure that the radionuclides present in the PG will not be available to the environment. The availability of  $^{238}\text{U}$  and  $^{232}\text{Th}$  in samples of soils amended with PG through percolation with water, by calculating the available fraction, was determined. This fraction was obtained by the ratio of the concentration of the radionuclides in the leachate by a radiochemical procedure based on a publication from International Atomic Energy Agency over the total concentration in the samples, by Instrumental Neutron Activation Analysis and gamma spectrometry. The results demonstrated that the available fraction of the radionuclides were in all cases lower than 0.2%. This indicates that the use of phosphogypsum as agricultural input does not contribute to

increase the availability of  $^{238}\text{U}$  and  $^{232}\text{Th}$  to the leaching water.

#### **Dosimetry of $^{222}\text{Rn}$ in the air in environments located above and below ground level**

Exposure of the general population to ionizing radiation comes mainly from natural sources. The main contribution is due to inhalation of radon ( $^{222}\text{Rn}$ ), a gas that occurs naturally. The  $^{222}\text{Rn}$  concentration in the environment is controlled by factors such as soil permeability and water content, the weather variability, materials used in the foundation and the usual positive pressure differential between the soil and the internal environment. Studies indicate that the concentration of radon shows a wide variation in the basement, ground floor and upper floors of buildings. Radon levels in basements, ground floor and floors above ground level, at a university in the city of São Paulo and in one residential building in the city of Peruibe, were determined. Measurements of  $^{222}\text{Rn}$  were performed using the method with nuclear track of solid state detectors (CR39). The studied environments present  $^{222}\text{Rn}$  concentration well below the values recommended by the International Commission on Radiological Protection, published in the 2009 document, of  $300 \text{ Bq} \cdot \text{m}^{-3}$  for homes and  $1000 \text{ Bq} \cdot \text{m}^{-3}$  for the workplace. In the residential building, the concentration of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  in the materials used in the building construction was also analyzed, by gamma spectrometry. The effective total dose for the resident due to external exposure was  $0.8 \text{ mSv} \cdot \text{y}^{-1}$ , lower than the annual dose limit for the general public of  $1 \text{ mSv} \cdot \text{y}^{-1}$ .

#### **Assessment of natural radionuclides concentration from $^{238}\text{U}$ and $^{232}\text{Th}$ series in Virginia and Burley varieties of *Nicotiana tabacum L.***

Brazil is the largest exporter and second largest

producer of tobacco worldwide, according to the crop production of 2013/2014. The tobacco plant (*Nicotiana tabacum L.*) is used to manufacture all derivatives and the chemical composition of the resulting tobacco products varies with the type of tobacco leaves, how they are grown, the region where they are cultivated, the characteristics of preparation (compression, filter and paper) and the temperature variations resulting from the incomplete combustion of tobacco. Tobacco products are extensively used throughout the world, and the most consumed are cigarettes, cigars and narghile. The damaging effects that these products cause to human health are discussed globally, and many surveys are performed with the aim of relating the use of these products with various illnesses. There is a lack of information about the radiological characterization of the tobacco plant both in international and Brazilian literature. The concentration of radionuclides  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{230}\text{Th}$ ,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ , members of the  $^{238}\text{U}$  decay series, and the radionuclides  $^{232}\text{Th}$  and  $^{228}\text{Ra}$ , members of the  $^{232}\text{Th}$  decay series in the varieties Burley and Virginia, which are the most cultivated in Brazil, was determined. Plants from these varieties were cultivated in pots with organic substrate and fertilizer and also acquired from the producers and analyzed by alpha spectrometry for U and Th isotopes and  $^{210}\text{Po}$  determination, and gross alpha and beta counting,  $^{228}\text{Ra}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$  determination. The whole plant, from both places, was analyzed; root, stem, leaves, as well as the organic substrate, the fertilizers, and the soil. The results for U and Th isotopes presented values below the detection limits of the methods to the leaves and stems of all plants analyzed, with measurable results only in roots, soil, and substrate. The radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$ , and  $^{210}\text{Po}$  were determined in most parts of the plants, with the highest values obtained for  $^{228}\text{Ra}$ , which also had the highest value of the transfer factor. Plants grown at IPEN showed

lower concentration of radionuclides analyzed when compared with plants grown by the producer, as these were grown in pots with organic substrate and addition of fertilizer, whose analysis showed low concentrations of radionuclides studied. Based on data from national literature who studied the Brazilian fertilizer, it can be concluded, to the plants from the producer, the fertilizer has a great influence in the concentration of radionuclides studied.

### Assessment of natural radioactivity in commercial marble and granite of Espírito Santo State

Concentrations of natural radionuclides  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  in granite and marble samples were determined, considering the main extraction mining of Espírito Santo state, south-eastern Brazil. For all studied sites, three samples were sealed in 100 mL high density polyethylene bottles. Each sample rested for 4 weeks to reach the secular equilibrium of  $^{238}\text{U}$  and  $^{232}\text{Th}$  series before measured by high resolution gamma spectrometry, and the acquired spectra were analyzed with the software WinnerGamma. The self-absorption correction was considered for all samples, using an expression and method specially developed for this purpose. The concentration of  $^{226}\text{Ra}$  was determined by the weighted arithmetic mean of  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  concentrations, the concentration of  $^{232}\text{Th}$  by the weighted arithmetic mean of  $^{228}\text{Ac}$ ,  $^{212}\text{Pb}$  and  $^{212}\text{Bi}$  concentrations, and the concentration of  $^{40}\text{K}$  by its single 1460 keV transition. The radium equivalent and gamma index were calculated from the activity concentrations of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$ . The emanated radon was measured using an exhalation chamber and the passive detector technique, with a solid state nuclear tracks detectors (SSNTD) being exposed in NRPB/SSIH dosimeters. During exposure, a commercial detector CR39<sup>®</sup> and a national plastic called Durolon<sup>®</sup> were used. The last one was char-

acterized for this purpose using a technique called double exposure and sensitivity intrinsic factor. The characterized plastic was efficient for the application and the calibration factor corresponded to  $1.60 \pm 0.10 \text{ tracks} \cdot \text{cm}^{-2} \cdot (\text{kBq} \cdot \text{m}^{-3} \cdot \text{day})^{-1}$  in relation to the CR39 factor, equivalent to  $2.8 \pm 0.2 \text{ tracks} \cdot \text{cm}^{-2} \cdot (\text{kBq} \cdot \text{m}^{-3} \cdot \text{day})^{-1}$ . The detector showed a higher efficiency at a higher dose. The activities determined by passive detection varied from  $100 \pm 10 \text{ Bq} \cdot \text{m}^{-3}$  up to  $(2,4 \pm 0,3) \cdot 10^3 \text{ Bq} \cdot \text{m}^{-3}$ , highlighting the biggest exhalation rates for granite Iberê Mombasa. Considering the marbles, activity values varied from  $80 \pm 10 \text{ Bq} \cdot \text{m}^{-3}$  up to  $200 \pm 25 \text{ Bq} \cdot \text{m}^{-3}$  highlighting only the Cintilante and Branco Extra with higher values. The values obtained for surface exhalation rate were approximately equal, except for granites Iberê Mombasa and Iberê Prado with values above  $1 \text{ Bq} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ . The measures by gamma spectrometry showed that the  $^{226}\text{Ra}$  concentrations varied from  $1.9 \pm 0.2 \text{ Bq} \cdot \text{kg}^{-1}$  up to  $483 \pm 55 \text{ Bq} \cdot \text{kg}^{-1}$ , with the highest value for granite Iberê Mombasa. The  $^{232}\text{Th}$  concentrations ranged from  $3.2 \pm 0.4 \text{ Bq} \cdot \text{kg}^{-1}$  to  $224 \pm 6 \text{ Bq} \cdot \text{kg}^{-1}$ , whose largest value was observed for the gray granite Corumbá. The  $^{40}\text{K}$  concentrations ranged from  $8.8 \pm 1.8 \text{ Bq} \cdot \text{kg}^{-1}$  up to  $1642 \pm 67 \text{ Bq} \cdot \text{kg}^{-1}$ , with the largest value observed for granite Iberê Vitara. The radio equivalent value showed that most samples can be defined as category I, below  $370 \text{ Bq} \cdot \text{kg}^{-1}$ , except for the granites Cinza Corumbá, Iberê Crema Bordeaux and Iberê Mombasa that can be classified as class II (up to  $740 \text{ Bq} \cdot \text{kg}^{-1}$ ). The evaluated granites show internal and external exposure rates below  $1.0 \text{ mSv} \cdot \text{y}^{-1}$  except the granites Cinza Corumbá, Iberê Crema Bordeaux and Iberê Mombasa that exceed the value range of 1.0 to  $3.2 \text{ mSv} \cdot \text{y}^{-1}$  for this index. For the annual exposure dose, only the granites Gray Corumbá, Iberê Crema Bordeaux and Iberê Mombasa exceeded  $1.5 \text{ mSv} \cdot \text{y}^{-1}$ . For the alpha exposure index only the Iberê Crema Bordeaux and Iberê

Mombasa granites indicate limitations when applying as surface material. However, considering the gamma exposure index, the granites Cinza Corumbá, Cinza Andorinha, Amarelo Icarai, Cinza Ocre, Iberê Crema Bordeaux and Iberê Mombasa have controlled application. In conclusion, the evaluated granites and all marbles evaluated have viable applications in different activity sectors and for different purposes and the granites that exceeded the proposed limits should not be applied in the interior of residences.

### Assessment of natural radioactivity in wall paints of commercial use in Brazil

Natural radioactivity in soils, rocks and construction materials, due to  $^{40}\text{K}$  and the natural series of  $^{232}\text{Th}$  and  $^{238}\text{U}$ , is the main contribution to external exposure in mankind. Activity concentrations of  $^{226}\text{Ra}$  ( $^{238}\text{U}$  series),  $^{232}\text{Th}$  and  $^{40}\text{K}$  were determined for 50 white latex wall paints samples, commercialized in Brazil, namely 15 Economic quality samples, 15 Standard quality samples and 20 Premium quality samples and for a single titanium dioxide sample. The samples were tightly sealed and stored for a minimum period of 30 days, to reach the radioactive secular equilibrium from  $^{238}\text{U}$  and  $^{232}\text{Th}$  series, then measured by high resolution gamma-ray spectrometry. The activity concentration was determined using the weighted average concentrations of  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  for  $^{226}\text{Ra}$  and  $^{228}\text{Ac}$ ,  $^{212}\text{Pb}$  and  $^{212}\text{Bi}$  for  $^{232}\text{Th}$ . The  $^{40}\text{K}$  activity concentration was determined by its single transition of 1460.8 keV. Self-attenuation correction factors of the samples whose densities are higher than  $1.0 \text{ g} \cdot \text{cm}^{-3}$  were determined and used to make the necessary corrections. The radiological indices radium equivalent activity ( $\text{Ra}_{\text{eq}}$ ), activity concentration index ( $I_{\gamma}$ ), internal exposure risk index ( $H_{\text{in}}$ ) and external exposure risk index ( $H_{\text{ex}}$ ) and also the absorbed dose rate ( $D$ )

and annual effective dose ( $D_{\text{ef}}$ ) were calculated from the activity concentrations of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$ . The activity concentration values for  $^{226}\text{Ra}$  ranged from under the minimum detectable activity to  $38.7 \text{ Bq} \cdot \text{kg}^{-1}$ , for  $^{232}\text{Th}$  from under the minimum detectable activity to  $101.2 \text{ Bq} \cdot \text{kg}^{-1}$  and for  $^{40}\text{K}$  from under the minimum detectable activity to  $256 \text{ Bq} \cdot \text{kg}^{-1}$ .  $\text{Ra}_{\text{eq}}$  ranged from  $1.41 \text{ Bq} \cdot \text{kg}^{-1}$  to  $203 \text{ Bq} \cdot \text{kg}^{-1}$ ,  $I_{\gamma}$  ranged from 0.0047 to 0.720,  $H_{\text{in}}$  from 0.0076 to 0.653 and  $H_{\text{ex}}$  from 0.0038 to 0.549. The absorbed dose rate ranged from  $0.170 \text{ nGy} \cdot \text{h}^{-1}$  to  $21.3 \text{ nGy} \cdot \text{h}^{-1}$  and the annual effective dose ranged from  $0.83 \mu\text{Sv}$  to  $104.2 \mu\text{Sv}$ . The results show that the activity concentrations of the wall paints studied in this work are below the recommended limits by Hassan et al. for  $\text{Ra}_{\text{eq}}$  ( $370 \text{ Bq} \cdot \text{kg}^{-1}$ ), by European Commission for  $I_{\gamma}$  (limit of 2 for superficial materials) and by the Organisation for Economic Co-operation and Development for  $H_{\text{in}}$  and  $H_{\text{ex}}$  (both with limit of 1), for all the 50 samples, assuring the safety of these wall paints with respect to radiological protection.

### The use of representative person and critical group concepts for environmental control of nuclear facilities in Brazil

According to the National Commission for Nuclear Energy, CNEN, the assessment of environmental radiological impact from the release of radionuclides to the environment due to normal operation of nuclear facilities, for protecting the public, considers the concept of critical group. In 2006, the International Commission on Radiological Protection (ICRP), for the same purpose, proposed the adoption of the concept of representative person. Once, at some point, this new concept probably will be adopted in Brazil. The changes in terms of procedures for calculating and consequent results arising from the application of the representative person methodology are evaluated

and compared to the critical group methodology currently used for regulatory control of Brazilian nuclear facilities. As a reference, the predicted potential releases of radionuclides resulting from the normal operation of the Uranium Hexafluoride Production Plant (USEXA), located at Centro Experimental Aramar (CEA), were used. Specifically, the objectives are: to carry out the environmental radiological impact for CEA, using the two recommended methods (deterministic and probabilistic) for the representative person, as described by the ICRP (2006); to make the comparison of results obtained with these methods with those obtained with the methodology used for the critical group; and, make a critical analysis of the need and the availability of data for the application of these methodologies, as well as its consequences for the operational control of CEA. Based on the results obtained, it is emphasized that the use of the methodology for calculating critical group remains a simple and efficient way to evaluate radiological environmental impact when compared to the use of the representative person methodology, which makes the establishment of monitoring programs, and therefore the environmental radiological control, simpler and objectives.

## Natural Radioactive Tracers

### Evaluation of the activity concentration of $^{226}\text{Ra}$ , $^{228}\text{Ra}$ and $^{210}\text{Pb}$ in sediments from Antarctica in the Admiralty Bay region

The natural radionuclides from radioactive series of  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  have been applied as tracers in environmental studies for understanding the dynamics that occur in both marine and terrestrial environment, as for example, in research of oceanic processes and management of the coastal region. In the marine environment, these radionuclides can be used to estimate biogeochemical fluxes of

marine particles and nutrients that occur in the water column as well as in the sediment. Several research works applied the distribution and the respective disequilibrium degree of natural radionuclides in the environment, including geochronological models for obtaining historical information on samples of certain sediment profile. The radiochemical characterization of the distribution of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{210}\text{Pb}$  from a sedimentary column called 1B (248 cm long) collected in the Admiralty Bay, Antarctic Peninsula region, was performed. The methodology used included the acid leaching of sediment samples followed by the radiochemical sequential separation of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  by co-precipitation with  $\text{Ba}(\text{Ra})\text{SO}_4$  and  $^{210}\text{Pb}$  by co-precipitation with  $\text{PbCrO}_4$ . All measurements were carried out by counting of gross alpha and gross beta measures in a low background gas flow proportional detector. The activity concentrations of  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  were used to estimate the unsupported  $^{210}\text{Pb}$  activities present in sediment profile 1B. Based on unsupported  $^{210}\text{Pb}$  data and the application of the CIC model (Constant Initial Concentration), it was possible to determine the sedimentation rate of  $0.59 \pm 0.05 \text{ cm} \cdot \text{y}^{-1}$ .

### Study of natural radionuclides $^{226}\text{Ra}$ , $^{228}\text{Ra}$ and $^{210}\text{Pb}$ in marine sediment cores from Southwest Atlantic Ocean during the Holocene

Natural radionuclides from  $^{238}\text{U}$  and  $^{232}\text{Th}$  series have been successfully applied as tracers of environmental process and climate changes. The  $^{210}\text{Pb}$  (half-life of 22.2 years) is used in the geochronological dating technique of sediment cores of the last 100–150 years, and its respective sedimentation rate determination. The study of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  concentrations (half-lives of 1600 years and 5.75 years, respectively) helps calculate the activity of  $^{210}\text{Pb}$  in excess in the environment, besides being important tracers of marine processes, as ground water

discharge. The activity concentrations of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{210}\text{Pb}$  in four short marine cores, collected from the continental platform to upper slope of Southwest Atlantic Ocean, were determined. Taking into account the results obtained, sedimentation rates and the ages of each sediment layer were determined using the geochronological dating method with  $^{210}\text{Pb}$ . All sediment samples were totally acid-digested in microwave (Figure 31). The sequential radiochemical separation of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  were performed, obtaining in the end the precipitation of  $\text{Ba}(\text{Ra})\text{SO}_4$  and  $\text{PbCrO}_4$ . The gross  $\alpha$  measurements of  $^{226}\text{Ra}$  and gross  $\alpha$  measurements of  $^{228}\text{Ra}$  and  $^{210}\text{Pb}$  from the precipitates were carried out in a gas-flow low background proportional counter. Concerning all cores analyzed, the activities concentrations of  $^{226}\text{Ra}$  ranged from  $14 \text{ Bq}\cdot\text{kg}^{-1}$  to  $154 \text{ Bq}\cdot\text{kg}^{-1}$ ; the concentrations of  $^{228}\text{Ra}$  ranged from  $17 \text{ Bq}\cdot\text{kg}^{-1}$  to  $45 \text{ Bq}\cdot\text{kg}^{-1}$ ; and the concentrations of  $^{210}\text{Pb}$  ranged from  $20 \text{ Bq}\cdot\text{kg}^{-1}$  to  $2073 \text{ Bq}\cdot\text{kg}^{-1}$ . High values of  $^{210}\text{Pb}$  were observed on the top of all the cores studied, mainly related to atmospheric deposition. The results obtained in this work were of the same order of magnitude of those reported in the literature available on non-contaminated areas of Southeast Brazilian Coast. Sedimentation rates fall with the increase of water column depth and ranged

from  $0.049 \text{ cm}\cdot\text{y}^{-1}$  to  $0.40 \text{ cm}\cdot\text{y}^{-1}$ .

### Radon as an indicator of environmental contamination by hydrocarbons in free-phase

Contaminated sites by NAPL (Non-Aqueous Phase Liquids) may lead to safety risks to human health and to ecosystems, restrictions to urban development and decrease of real estate value. Radon gas as an indicator for the analysis of subsurface soil gas, once this noble gas presents good solubility in a wide range of NAPL, being partially retained in the NAPL contamination, was used. Therefore, a decrease of the activity of radon in the contaminated soil gas can be expected, due to the high capacity of partitioning of radon in NAPL, which allows that the NAPL retain part of the radon previously available in the soil pores. The survey was carried out at a disused industry, contaminated by low volatile NAPL, located at southeast of São Paulo city, from June 2014 to May 2015. Radon was evaluated by passive detection methodology with CR39 solid state nuclear track detectors (SSNTD) in ten monitoring stations installed in the contaminated area investigated and named "A" to "J" (Figure 32). Radon concentrations average for the eight monitoring stations at non-contaminated locations varied from

Figure 31. Vertical profile (cm) of natural isotopes  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , total and unsupported (ns)  $^{210}\text{Pb}$  concentrations ( $\text{Bq}\cdot\text{kg}^{-1}$ ) along a short marine sedimentary profile in SW Atlantic Ocean.

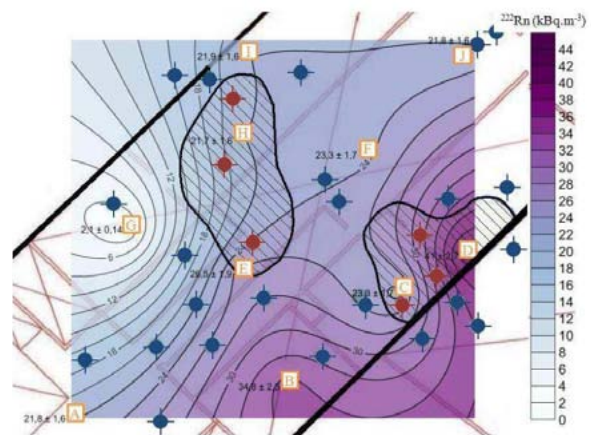
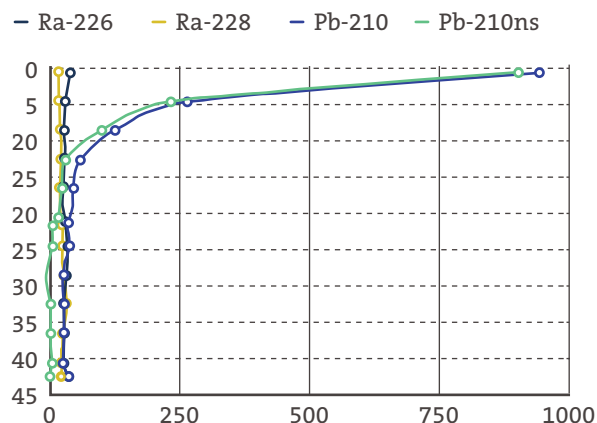


Figure 32. Map of isoconcentrations of  $^{222}\text{Rn}$  activity obtained with SSNTD detectors in winter.

$22 \pm 4 \text{ kBq}\cdot\text{m}^{-3}$  to  $39 \pm 4 \text{ kBq}\cdot\text{m}^{-3}$ . For the two monitoring stations assumed as contaminated locations, radon concentrations average were  $1.4 \pm 0.4 \text{ kBq}\cdot\text{m}^{-3}$  and  $13 \pm 9 \text{ kBq}\cdot\text{m}^{-3}$ . The results have shown good agreement between the used method and the conventional environmental investigation techniques, for the majority of the monitoring stations in different seasons. Results obtained with CR39 detectors varied over the exposure time due to the different seasons. No relation was observed between radon activity concentrations and rain volume accumulated over the different CR39 exposure times. The lowest  $^{222}\text{Rn}$  activity concentrations occurred in “G” and “H” monitoring stations, also verified by gamma-ray spectrometry, that the low activities are not related to the activity concentration of its father  $^{226}\text{Ra}$  from the  $^{238}\text{U}$  decay chain, reinforcing the theory that radon gas is retained in sites where NAPL contamination is present. Results obtained during environmental remediation proved that the methodology employed in this study was more efficient than the conventional investigation techniques, especially for the “D” and “G” monitoring stations to the investigated site.

### **Inorganic chemical characterization of sediment cores from Pantanal da Nhecolândia, MS, dated by the $^{210}\text{Pb}$ method**

Pantanal da Nhecolândia, geographically located in the state of Mato Grosso do Sul, is part of the Brazilian Pantanal, and has its specific characteristics, one being the existence of saline lakes, commonly known as Salinas (Figure 33). Therefore, to estimate a possible human influence, a study was initiated in Pantanal da Nhecolândia in 2010, where four sediment cores were collected in Salinas A, 6, M, and V. The elements As, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb, and Zn were determined using instrumental neutron activation analysis (INAA), in the fine (silt + clay) and coarse (medium sand + fine sand) fractions of the sediment. The sedimentation rates and age of the sediments were determined using the  $^{210}\text{Pb}$  method. The grain size analysis and the water content of the sediment samples were also determined to assist in the interpretation of the results. The four sediment cores showed different sedimentation rates, which is probably related to drought and flood periods. The grain size analysis showed that the Salinas have a percentage of the fine fraction oscillating from 3.5% in Salina M to 70% in Salina A, which is characteristic of this region. The results were compared with the values of the Upper Continental Crust – UCC and the North American Shale Composite – NASC, and some elements showed values above these, including the elements As, Hf, Rb and Sb, in the two fractions of the sediment. These results of concentration of the elements in the four Salinas suggest the existence of natural deposits of these elements. The results of concentration of the studied elements in the present work suggest that there is no anthropogenic influence in the region. To evaluate these concentration values the enrichment factor – EF was calculated using



Figure 33. Salina and vegetation in Pantanal da Nhecolândia, MS.

reference values from the UCC, NASC and values of the core basis – BEF. It was possible to conclude that the best methodology to evaluate the elements enrichment in the Pantanal, for the present study, was the BEF.

## Ionizing Radiation Metrology

### Development and characterization of special ionization chambers for computed tomography beams

The use of computed tomography (CT) for imaging procedures is growing due to advances in the CT equipment technology, because they allow the acquisition of images with better resolution than through other techniques. Therefore, they are responsible for increasing the dose radiation of patients during the procedure. This fact led to a greater concern about the doses received by patients who undergo this type of examination. To perform the dosimetry in CT beams, the most widely used instrument is the pencil type ionization chamber, because this dosimeter has a uniform response to the incident radiation beam for all angles. The conventional ionization chamber, which is available on the market, has a sensitive volume length of 10 cm; however, some studies have shown that this dosimeter has underestimated the dose values. Therefore, in this study two ionization chambers with sensitive volume lengths of 10 cm and 30 cm, making use of low cost national materials, were developed at the Calibration Laboratory of Instruments. The characterization of these chambers was performed, and the results were obtained within the international recommended limits. As an application, the developed ionization chambers and a commercial chamber were tested in a clinical tomographer. The developed ionization chambers were analyzed in a complete way for their possible uses.

### Establishment of a primary standard system for low energy X-rays using a free air ionization chamber

A primary standard system was established for low energy X-rays (10 kV to 50 kV), using a free air ionization chamber with concentric cylinders, Victoreen (Model 481-5), at the Calibration Laboratory of Instruments (LCI). A new ionization chamber alignment protocol was developed for the radiation system and a modification on the micrometer housing used for the movement of the internal cylinders was made. The results obtained for the stability and characterization tests showed to be within the limits established by the standards IEC 61674 and IEC 60731. The correction factors for photon attenuation in the air, transmission and scattering in the diaphragm, scattering and fluorescence and ion recombination were also determined. These values were compared with those obtained by the German primary standard laboratory, Physikalisch-Technische Bundesanstalt (PTB), showing good agreement. Finally, the absolute values of the quantity air kerma rate for the standard qualities direct beams MWV28 and WMV35 and the attenuated beams WMH28 and WMH35 were determined; the results are in agreement, with a maximum difference of 3.8%, with the values obtained using the secondary standard system of LCI.

### Application of special ionization chambers for quality control in mammography

Mammography is an examination which uses X-rays to obtain images of the internal anatomy of the breast. To provide a correct diagnosis, it is necessary that the equipment constantly undergoes quality control programs to ensure that patients submitted to this examination do not receive more than the necessary dose, thus avoiding unwanted possible biological



effects. The ionization chambers are widely used as detectors to perform the quality control program of equipment with radiation, as mammographers. Four different special ionization chambers, developed at the Calibration Laboratory of Instruments of IPEN, were submitted to the characterization tests in standard X radiation beams at the LCI. The results were satisfactory, within the limits established by national and international standards. As an application, the ionization chambers were used for quality control tests in four mammography clinics from different institutions, as the repeatability and linearity of the air kerma rate. The results obtained in these tests were within the limits recommended by national and international standards.

### Internal dosimetry

The internal dosimetry program at the Instituto de Pesquisas Energéticas e Nucleares, IPEN, was accomplished in two steps: the activity measurements performed at the In Vivo Monitoring Laboratory and subsequent data analysis and dose evaluation by the Dose Calculation Group, according to the ICRP models. The purpose of this study was to take the whole body and thyroid monitoring results recorded from 2005 to 2015 to see whether the internal contamination control procedure for workers were suitable even with the increase in the radiopharmaceutical production. The study were based in a research called "Search of Variables", taking into account the dose distribution data for all the tasks recorded by the radioprotection service in the restricted areas of radiopharmaceutical production plant. This methodology aims to identify and determine the relevant variables that impact on the worker's dose. The results presented the following variables: occupationally exposed individual, operation variable, area/cell and type of operational task, which depends on

the variable dose. In spite of growth rate in the production of radiopharmaceutical, this study has shown that the improvements in the plant have contributed to the dose reduction of the workers.

### Dosimetric Materials

The main objective of this research area is the development of new dosimetric materials with high sensitivity, low cost and easy obtaining to be applied in external dosimetry.

#### Fricke/Alanine Gel Dosimeter

DL-Alanine ( $C_3H_7NO_2$ ) is an amino acid tissue equivalent traditionally used as standard dosimetric material in EPR dosimetry. Recently, it has been studied to be applied in gel dosimetry, considering that the addition of alanine in the Fricke gel solution improves the radiation induced ferric ions production. The performance of the Alanine gel solution developed at IPEN is being studied using spectrophotometry and magnetic resonance imaging evaluation techniques.

#### Ceramic materials based on rare earth doped yttria

The following research area aims to develop new dosimetric materials with high sensibility using facile low-cost processing. Rare earths (RE) which exhibit excellent chemical and physical proprieties are promising materials for dosimetry. Among RE group, yttrium oxide also known as yttria ( $Y_2O_3$ ) exhibits structure characteristics that offer great possibilities for doping with RE. Ceramic micro rods based on undoped yttria ( $Y_2O_3$ ) and RE doped yttria ( $Y_2O_3:RE$ ) have been produced from assembling of nanoparticles via bio-prototyping, followed by sintering. Sintering of rods, which aims to improve nanoparticles bond, was performed

by thermal treatment at 1600°C for 4h. As sintered yttria based rods exhibited dense surface microstructure, homogeneous size, shape, and cleavage planes characteristics of transgranular fracture, as illustrated in Fig.34. Furthermore, doping yttria with europium ( $Y_2O_3:Eu$ ) led to formation of new defects, which in turn, supplied more effective EPR response.  $Y_2O_3:Eu$  rods exhibited linear EPR dose response-behavior from 0.001 up to 10kGy. Thermal fading of EPR signal was less than 20% during 162h. Complete cleaning of EPR signal was achieved by thermal treatment at 1000°C/2h in air. These innovative results show that rare earth based ceramics are promising materials for dosimetry.

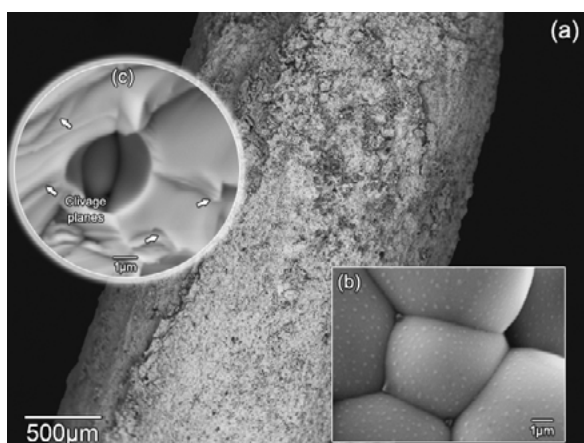


Figure 34. SEM images of  $Y_2O_3:Eu$  rods sintered at 1600°C for 4h at room atmosphere, (a) general view of ceramic rod; (b) surface microstructure; (c) fracture surface, exhibiting cleavage planes in transgranular fracture.

## External Dosimetry

### Dosimetry in computerized tomography and evaluation of the dose profile

A new method for determination of absorbed doses in computed tomography examinations was developed using the Fricke gel solution developed at IPEN. Absorbed doses were determined by different methods of analysis: optical absorption spectrometry – O.A., magnetic resonance imaging - MRI and ionization

chambers. Lower detection limit, detection sensitivity and signal response repeatability of the Fricke gel solution for the measuring methods was determined. The stability of the different computerized tomography equipment with multiple detectors was also evaluated. The Fricke gel solution presented repeatability better than + 5.5% using the O.A. spectrophotometry technique and + 3.5% using MRI technique. The CT equipment presented repeatability better than + 0.2%. A skull phantom filled with the Fricke gel solution was developed to determine the total collimation of the CT equipment and the dose distribution using the three-dimensional magnetic resonance imaging technique. The Fricke gel solution is easy and relatively quick to prepare, but care must be taken to avoid contamination and lose the solution. The results obtained confirmed the application of this type of dosimetry to the CT equipment.

## Metrology in Radiotherapy

### TL response and intrinsic efficiency of dosimeters irradiated using different phantoms in clinical electron beam dosimetry

Different phantom materials affect the electron spectrum incident on the detector and it can alter the response of dosimeters to different radiation types, so this fact should be considered in clinical dosimetry. The TL response of  $LiF:Mg,Ti$  microdosimeters and  $CaSO_4:Dy$  dosimeters were studied for 12 MeV electron beams using PMMA, liquid water and solid water (SW) phantoms. The dosimeters were irradiated with doses ranging from 0.1 up to 5 Gy using a Varian Clinac  $^{210}OC$  linear accelerator using a  $10 \times 10 \text{ cm}^2$  field size and 100 cm source-phantom surface distance, with the dosimeters positioned at the depth of maximum dose.  $CaSO_4:Dy$  dosimeters produced at IPEN presented higher TL sensitivity and intrinsic efficiency than  $microLiF:Mg,Ti$  from Thermo

Scientific dosimeters for all phantoms. For the three phantoms studied, the dose response curves to 12 MeV electrons presented a linear behavior for doses from LDL up to 5 Gy. All repeatability values are better than +3.5%.  $\text{CaSO}_4:\text{Dy}$  dosimeters showed maximum variation of TL sensitivity relative to  $^{60}\text{Co}$  of 11.6% between solid water and PMMA phantoms and  $\text{microLiF}:\text{Mg,Ti}$  dosimeters showed maximum variation of TL sensitivity relative to  $^{60}\text{Co}$  of 9.5% to liquid water and solid water phantoms. According to the results, the phantom material affected the electron spectrum incident on the detector and altered the response of the dosimeters to 12 MeV clinical electron beam using  $\text{microLiF}:\text{Mg,Ti}$  and  $\text{CaSO}_4:\text{Dy}$  as thermoluminescent detectors.

#### **TL and OSL dose response using a PMMA phantom for IMRT technique quality assurance**

The principle of IMRT is to treat a patient from a number of different directions (or continuous arcs) with beams of non-uniform fluences, which have been optimized to deliver a high dose to the target volume and an acceptably low dose to the surrounding normal structures. This study had as objective to provide information to the physicist regarding the application of different dosimeters type, phantoms and analysis technique for Intensity Modulated Radiation Therapy (IMRT) dose distributions evaluation. The measures were performed using dosimeters of  $\text{LiF}:\text{Mg,Ti}$  and  $\text{Al}_2\text{O}_3:\text{C}$  evaluated by techniques of thermoluminescent (TL) and Optically Stimulated Luminescence (OSL). A polymethylmethacrylate (PMMA) phantom with five cavities, two principal target volumes considered like tumors to be treated and other three cavities to measure the scattered radiation dose was developed to carry out the measures Fig. 35. The doses evaluated to the tumor simulators cavities using  $\text{LiF}:\text{Mg,Ti}$  dosimeters corresponding to the estimated doses

given by IMRT planning and the repeatability of TL responses is better than + 4.12%, lower than 5% acceptable for radiation therapy. The scattered radiation doses received by structures 3, 4 and 5 corresponded on average to 16.14% of the highest dose received by the structure 1, according to the planning. The  $\text{LiF}:\text{Mg,Ti}$  dosimeters demonstrated to have good accuracy in all measures of IMRT planning. Comparing the doses calculated by  $\text{Al}_2\text{O}_3:\text{C}$  dosimeters using OSL technique with the doses provided by the planning system, it was observed that the dose for the cavity 1 was underestimated

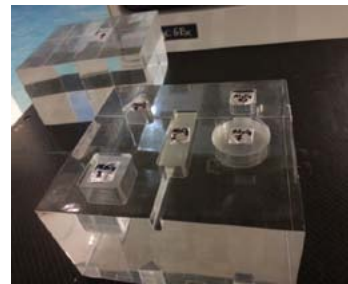


Figure 35. PMMA phantom developed to IMRT technique quality assurance

#### **Three-dimensional dosimetric verification system using Fricke gel solution applied to verification of Volumetric Modulated Arc Radiation Therapy (VMAT) in the treatments with respiration target movement**

Volumetric Modulated Arc Therapy (VMAT) is one of the methods most commonly used in teletherapy to treat cancer. The various technological advances and the evolution of treatment techniques made the VMAT as one of the state of the art methods for the treatment of some cancers. Such advances require quality control of these tools in order to ensure that the entire treatment process is satisfactory and accurate. To date, the community lacks an experimental system capable of evaluating, considering the uncertainty levels, if the computerized planning systems are able to consider the movement of targets in the treatments with VMAT. In this work, it was

projected and developed a Fricke Xylenol Gel phantom capable of measuring the differences introduced by movement using the Magnetic Resonance Image - MRI and compared qualitatively and quantitatively with other systems. The congruence of the isodose curves, with the signal intensity of the MRI image and the large difference in signal intensity of the MRI image with the isodoses, shows that the movement generates a blurring are shown in figure 37.

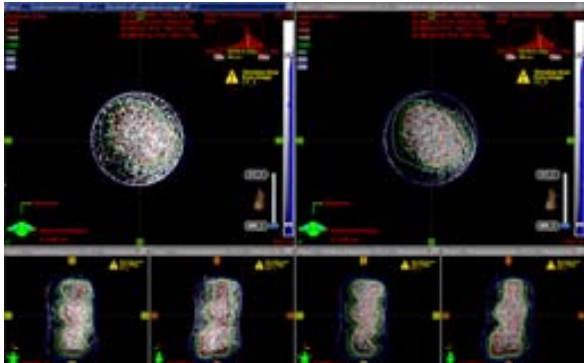


Figure 37- Fricke Gel Phantom VMAT Irradiation and congruence between dose distribution and MRI signal.

### Comparative study of the TL response in clinical electron beams dosimetry applied to Total Skin Irradiation – TSI Treatments

Total Skin Irradiation - TSI is a radiotherapy technique applied in the treatment of certain generalized malignant diseases of the skin. This treatment aims to irradiate the patient's entire skin evenly with large electron fields. The radiation penetrates a few millimeters into the skin and reaches the affected part completely without penetrating the internal organs. The application of electrons in therapy requires great accuracy in the dose absorbed by the tumor since a variation of  $\pm 5\%$  is determinant in the risk of relapse or sequelae. In the TSI Stanford technique, the patient is treated by a two-day cycle with three dual fields per day. When the patient is placed in the six positions with a double field irradiation at each position, the dose is considered less uniform

due to the curvature of the patient's body, the angles of electron incidence that are varied and the orientation of the bundles. In this study, LiF:Mg,Ti and CaSO<sub>4</sub>:Dy dosimeters were used to evaluate the entrance dose distribution to the skin. The LiF:Mg,Ti showed uncertainty of  $\pm 0,1\%$  and CaSO<sub>4</sub>:Dy,  $\pm 0,2\%$ . In the TSI irradiation procedure, the real conditions for the patient's treatment were implemented. An anthropomorphic phantom (Figure 38) was positioned on a turntable and the TL dosimeters were positioned in several anatomical regions such as abdomen, thorax center, thorax right, thorax left, posterior, right side, right thigh, perineum and front. The doses were acquired on alternate days, allowing a better study of the skin. Other factors were analyzed in this study, such as the homogeneity of the field and the dose at the calibration point (ZRef). Considering the characteristics of the irradiation field, the maximum dose deposition should be delivered in a few millimeters of the skin surface (5 - 15 mm). Comparing the dose at the calibration point, a small variation was observed in relation to the other points studied such as the posterior region and the right side of the anthropomorphic phantom. The TL dosimeters presented good results for dose evaluation in TSI treatment.

Figure 38  
- Phantom AldersonRando® used in clinical electron beams dosimetry applied to Total Skin Irradiation – TSI Treatments.



### The comparison between Varian AAA and ACUROS XB dose calculation algorithms for VMAT treatment planning of brain multiple metastases

The Optically Stimulated Luminescence dosimetry has become one of most used techniques for radiation dosimetry nowadays. The “Alabama Technique” demonstrates plan quality and provides a practical, systematic approach to the treatment planning technique for single isocenter cranial radiosurgery with volumetric modulated arc therapy (VMAT) used in metastatic carcinoma treatments. An anthropomorphic skull 3D printed phantom was submitted to a CT scan and planed five target volumes. In order to compare, two dose calculations were performed in the Varian Eclipse with VMAT planning with “Alabama Technique” using the Varian’s AAA and Acuros XB algorithms. The treatment was delivered with a VARIAN True Beam linear accelerator with Multileaf Collimator HD and 6 MV photon beam was used. Landauer nanoDot dosimeters were positioned inside each of the five target volumes planned and the experimental dosimetry results were compared with the two calculation algorithms. The experimental results using the OSLDs show agreement of 97.26 %, 99.12 %, 99.99 %, 95.94 % and 98.79 % for the targets 1 to 5 respectively for the ACUROS XB calculated doses. The findings of this work indicate that ACUROS XB calculates more accurate doses compared with AAA, with all the experimental agreements better than 96 %. The intrinsic precision and uncertainty of the InLight system device is sufficient to sustain the dosimetry



Figure 39- Landauer nanoDot dosimeters and anthropomorphic skull 3D printed phantom.

uncertainties below 2 %, validating the results. Figure 39 presents the anthropomorphic skull 3D printed phantom.

### 3D Phantoms

#### Attenuation coefficient determination of printed ABS and PLA samples in diagnostic radiology standard beams

IAEA code of practice TRS-457 states that standard phantoms should offer the same primary attenuation and scatter production as relevant body section of a representative patient. Material cost, availability and dimensional stability must also be considered. The goal of this study was to determine the attenuation coefficient of printed ABS and PLA samples in standard X-ray beams, verifying if phantoms printed with these materials could be an easier-handle substitute for PMMA, enabling the creation of different designs in an easier and cheaper way. Results show that PMMA presents higher attenuation coefficient, followed by PLA and ABS, which means that thinner PMMA layer creates higher radiation attenuation.

#### Equivalence between Solid Water and printed PLA plates for 6 MV clinical photon beam – An assessment using thermoluminescent dosimetry

Three dimensional models of anatomical structures, produced by rapid prototyping are being adopted for medical application as hemodynamics studies and maxillofacial surgery planning. Models with geometrical accuracy can be achieved using medical images as MRI or CT and produced using polyurethane, polylactic acid and epoxy resins. By changing materials and densities, it is possible to achieve the desired tissue-equivalence. This work was developed in order to analyze the equivalence between the printed PLA and the Solid Water plates by using the thermoluminescence

dosimetry, in order to assess the viability of building a phantom for radiotherapy with a 3D printer. The results indicate that the PLA printed plates can be considered tissue-equivalent and agree with the obtained using solid water plates.

#### Development of tissue equivalent phantoms using 3D printer for application in quality assurance in veterinary medicine

3D printing is a revolutionary technology that allows us to change the way we consume, create and even live in the world. Today(,) it is possible to print 3D anatomical models based on images of computed tomography (CT), Magnetic Resonance Imaging (MRI). This work aims to use a 3D printer to build a dog phantom named “canis morphic”, a veterinary phantom that can be used in quality control of radiodiagnostic images and quality assurance of dosimetry in radiation therapy area. The development of simulators using 3D printers and tissue-equivalent materials proved to be quite feasible for use in the field of veterinary radiology. The images obtained by CT exams showed good agreement with real exams with animals, thus this dog’s phantom has demonstrated to be very useful for quality control in radiodiagnostic and radiation therapy areas. The methodology used in this study enabled the development of personalized exams for the verification of a better protocol on the evaluation of absorbed doses in patients. This work will allow the creation and development of phantom of different shapes and sizes with

tissue-equivalent material that will be used for application in veterinary medicine (radiodiagnosis and radiation therapy). Parts of the printed dog phantom are presented in Figure 40 and 41.

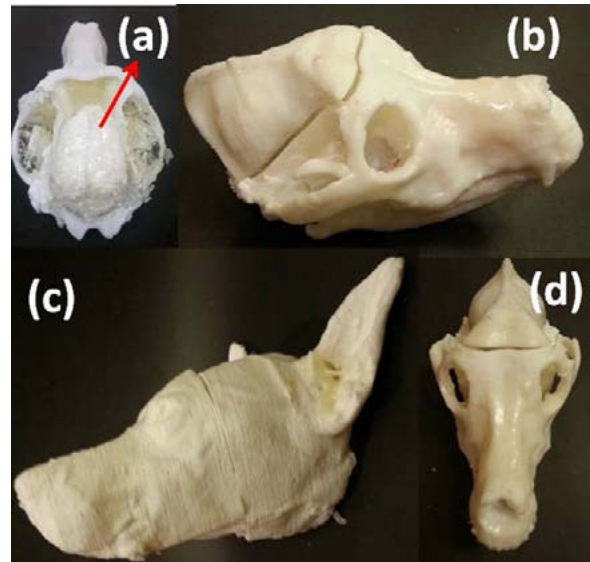


Figure 40 - Printed parts: (a) Brain; (b) Skull – lateral view; (c) Dog head – external view; (d) Skull – frontal view.

#### Metrology in Diagnostic Radiology

During the period of 2014-2016, a new calibration methodology in terms of absorbed dose to water for parallel plate ionization chambers to be used in low energy X rays beams (10kV to 100kV) was established. In order to establish this calibration methodology, two ionization chambers PTW models 23344 were used. Both chambers were characterized and tested qualitatively according to recommendations of international standards. The characterization tests performed were: measuring effective minimum dose rate measurements, the satu-



Figure 41- Printed parts: (a) cervical spine; (b) lumbar spine.

ration curve, ions collection efficiency, polarity effect and the linearity of the ionization chamber response. For the implementation of the methodology, the radiation qualities the T-10 to T-100 were established, following the recommendations of the IAEA code of practice, TRS 398. The reference ionization chamber positioned in the PMMA phantom is shown Fig. 42.

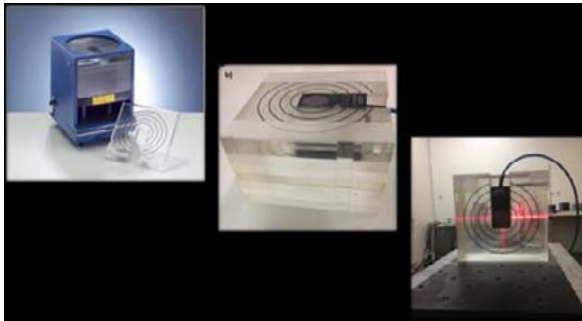


Figure 42. Parallel plate ionization chamber positioned in the PMMA phantom.

To improve the dosimetry in computed tomography procedures, a guide providing information to the adequate use of a calibrated pencil ionization chamber was developed. The guide includes guidance prior knowledge of half value layer (HVL), as it is necessary to know the effective beam energy for application quality for correction factor ( $k_q$ ). In this work, it was decided to test a Tandem System consisting of five aluminum and three PMMA cylindrical absorbing layers coupled to the pencil ionization chamber. Using Tandem curves, it was possible to assess HVL values and the calibration coefficients to the appropriate beam.

To contribute to the Diagnostic Reference Levels determination to pediatric CT scans, a head pediatric phantom using materials to simulate the skullcap was developed: cortical bone (aluminum) and cancellous bone (PVC). It was filled with distilled water. Its dimension follows the recommendation of the World Health Organization and the UCRU (Uclan Cybercrime

Research Unit) for children from 0 to 5 years old head size. It can be seen at Fig.43. The results showed attenuation up to 23% when different materials are used as skullcap, demonstrating that the DRLs adopted could be overestimating the dose received by pediatric patients.

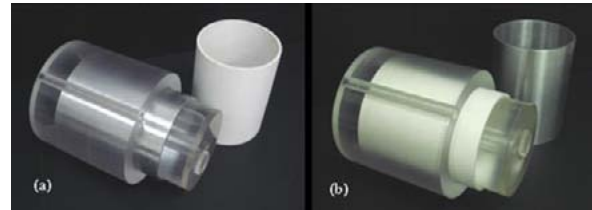


Figure 43. Head pediatric phantom: cortical (aluminum) and cancellous (PVC) bone.

## PRODUCTS AND SERVICES

### Institutional Environmental Radiological Monitoring Program

The Environmental Radiometry Laboratory of the Radiation Metrology Center is responsible for the planning and execution of the Institutional Environmental Radiological Monitoring Program (PMRA). This Program is developed in a two-fold approach (Figure 44).

Preventive evaluation involves collection of effluent samples generated at IPEN, including those from Radiopharmacy Program and Research Reactor Center, and the characterization of their radioactive contents. Subsequently, the radiation effective doses of the critical groups of population are assessed on an annual basis, by using dispersion models recommended by IAEA.

The confirmatory evaluation is performed by collection and analysis of samples from environmental matrices including atmospheric air, soil, groundwater and rainwater in IPEN's surroundings, in order to determine their radioactive contents. Several analytical techniques such as gamma-ray spectrometry, liquid scin-

tillation, gross alpha and beta counting, and thermoluminescent dosimetry are employed.

The Institutional PMRA has shown over the years that the radiological environmental impact of IPEN's facilities is negligible, as the effective doses to members of the public are several orders of magnitude lower than the recommended levels.

#### Determination of radionuclides in foodstuff and commodities

Several analytical techniques are available and offered in the form of providing services to the private sector. Available analyses include: determination of gross alpha and beta activities; determination of natural and artificial gamma emitters; determination of uranium, thorium and radium isotopes; determination of  $^{210}\text{Pb}$  and  $^{222}\text{Rn}$ ; determination of radionuclides in foodstuffs and commodities imported and exported by Brazil; and determination of  $^{90}\text{Sr}$  in foodstuffs and food commodities; and determination of  $^3\text{H}$  in water.



Figure 44. The renewed sample preparation laboratory for the characterization of radioactive effluents produced by IPEN's facilities, for the execution of the Institutional Environmental Radiological Monitoring Program.

#### Internal dosimetry: Routine

The workers that carry out activities with unsealed sources are routinely monitored to demonstrate that they are receiving adequate protection to internal contamination. Direct measurements of whole-body and thyroid contents provide an estimation of the radionuclide activity incorporated by the potentially exposed workers. These measurements are carried out for workers, trainees and visitors and are routinely performed by the In Vivo Monitoring Laboratory, LMIV. The frequency of measurements is defined by the Radioprotection Service (SRP) and the Dose Calculation Group of IPEN. For this purpose, LMIV are equipped with two measurement systems: the whole body counter, NaI(Tl) (8x4"), and the thyroid counter, NaI(Tl) (3x3"). The counting room dimensions are 2.6 m x 1.7 m x 1.85 m and the walls are made with 130 mm-thick steel sheet lined with 5 mm of lead and 5 mm of copper. This room is climatized and the temperature is maintained at 25°C. The measurement system is calibrated in energy and efficiency, with sources of  $^{152}\text{Eu}$ ,  $^{241}\text{Am}$  and  $^{60}\text{Co}$  with gamma emissions between 59.54 and 1,408.08 keV, positioned within Alderson Research Labs anthropomorphic phantom. The background measurements spectrum is obtained from workers that were not exposed occupationally. The concepts adopted in the HPS N13.30 Standard and proposed in ISO documents for standardization are used for activity measurements. The dose calculation follows the measurements of the activity in excreta or in body tissues. The calculation of activity in body compartments and the committed dose estimates are carried out with the software "Activity and Internal Dose Estimates", AIDE. These calculations are based on the mathematical models recommended by the International Commission on Radiological Protection, and adopted by the Brazilian



Nuclear Energy Commission, according to the type of the radionuclide and the practice. Continuous improvements in IPEN's installations which handle radioactive materials have required actualization in safety programs.

During the period from January 2014 to December 2016, approximately 2,400 direct measurements of both whole-body and thyroid contents have been carried out in workers as well as the internal dose evaluation. The committed effective dose higher than the annual limit on intake in this period was not achieved. In addition, the LMIV have participated in a research group of the National Council for Scientific and Technological Development which involves eight other institutions.

#### **Dosimetric material production - pellets of $\text{CaSO}_4:\text{Dy}$**

The Dosimetric Materials Laboratory developed and patented the  $\text{CaSO}_4:\text{Dy}$  crystals growth system and the method to produce the Teflon<sup>®</sup> sintered pellets. The  $\text{CaSO}_4:\text{Dy}$  crystals grow in the sealed system and are cold pressed with the binding material to

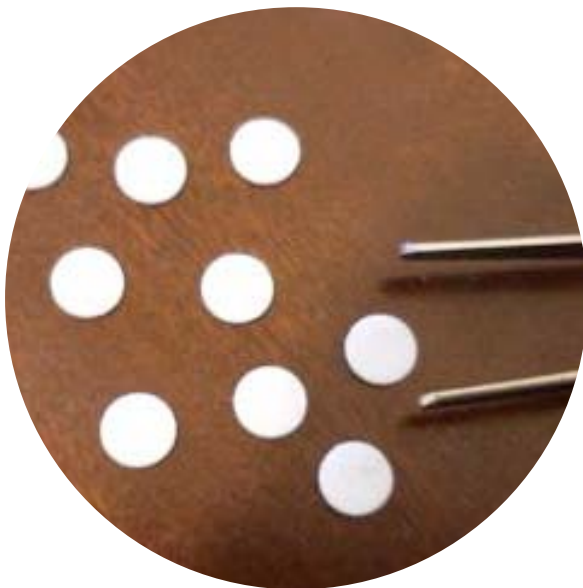


Figure 45-  $\text{CaSO}_4:\text{Dy}$  dosimeters.

make the 6 mm diameter pellets (Figure 45). The  $\text{CaSO}_4:\text{Dy}$  pellets are destined to the individual, area and environmental monitoring through the thermoluminescence dosimetry. Besides, they could be applied to the high doses, retrospective and clinical dosimetry as well as solid state dosimetry research. Pellets of several materials such as quartz, emerald, topaz, jade for instance can be also produced by means of the same referred method. The requests of  $\text{CaSO}_4:\text{Dy}$  crystals and pellets from many institutions have been attended by the laboratory.

#### **Routine External Dosimetry**

The external dosimetry laboratory applies the thermoluminescent (TL) technique and  $\text{CaSO}_4:\text{Dy}$  based dosimeters developed at IPEN to carry out individual, area and environmental monitoring.

The individual monitoring service is authorized by the Brazilian Nuclear Energy Commission - CNEN by mean of the Essays and Calibration Services Evaluation Committee - CASEC. It completely satisfies CNEN's regulatory norms, besides presenting a brake in IPEN's quality control system, being responsible for the external exposure monitoring of all occupationally exposed individuals at IPEN, other autarchies, governmental offices and even some private facilities.

The area and environmental monitoring are performed to different society sectors, such as research institutes, universities and private foundations and companies.

#### **High Dose Dosimetry**

Alanine/Electron Paramagnetic Resonance (EPR) dosimetric system provides a secondary standard for routine radiation dosimetry

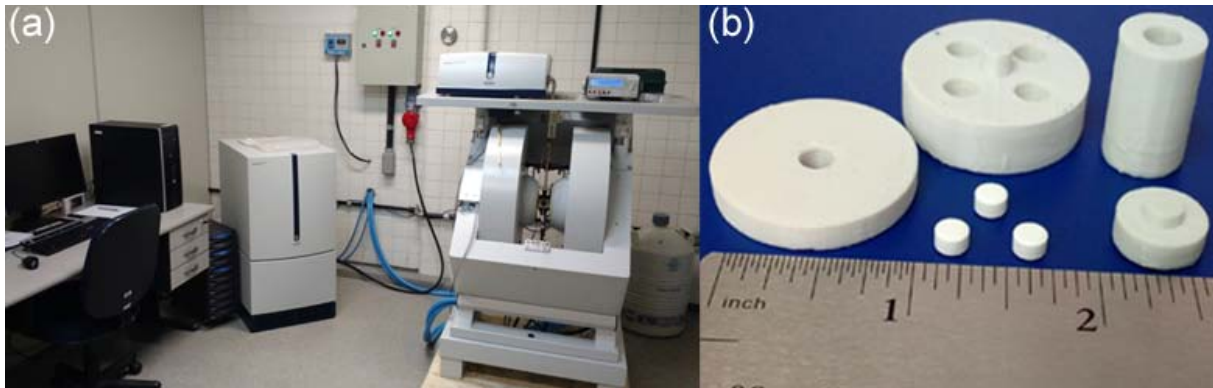


Figure 46 – Alanine-EPR dosimetric system: (a) Bruker ESR spectrometer ( -band); (b) alanine encapsulated in polyethylene tube and buildup cap in polymethylmethacrylate.

in gamma rays, X-rays and electron beams sources (Fig. 46a).

The amino acid alanine is tissue-equivalent material with several features for dosimetric applications: low fading, low uncertainty ( 3%), no dose rate dependence and non-destructive EPR signal readout.

For therapeutic dose range, the High Dose Dosimetry Laboratory of IPEN developed a dosimetric system based on alanine/EPR. The detector is encapsulated in special polyethylene tube that reduces the humidity problems and improves the mechanical resistance. A computer program to extract signals from noise spectra based on the wavelet transform was developed in order to allow the use of the dosimetric system at radiotherapy dose ranges (1 to 20 Gy).

For industrial applications, the dosimetric system is based in commercial alanine pellets which offer wide dose range from 0,01 to 100 kGy (Fig. 46b).

EPR spectrometry is powerful instrument for radiation dosimetry accident evaluation. Inorganic or organic substances present in the accident scenario are candidates for retrospective dose study by the EPR technique. These items included nails, plastics, clothes,

glasses, sugar, ceramic and pharmaceuticals.

### Radioprotection Level

An improvement on the calibration procedure in high exposure rate field was implemented for portable survey meters used in radioprotection routines. These equipments were tested in relation to their response as: repeatability, reproducibility, and exposure rate measurements. According to the calibration results obtained in a Cs-137 gamma radiation field, the procedure for portable survey meters used in a high exposure rates was established at Calibration Laboratory of IPEN-CNEN/SP. It was also introduced an improved test program to be applied before the calibration procedure starts in a gamma radiation field. Several problems related to the equipment operation as: check of the battery voltage, display malfunction, could be avoided with these actions. About 15% of the equipments have shown this type of problems during the calibration procedures. The qualification test was made with Geiger-Müller detectors, from different manufacturers and models, according to energy dependence in standard field of gamma radiation. The qualification results obtained from two hundred detectors agree with the national and international standard recommendations. The data sheets and all

information in relation to the new procedures were integrated in one database. The improvements implemented have reduced costs and increased productivity.

## Diagnostic Radiology

It was developed the improvement of one calibration procedure of mammography dosimeters (ionization chambers) to be applied at clinical X-ray system of the calibration laboratory (IPEN-CNEN/SP). The clinical X-ray system was studied in their behavior, or tested with respect to their response such as: repeatability, reproducibility of the nominal voltage, current and air kerma rate. The results obtained show the possibility to use the clinical X-ray system in calibration procedures. After those studies, one calibration procedure of mammography dosimeters (ionization chambers) was established at calibration laboratory.

## Metrology in Diagnostic Radiology

The Calibration Laboratory has since 1980 been calibrating instruments used in radiation protection and therapy measurements and belonging to hospitals, industries, clinics and other users located in São Paulo and in other parts of Brazil.

Since 2000, calibration service is being offered to users of diagnostic radiology instruments with the establishment of standard radiation quality at this level.

At the radiation protection level, there are special set-ups with gamma ( $^{60}\text{Co}$  and  $^{137}\text{Cs}$ ), beta ( $^{90}\text{Sr} + ^{90}\text{Y}$ ,  $^{204}\text{Tl}$  and  $^{147}\text{Pm}$ ), alpha ( $^{241}\text{Am}$ ,  $^{233}\text{U}$ ,  $^{238}\text{Pu}$ ,  $^{244}\text{Cm}$ , etc.) and low energy X radiations (60 kV).

Clinical dosimeters (radiotherapy level) can

be calibrated, using gamma ( $^{60}\text{Co}$ ) or low energy X radiation. As a reference system, a secondary standard ionization chamber is used, traceable to the Physikalisch-Technische Bundesanstalt, PTB, Germany, and to the National Laboratory of Metrology of Ionizing Radiation, Brazil.

Instruments used in diagnostic radiology measurements can be tested in X radiation qualities, using a Seifert X radiation system (160 kV) and a reference system with four ionization chambers for diagnostic radiology measurements (mammography, computed tomography, fluoroscopy, radiation protection and conventional diagnostic radiology ionization chamber) traceable to the PTB, Germany (Fig. 47).



Figure 47 - radiation calibration system.

The types of instruments calibrated are: several kinds of ionization chambers, pen dosimeters, survey meters (including superficial contamination detectors), alarm dosimeters, clinical dosimeters and others. The distribution in terms of levels of calibration is: 13 % for radiation therapy, 10% for diagnostic radiology and 77% for radiation protection level.

Besides this service, 686 samples including thermoluminescent dosimeters, alanina and others, using beta, gamma and X radiation were irradiated.

Since 2015, the LCI is undergoing an accreditation process at National Institute of Metrology, INMETRO according to the ISO IEC 17025 standard. All quality System documentation was analyzed and the external audit will be in 2017.

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