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, the Radiation Metrology Center and the Radioactive Waste Management Laboratory. 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 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 instrumental neutron activation analysis, with comparative or *ko* 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 radiography, scientific computation and nuclear instrumentation.

During the last several years a special effort was made to refurbish the old components and systems of the reactor, particularly those related with the reactor safety improvement, in order to upgrade the reactor power. The primary objective was to modernize the IEA-R1 reactor for safe and sustainable operation to produce primary radioisotopes, such as ^{99}Mo and ^{131}I, among several others, used in nuclear medicine, by operating the reactor at 5 MW on a schedule of 120 hours/week continuous operation. From 2011 to 2012 the reactor's operating power was increased from 4.0 MW to 4.5 MW, with the exception of one month, where the power reached 5MW for tests. In 2013 the reactor operated until early July at 4.5 MW, when it was temporarily shut down for maintenance replacing most of the primary cooling circuit, which was essentially the same since the 60's.

At the Radiation Metrology Department, all activities of research and development, services, supervision of graduate and undergraduate students and courses performed at the Department are related to the development, improvement and establishment of new methodologies or products in radiation metrology, aiming to assure the safety of IPEN workers, community and environment. Services such as 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) are offered to internal and external communities. The financial resources for research and development are supported by scientific governmental agencies.

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

The high-resolution neutron powder diffractometer Aurora resulted from an upgrade of an old multipurpose diffractometer with the same name. The former Aurora was constructed in the middle of the sixties. Its upgrading to a high-resolution instrument was carried out in the past decade. It is installed on the IEA-R1 research reactor at IPEN-CNEN/SP. Although IEA-R1 is a low-flux reactor (5 MW thermal), the position sensitive detector (PSD), installed in Aurora, allows a quite fast measurement of powder patterns with good resolution. The PSD measures 20^0 of a pattern at once. An extensive pattern can be obtained

by collecting data in contiguous 20º segments, in an angular interval ranging from 5 to 130°. A double-bent silicon monochromator permits measurements with four different wavelengths namely 1.111, 1.399, 1.667 and 2.191 Å (nominal values). The IPEN Neutron Diffraction Group staff, which is in charge of the operation of Aurora, has participated in several studies carried out in cooperation with other groups or by itself. In the following sections, papers published in the past three years are presented.

Neutron single and multiple diffraction studies

With data obtained in the first Aurora, a paper dealing with the crystalline perfection of an aluminum single crystal was published. This paper shows how one can take advantage of the great penetrability of neutrons in the matter. The study showed that, from three-dimensional neutron diffraction rocking curves, it became possible to characterize the individual crystalline domains of a large multi-domain aluminum crystal. Construction of a contour map of the individual domains made it easier to determine breadth and relative intensity of each domain. The angular distances between them were also determined. Figure 1 shows three-dimensional rocking curves constructed before and after an initial data treatment of the raw experimental data, obtained from the aluminum crystal. Figure 2 shows the contour map for the crystal, constructed with the individual domains found in the crystal.
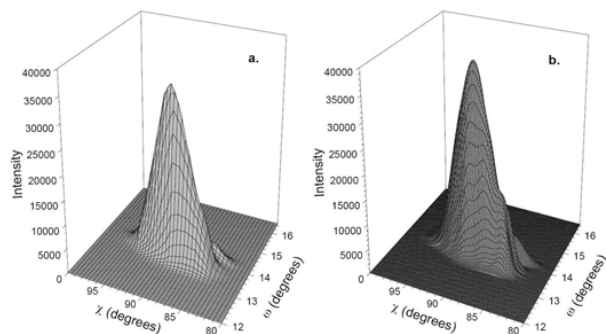

Figure 1. Three-dimensional neutron diffraction rocking curves I x ω x χ constructed before (a.) and after (b.) interpolation and deconvolution of the raw experimental curve obtained with the aluminum crystal.
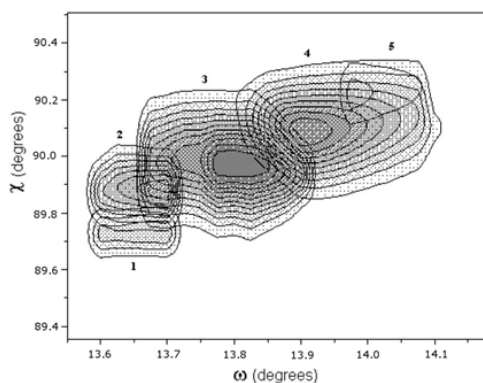

Figure 2. Contour map constructed with the 5 individual domains found in the aluminum crystal.

Another work is a study of the symmetry mirrors in multiple diffraction patterns of face-centered cubic crystals. In this work, the authors simulated several X-ray and neutron multiple diffraction patterns, employing the program Multi, for different crystals and primary reflections. They found that two types of mirrors coexist in the patterns: isomorphic and anamorphic mirrors. Number and types of mirrors depend on the *n*-fold symmetry of the scattering vector associated with the primary reflection. For *n* even, only *n* isomorphic mirrors appear in the patterns. For *n* odd, *n* isomorphic mirrors are formed intercalated between *n* anamorphic mirrors. These results have contributed to solve the problem of indexing a multiple diffraction pattern.

Rietveld analyses of neutron and X-ray diffraction patterns

The IPEN Neutron Diffraction Group is presently involved in studies of Rietveld quantitative phase analysis employing both neutron and X-ray diffraction patterns. The studies presented in this section 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. Structural, ferroelectric and magnetic arrangements, and electron density in the vicinity of cations, were modeled from high-resolution X-ray and neutron powder diffraction data in La modified $BiFeO_3$-$PbTiO_3$ compounds.

Another study makes a comparison between the luminescence of the system $MgGa_2O_4$-Ga_2O_3 with the single phases $MgGa_2O_4$ and Ga_2O_3. It also relates the structural changes observed in the system to its optical properties. A comparison between Aurora and the high-flux diffractometer D2B at Institut Laue-Langevin (ILL - Grenoble, France) is additionally presented.

Two other studies were published. They are related to the characterization of $LiLa_{(1-x)}Eu_x(WO_4)_2$ and $Nd:LiLa(MoO_4)_2$ single-crystalline fibers. All fibers were grown by the micro-pulling-down method. Different characteristics of the fibers were analyzed in the papers. Concerning the structural characterizations, Rietveld quantitative phase analyses were carried out by using X-ray diffraction patterns.

Hyperfine interactions in solids, nanoparticles, and biomolecules

Phenomena in solid materials, in general, originates from small differences in their electronic structure, which makes specifically interesting to investigate new material and compounds in order to understand the origin of such phenomena from an atomic view. 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.

The hyperfine interactions technique involving the measurement of Perturbed gamma-gamma Angular Correlation (PAC) is being used to investigate a series of intermetallic compounds and metal oxides which present interesting properties like superconductivity, magnetic order, phase transitions, etc. Biological materials like proteins and DNA are also a recent subject of investigation. The PAC techniques uses radioactive nuclei implanted in the solids, which 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 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.

Due to the proximity of a nuclear research reactor, our laboratory can use a variety of special radioactive probe nuclei such as ^{140}La, ^{111}Ag, ^{111m}Cd which are produced by neutron irradiation in the IEA-R1 research reactor of IPEN, besides the usual ones like ^{111}In and ^{181}Hf. Two PAC spectrometers: one with 4-BaF_2-detectors setup and other with 6-detectors are available in the Hyperfine Interactions laboratory. A methodology using the ^{6}Li ion beam from the Pelletron accelerator

in IFUSP to implant ^{111}In probe into the sample through ^{108}Pd(^{6}Li,3n)^{111}In nuclear reaction is also available. The compounds which have been investigated are:

- Diluted Magnetic 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. In_2O_3, ZnO, SnO_2, TiO_2 doped with Co, Mn, Fe, Ni, Cr and V are being investigated by PAC in order to understand the origin of the magnetism in these compounds.

- Insulator oxides with large bandgap as HfO_2 and CeO_2 are promising materials to replace 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.

- 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 $REIn_3$ (RE = rare-earth element), CeT_2X_2 where (T = Mn, Pd, Rh and X = Ge, Si), and $LaMn_2X_2$ (X = Si, Ge) with PAC technique using ^{140}Ce and ^{111}Cd probe nuclei.

- Magnetic nanoparticles of Fe_3O_4 with sizes homogeneously smaller than 30 nm are also being investigate with PAC spectroscopy using ^{111}Cd as probe nuclei. These nanoparticles are important materials for biomedical applications such as drug delivery, hyperthermia treatment of tumors and imaging.

- PAC spectroscopy are also being used to investigate biomolecules of EDTA, nucleobases, and DNA molecules of different mouse lineages (A/J, C57BL/6, B6AF1, BXA1 and BXA2) infected by the strain Y of *T. cruzi*. This parasite may cause the Chagas disease when transmitted to humans. The main objective of the present work is to investigate the neighborhood of the sites to which the ^{111}In-^{111}Cd probes are bond in the DNA molecules of the different mouse lineages by measuring nuclear quadrupole interactions in order to in order to compare them and establish which nitrogenated base the probe are bonded to.

- Very precise ab-inito 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 REAg, $REIn_3$ (RE = rare-earth element) and $LaMn_2Ge_2$. Ab-initio calculations for the series of compounds like oxides such as HfO_2, ZnO and In_2O_3 are also being carried out.

Figure 4. PAC spectrometer set up with six BaF_2 detectors.

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.

Radiation spectroscopy and spectrometry radioactive decay

The Radiation Spectroscopy and Spectrometry laboratory (LEER) focuses its activities in measurement of radiations, especially beta and gamma transitions and its scope can be divided in three main lines:

Gamma spectrometry applied to health and environment areas
For clinical analysis biological materials in humans and animal models and obtain reference values for use in diagnosis of different pathologies. These data are relevant to both veterinary medicine and to public health areas. These investiagtions are performed using Neutron Activation Analysis (NAA) and X -ray Florescence (EDXRF) techniques.

Nuclear data
Using single beta and gamma spectroscopy coupled to coincidence and angular correlation analyses, the group have been measuring nuclear data on nuclei produced via neutron irradiation in the IEA-R1 reactor, as gamma and beta transition energies, intensities and electromagnetic nature, beta feeding for the excited levels and measuring of thermal neutron cross activation sections and half live of beta decay.

Nuclear instrumentation and methodology
The group has been developing methods and methodologies to allow a better and quicker analysis of the experimental data: this includes the development of both data reduction and analysis procedures. Also, preparation of texts for teaching physics as well as didactic proposals involving gamma spectroscopy measurements for high school students.

Highlights 2011-2013

- Reference Values in Whole Blood of DMGR using Neutron Activation Analysis and XRF Techniques (LEER, CQMA and CBT at IPEN, Butantan Institute and IFUSP);
- Investigation of different strategies for radiolabelling of nanoparticle-PAMAM dendrimers (LEER and UDELAR);
- The use of portable X-ray Fluorescence Spectrometry (PXRFS) for clinical practices (LEER and CQMA at IPEN and IFUSP);
- Concentrations of ions and metals in blood of Brazilian runners using NAA (LEER and LABEX/UNICAMP);
- Quantitative study of non-stimulated human whole saliva using NAA (LEER and UNIBAN);
- Analysis of saliva and hemolinphy from Amblyomma cajennense (Acari: Ixodidae) species from Brazil by NAA and EDXRF (LEER and Butantan Institute);
- Reference values in biological materials (blood, bone and organs) for Elemental analyses C57BL and DMDMDX mice using NAA (LEER , and CBT at IPEN and Butantan Institute);
- Elements in Bone of the Pleistocene mammal determined by NAA (LEER, UFF and UDELAR)
- Sugar Cane Nutrient Distribution Analysis using NAA (LEER and FEI);
- Sulfur determination in blood from inhabitants of Brazil using neutron activation analysis (LEER and UNISA);
- Variability of ^{137}Cs and ^{40}K soil-to-fruit transfer factor in tropical lemon trees during the fruit development period (LEER and UFF);
- Quantitative evaluation of Cl and Na in Hyperimmune Sera by NAA (LEER and Butantan Institute);
- Development and application of software for Beta-gamma decay lifetimes analyses for high school students (LEER and IFUSP).

The facility for neutron imaging of IPEN-CNEN/SP and its use in technology

Neutron imaging is a set of techniques that make use of neutrons as penetrating radiation to investigate the internal structure of a sample. Because of the neutron - matter interaction characteristics, this technique is largely employed to inspect hydrogenous rich substances (oil, water, adhesives, rubber, etc) even wrapped by thick metal layers. The facility for neutron imaging of IPEN was designed in 1988, becoming operational in 1992, and installed in the beam-hole, BH - 08,

of the 5MW IEA-R1 Nuclear Research Reactor. From 1992 to 1997, the working group has developed the film imaging technique by using conventional X-ray films and track-etch foils. In 2001 the facility has been improved and a real - time imaging system was also installed. Between 2002 and 2008 a digital system for image processing as well as three new imaging techniques to inspect thin samples (μm) were developed. In October 2009 we start to construct a facility for neutron tomography to obtain 3D images and in the beginning of 2011 it was operational and installed in the BH - 14 of the same reactor (Fig. 5). A tomography can be obtained in 5minutes with a resolution of 260 μm. These parameters are comparable to the parameters of the top five facilities installed in Germany, South Korea, Japan, Switzerland and United States of America.
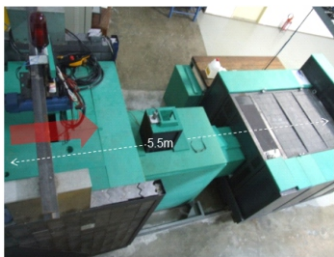

Figure 5. Top view of the facility for neutron tomography.

The figures below are some images to demonstrate the capability of the present neutron imaging facility. Figure 6 are 2D images obtained in films: at left a turbine blade where the white spots are organic substances blocking the air ducts for cooling, emphasizing the high contrast of the method; at right a colony of bacteria, emphasizing the high resolution of the method. Figure 7 shows the 3D image of a wood sample which was impregnated with kerosene. Since the depth of kerosene is easily visible in the image, and since other impregnation solutions are also based on hydrogen rich substances, the studies for the preservation of cultural heritage objects, for example, are also feasible in our facility.
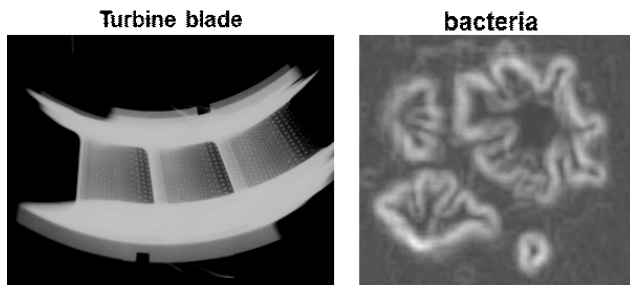

Figure 6. Examples of film images: Left - the clogging of the air ducts of a turbine blade; Right - a bacteria colony (obtained in 20sec. resolution < 50μm).

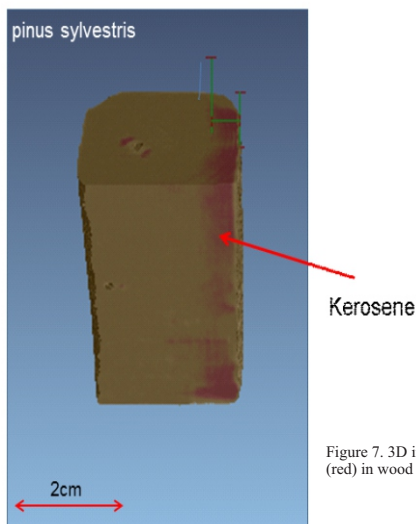Figure 7. 3D image: penetration of Kerosene (red) in wood (light brown).

Applied nuclear physics, instrumentation and scientific computing

Instrumentation

Different types of position sensitive detectors for annihilation radiation based on silicon photomultipliers (SiPM) and LYSO scintillators have been tested. A monolithic LYSO scintillator have been coupled to a Matrix9® SiPM system of SensL. The results have shown that this system is not adequate to be used with monolithic scintillators, since a significant part of the events are assigned to wrong positions. The wrong positioned events are caused by the "scrambled cross-wired" logic used by this system, which was discarded for the next tests. Experiments with long scintillator bars (3 x 3 x 100 mm^3) coupled to two SiPMs have been also performed. Two different scintillators (LFS from Zecotec and LYSO from Proteus) and two different 3 x 3 mm^2 SiPMs (from Zecotec and Hamamatsu) were employed. The results revealed that the LFS has a higher light yield in comparison with LYSO, and the Hamamatsu SiPM has a higher gain in comparison with Zecotec. A XY positioning system based on step motors controlled by an Arduino board has been developed to be used in the positioning of either gamma-ray sources or position sensitive detectors. A data acquisition system with two CAEN V1720 8-channel digitizers will be used in the forthcoming experiments, which will involve scintillator blocks coupled to SiPM matrices and long bars coupled to pairs of SiPMs. New algorithms to reconstruct the position of interaction between the gamma rays and the scintillator block have been developed using simulated data. These algorithms will be used to obtain the position of positron sources placed in the field of view of the position sensitive detectors.

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. Also, in order to address dead-time issues discovered in half-life measurements, a programmable, time-variable pulser was built using an ArduinoUNO board and an in-house built pulse shaper, and its performance was found out to be adequate for the intended measurements of 2-20 minutes half-lives.

Applied nuclear physics

A method for detector efficiency calibration for extended gamma-ray sources was developed that depends only on measurements performed with point-like standard sources; its performance was assessed in measurements with soil samples, and the comparison to results obtained using a standard calibration technique with a doped soil sample proved that the proposed methodology is suitable for this type of experiment.

Scientific computing

Glass and resin microspheres loaded with radioactive isotope are used in treatments of liver cancer. Studies for the production of glass microspheres for radiotherapy are being carried on presently at the Center of Materials Technology of IPEN. Simulations with the GEANT4 Monte Carlo toolkit were performed to investigate the application of 166Ho-loaded microspheres in liver brachytherapy. In comparisons with ^{90}Y and ^{32}P used in the previous studies, ^{166}Ho has the advantage of allowing the determination of the microspheres position inside the human body, because it has a low-energy low-intensity gamma ray (81 keV, 6.7%) that can be imaged using SPECT. The simulations confirmed the capability of imaging the ^{166}Ho-loaded microspheres with dose deposition approximately similar to the ones delivered by ^{90}Y-loaded microspheres.

Simulations were also started for the new Prompt-Gamma Activation Analysis facility beam filters. They are being carried out using GEANT4 and MCNP5 Monte Carlo software. As part of a modernization effort of the SAANI (Instrumental Neutron Activation Analysis Software), a project was started in order to use its base libraries to a web based version of a Gamma Spectroscopy Analysis Software suitable for comparative and k0 neutron activation analysis methods.

A new procedure for robust data fitting was developed which is able to properly fit a given mathematical function to experimental data while properly treating outliers, yielding good results even for very large data samples (n > 1000 data points) with a great number of randomly-distributed outliers (~5% of the dataset).

A software for the automation of Comparative INAA data analysis is under development; this software incorporates the use of the Canberra® Genie2k software to import spectra from different acquisition systems as well as to perform the spectra analysis, then performs all the individual concentration calculations, employing robust statistics to deliver the final concentration results for each of the samples included in the batch. The results obtained so far show that the software delivers more accurate values than the present "manual" analysis, with a huge reduction in the time required to do so (from several hours to a few minutes, including the process of data input and all the calculations).

Implementation and utilization of the *k0*-standardization method for neutron activation analysis using the *k0*_IAEA software.
The neutron activation analysis laboratory (LAN) at IPEN has been analyzing different kind of samples for decades, using the comparative method of analysis by neutron activation with 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 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 can not be analyzed due to the absence of a corresponding element standard. The *k0*-NAA method, developed by the Institute of Nuclear Sciences, Gent, Belgium, has been increasingly used, as it requires only a single comparator such as [197]Au for multielement determination instead of multielement standards required in the relative method.

The INAA comparative method is still considered one of the most accurate methods of INAA, but more and more neutron activation laboratories in Brazil and in other countries all over the world are using the *k0*-NAA method, due to the improvement of the analysis procedure and time and still quite accurate results.

Many INAA laboratories developed *k0* software using different approaches. The *k0*_IAEA program was developed to be distributed free of charge by the IAEA, in order to assist users of the *k0*-approach in NAA to harmonize their results, and to encourage NAA laboratories to adopt the *k0*-standardization method.

For the implementation of the *k0*-NAA method for use of all the researchers and students from LAN, that use NAA as analytical technique, it is necessary to determine the physical parameters of the different irradiation positions at the IEA-R1 nuclear reactor of IPEN (for long and short irradiation), and to characterize the gamma-ray spectrometers used at LAN. An intensive training of the *k0*_IAEA software use was performed, including the study of the software routine, irradiation of flux monitors and of reference materials. For this purpose, several experimental parameters were determined, such as the neutron flux parameters of the IEA-R1 nuclear reactor (for short) as well for the gamma-ray spectrometers (efficiency curves at different counting positions).

The LAN-IPEN has performed a Master Degree study, supported by FAPESP, for the implementation of the *k0*-NAA method for geological sample analysis, with quite good results. In this study the thermal to epithermal flux ratio f and the shape factor α of the epithermal flux distribution of the IEA-R1 nuclear reactor of IPEN were determined for the pneumatic irradiation facility and one selected irradiation position, for short and long irradiations, respectively. To obtain these factors, the "bare triple-monitor" method with [197]Au-[96]Zr-[94]Zr was used. In order to validate the methodology, the geological reference materials basalts JB-1 (GSJ) and BE-N (IWG-GIT), andesite AGV-1 (USGS), granite GS-N (ANRT), SOIL-7 (IAEA) and sediment Buffalo River Sediment (NIST–BRS-8704), which represent different geological

matrices, were analyzed. The concentration results obtained agreed with assigned values, with bias less than 10% except for Zn in AGV-1. The U-score test showed that all results, except Mg in JB-1, are within 95% confidence interval. These results indicate excellent possibilities of using this parametric method at the LAN-IPEN for geochemical and environmental studies.

The *k0*-standardization method has been applied, in our laboratory, for biological sample analysis, by using the *k0*_IAEA software. To evaluate the accuracy of the results, bias (%) and En-number test were applied to the results obtained in the analysis of the biological reference materials NIST SRM 1547 Peach Leaves, INCT-MPH-2 Mixed Polish Herbs and NIST SRM 1573a Tomato Leaves. Bias (%), for most elements, ranged from 0 to 30%, in relation to certified values. En-number values showed that, with few exceptions (Na in NIST SRM 1547 and NIST SRM 1573a, and Al, Cr, Sc and Zn in INCT-MPH-2), the results were within a 95% confidence level. These results pointed to the possibility of using the *k0*-INAA method with the *k0*_IAEA software for analysis of biological samples at LAN-IPEN.

Nutritional studies in foodstuffs and diets

For humans, food is the major route of exposure to essential and toxic elements. The necessity of healthy and good quality diets requires the ability to detect the presence of possible contaminants, as well as, nutritional composition of the diets. Therefore, knowledge of the nutrients and/or toxic element levels in foodstuffs has become of great importance for human health. In the period 2011-2013 Neutron Activation Analysis was applied to analysis foodstuffs and diets in the following studies (Partnership: CNEN/LAPOC):

Total diet study: Estimative of dietetic ingestion of toxic and essential elements, according to Household Budget Survey 2008-2009

Total Diet Study (TDS) is the approach to estimate dietary exposure to essential and toxic elements for a large-scale population over a specific period of time by food sample evaluation, represented by a Food List, which presents the types and quantities of the foods consumed by this population. For the development of the Food List, the following steps are necessary: the sampling, the kitchen preparation of the samples as they are normally consumed; the analysis in laboratories, and the combination of the analytical results with food consumption data. Since the food is prepared as ready to eat, consequently chemical changes during food preparation are considered. Because dietary habits are different in each country, the World Health Organization (WHO) has encouraged countries to carry out their own TDS. Although TDS has been conducted worldwide on or off or, even continuously, there has been just one previous TDS in Brazil, and this is for the State of São Paulo. In this study a methodology for constructing a Food List for the southeastern States of Brazil was developed using the food consumption data source from 2008-2009 Household Budget Survey conducted by the Brazilian Institute for Geography and Statistics (IBGE). This resulted Food List reflects the food consumption inside and outside of the households of the Brazilian southeastern region, corresponding to 100% of the daily individual food intake average weight for the Brazilian southeastern State population. It is based on the TDS Mixed food approach, presenting 82 food items grouped into 19 food groups. After the preparation of these food groups, the concentration of essential and toxic elements will be determined applying the Neutron Activation and Absorption Atomic Spectrometry methodologies.

Determination of essential elements in commercial infant foods by Neutron Activation Analysis

Breast milk is recognized as the most complete and most suitable food for the health growth and development for babies and infants. The World Health Organization (WHO) recommends exclusive breastfeeding up to six months of age. After this age, WHO recommends the introduction of complementary foods and maintenance of breastfeeding up to two years old. Complementary foods play a critical role in providing adequate quantities of many minerals. Inadequate complementary feeding is a major cause for high prevalence of malnutrition in developing countries. Some elements may be a potential health risk when consumed above the tolerable levels of intake for an extended period. Eating habits are important determinants of health conditions during childhood. Commercial infant food is an important part of the diet for many babies. As such it is necessary that such food contain sufficient amounts of essential elements. Inadequate complementary feeding is a major cause of high rates of malnutrition throughout the world. Commercial infant food is classified into four different stages: Stages 1 and 2 are adequate for babies older than 6 months, but new flavors and food are introduced in stage 2; Stage 3 is offered to 8 month old babies; Junior Stage is recommended to children over 1 year old. In this study, essential elements: Ca, Cl, Co, Cr, Fe K, Mg, Mn, Na, Se and Zn were determined in commercial infant food samples by Instrumental Neutron Activation Analysis (INAA). Twenty-seven infant food samples were bought in stores around São Paulo city during 2011. These samples were freeze-dried and homogenized before analysis. The powdered samples were irradiated in the IEA-R1 nuclear research reactor of IPEN-CNEN/SP. For validation of the methodology, INCT MPH-2 Mixed Polish Herbs and NIST-SRM 1577b Bovine Liver reference materials were analyzed. Most of the concentration results

were below the World Health Organization´s recommended daily intake for infants from 6 to 12 months old. These low essential element concentration results in commercial infant foods obtained in our study indicate that infants should not only be fed with commercial baby foods.

Evaluation of U, Th, ^{226}Ra, ^{228}Ra and ^{210}Pb levels and other elements in wild mushrooms from a high natural radiation region of Brazil

Mushrooms are fungi species capable of retaining radionuclides and stable elements that are important to the environment from the toxicological and radiological point of view. Studies have shown that mushrooms can be used as bioaccumulators in monitoring and evaluation of contamination and quality of ecosystems. The present study determined the radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb and the elements As, Co, Cr, Cs, Fe, K, La, Mn, Na, Sc, U, Th and Zn in 24 samples of mushrooms and soils collected on the Poços de Caldas plateau. The Poços de Caldas plateau has around 70 radioactive anomalies. In the present study, two groups of samples (of a total of seven groups) were taken from areas with radioactive anomalies. The determination of the stable elements was carried out by Neutron Activation Analysis. The determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in mushroom samples was carried out by radiochemical separation and their activities were measured in a Total Alpha and Beta Gas Flow Proportional Counter. These radionuclides were determined in soil by Gamma Spectrometry. The determination of thorium isotopes in mushrooms was carried out also by radiochemical separation and measured by Alpha Spectrometry. The analytical control of the methods utilized in this study was carried out with certified reference materials. Samples of mushrooms of a region that presented no radioactive anomaly were analyzed and compared with values obtained from the Poços Caldas Plateau, in order to identify the behavior of mushrooms as radioactive contamination indicators in their natural environment. Higher concentrations and activities were found in samples collected in the rural area of the Poços de Caldas plateau, which has the largest radioactive anomalies in the region. The results show that mushrooms are efficient indicators of environmental radioactive contamination and are appropriate to evaluate levels of radioactivity in areas which contain naturally occurring radioactive materials.

Determination of essential elements in marine algae by Neutron Activation Analysis

Algae are increasing in importance and use in the global trade. Algae are suitable for human and animal feed, as well as for fertilizer, fungicides, herbicides, and phycocolloids. The consumption of algae has increased considerably in recent years. Eastern and vegetarian diets have gained popularity in recent years and in turn increased the demand for these marine vegetables. Marine algae or edible seaweeds are rich in proteins, fiber, vitamins and are excellent sources of essential elements due to their ability to concentrate elements from the ocean. The chemical composition in seaweeds varies with the species, habit, maturity and environmental conditions. The algae species more consumed are: red (Nori, Agar-Agar, Dulse), green (Wakame) and brown (Hijiki and Kombu) species. This study analyzed samples of red (Nori), green (Wakame) and brown (Hijiki and Kombu) algae from Japan, China, Korea and the United States. The samples were acquired in the markets of São Paulo city. The concentrations of As, Br, Ca, K, Mn and Na were determined by Instrumental Neutron Activation Analysis. Samples of algae and elements were irradiated for 20 seconds or 8 hours depending on the element under thermal neutron flux at the IEA-R1 nuclear research reactor. The reference materials INCT-MPH2-Polish Mixed Herbs, Peach Leaves and Bovine Liver were used to validate the methodology. The brown species (Kombu and Hijiki) presented the highest values of As, Br, Ca, K and Na while the red specie (Nori) presented the highest level of Mg and Mn. All algae samples analyzed presented As values much higher than the maximum permissive level established by Brazilian legislation.

Characterization of potentially toxic elements in plants, grains and nuts

In most cases, the concentration of microelements and toxic elements found in soil does not pose a risk to the environment. However, in recent decades the mining, industrial process, the use of agricultural

inputs such as fertilizers, limestone and pesticides have greatly contributed to the enrichment of inorganic elements in areas close to events. Cadmium, lead, mercury and arsenic, classified as potentially toxic elements (EPT) are a huge problem for the Public Health. When they are present in the soil may persist due to their long life-time in soils, and could be readily available for plants, especially in acid soils, and being transferred to the human food chain. Thus, soils enriched with EPT have limited use for agricultural purposes. In this case, the corresponding site should be isolated and then procedures for decontamination or stabilization of EPT in the soils must be applied. The addition of chemicals to contaminated soil is one of the pratices used for immobilization of EPT through reducing the solubility and bioavailability of these elements, due to the complex formation and/or precipitation. Phosphates, limestone, Fe or Mn oxides, organic materials and zeolites are the chemicals used for the reduction and bioavailability.

Within this context the following study was conducted in the period of 2011-2013: **"Evaluation of the influence of adding different doses of phosphate (triple superphosphate - TSP) on the absorption of Hg and Pb by lettuce grown in contaminated soil."** The quantification of Hg was performed with cold vapor atomic absorption spectroscopy (CV AAS, Perkin Elmer® FIMS), where it was used stannous chloride as reducing agent. Eletrothermal atomic absorption spectroscopy (ET AAS, Perkin Elmer® Analyst 800 spectrometer with Zeeman background correction) was employed to quantify Pb. The concentrations of Hg and Pb absorbed in the leaves from lettuce treated with phosphate were compared with those absorbed in the leaves of a control plant. It was found that the absorption of mercury by lettuce leaves were not influenced by addition of phosphate. However, in the case of the lead, it was observed that the treatment with 250 mg kg^{-1} (P) absorption of Pb by lettuce leaves was lower when compared with absorption by the control plant. This project was conducted in partnership with CENA/USP.

Another project that began during this period and that is in progress is **"Establishment of the best experimental conditions for the determination of Barium in a number of foods, by method of neutron activation analysis (INAA)"**. Barium is an alkaline earth metal naturally present in soils. When available at a high level in the soil it can cause toxicity to plants and animals. Not all the Ba is readily available to living organisms. Barium is present in different forms in the soil: soluble, insoluble, inorganic and organic. In case of animals, barium tends to be concentrated in the bones which may compete with calcium, although only about 2% barium ingested in dietary is absorbed by the body. Another effect is that the barium can interfere with the availability of sulfur in the soil due to the sulphate formation of low solubility. The Ba can be determined through ^{139}Ba radionuclide, half life of 82.90 min, in about 40 minutes. The detection limit under the experimental conditions established for biological matrices was 7µg g^{-1}. The method validation was carried out from the analysis of various biological reference materials and, it was shown that the method had a satisfactory performance. Concentrations of approximately 11 µg g^{-1} of Ba were found in samples of soy flour. (Partnership: CENA/USP, UNICENTRO).

Applications of neutron activation analysis in the study of human health

With the improvement of analytical techniques and knowledge of the role of trace elements in human organism, the correlation studies between trace elements and their effects have become a challenge of many researchers. The NAA laboratory of IPEN over these years has analyzed different types of human tissues such as bone, teeth, lungs, hair, serum, nails and brain and interesting results have been obtained. In the period of 2011-2013 we continued the project below described.

Trace element determinations in human brain tissues
In Brazil, as in most developing countries, the increase in life expectancy and of the elderly population has led to a greater number of demented individuals or patients with Alzheimer's diseases. As a result, the rate of dementia has become one of most serious problems facing

public health. Numerous hypotheses have tried to explain the etiology of degenerative diseases including genetic defects, defects in the metabolism of membrane processes mediated by free radicals, neurotoxicity of trace elements, or combination of these factors. Of these hypotheses, one that has gained considerable attention is the involvement of trace element toxicity. Several elements are essential in many biological reactions; however, any variation in their levels may influence cognitive function. In several countries, mainly in Europe and North America, determinations of elements in brain tissue have been performed to study mental illness. However in Brazil, this type of data is very scarce.

In this study the analyses were extended to various regions of the brains that were provided by the Brain Bank of the Brazilian Aging Study Group (BBBABSG) of the São Paulo University, Medical School. The samples were dissected from the regions: hippocampus, cerebellum, frontal, parietal, temporal and occipital. They were isolated using a titanium knife, cleaned, homogenized and then freeze-dried for neutron activation analysis. The study population consisted of a group of an over 50 year individuals (range: 51-95 years) of both genders. Cognitive status was evaluated through a collateral source using the Clinical Dementia Rating scale (CDR).

Concentrations of Br, Fe, K, Na, Rb, Se and Zn showed that the distribution of elements in cognitively normal brains is heterogeneous for the elements determined in this study. These findings demonstrate the importance in selecting a specific brain region to study the effect of the trace element composition on neurological disorders. Comparisons of our results with reported data for normal individuals showed good agreement for most elements. Some elements showed wide interregional and interpersonal variability in concentration. The cluster analysis using element concentration data grouped the brain regions in different clusters probably due to their distinct functional activities or morphology. Significant Pearson correlation coefficients (r) for the pairs of hippocampus region elements Fe-Br (r=0.72), Na-K (r= 0.44), Rb-K(r=0.32), Zn-Na (r=0.53) and K-Br (r=0.35) (p<0.05) were obtained. The knowledge of these correlations is important to increase the understanding the role of these element interactions in normal and disturbed trace element metabolism. (Partnership: FMUSP).

Environmental applications of neutron activation analysis

Nowadays one of the most dangerous types of pollution in the Earth's ecosystem is resulting from heavy metals dumping. Its increasing use in industries and other activities considered to be essential in modern human life, has resulted in a modification of natural geochemistry cycle of these elements, increasing their dispersion in the environment. Pollution studies require highly sensitive analytical techniques, with high precision and accuracy. Instrumental neutron activation analysis (INAA) has been used for the determination of heavy metals and other trace elements in different environmental samples.

Sediments
The study of the distribution of metals 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 which have been polluted by heavy metals represent the comprehension of transportation phenomena in these complex ecosystems and the discovery of the pollution history.

A new methodology to study contamination, bioavailability and mobility of metals (Cd, Cu, Ni, Pb, and Zn) using chemical and geostatistics approaches in marine sediments of Sepetiba Bay (SE Brazil) was proposed. The chemical model of SEM (simultaneously extracted metals)/AVS (acid volatile sulfides) ratio uses a technique of cold acid extraction of metals to evaluate their bioavailability, and the geostatistical model of attenuation of concentrations estimates the mobility of metals. By coupling the two it was observed that Sepetiba Port, the urban area of Sepetiba and the riverine discharges may constitute potential sources of metals to Sepetiba Bay. The metals are concentrated in the NE area of the bay, where they tend to have their lowest mobility, as shown by the attenuation model, and are not

bioavailable, as they tend to associate with sulfide and organic matter originated in the mangrove forests of nearby Guaratiba area. (Partnership: Universidade Federal Fluminense, Instituto Federal de Educação, Ciência e Tecnologia de Sergipe, Instituto Oceanográfico-USP).

The contamination of two estuarine systems, a lagoon-estuary complex area of Iguape-Cananéia and of Santos-São Vicente, both located in the coast of São Paulo State, was evaluated. Cananéia is considered as part of Biosphere Natural Reserve due to its environmental and cultural importance and is considered unpolluted. Santos - São Vicente estuary is an example of environmental degradation in coastal systems of industrial origin. Another project developed in the Iguape-Cananéia lagoon-estuary complex was a comparative study of biogeochemical impacts in this area with emphasis of the Valo Grande influence, analyzing sediment samples collected along the region. Continuing the project "Toxic metal and trace elements assessment in sediments from water supply reservoirs from São Paulo State", four important reservoirs, Rio Grande, Guarapiranga, Itupararanga and Salto Grande/Ribeira de Iguape river were studied. In all these studies the toxic metal concentration and trace elements 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 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. (Partnership: Oceanographic Institute - IOUSP, Environmental Company of the São Paulo State - CETESB).

Soils

The urban environment quality is of vital importance as the majority of people now live in cities. Metals occur naturally in soil, but contents are generally increased in the urban environment due to anthropogenic activities. The platinum group elements Pt, Pd and Rh are the active components of car catalysts and are being spread into the environment to an as-yet incompletely known extent due to surface abrasion of the catalyst during car operation. São Paulo is a city with 19 millions of inhabitants and an ever increasing seven million motor vehicle fleet which shows severe pollutions problems. There has been little research on metal concentration levels in soils of São Paulo and there has never been an investigation regarding Pt, Pd, and Rh levels in the city.

In the present study, Pt, Pd, and Rh concentrations were determined in soils adjacent to seven main high density traffic avenues in the metropolitan region of São Paulo City. Inductively coupled plasma mass spectrometry was employed - after ultrasound-assisted aqua regia leaching - as analytical technique. The results showed concentration levels up to 378 ng g^{-1} for Pd, 208 ng g^{-1} for Pt, and 0.2 to 45 ng g^{-1} for Rh. These levels are much higher than those considered for the geochemical background of soils, indicating a catalytic converter source. Due to the different Pt/Pd/Rh ratio in Brazilian automobile catalytic converters, lower levels f Pt/Pd ratios compared with other similar studies were bserved. The obtained results are the first data for monitoring Pt, Pd, and Rh pollution in São Paulo City soils.

The elements As, Ba, Co, Cr, Sb, and Zn concentrations were determined in soils adjacent to avenues of highly dense traffic in São Paulo city to assess their levels and possible sources. The analytical technique employed was Instrumental neutron activation analysis. The results showed, except for Co, concentration levels higher than the reference values for soils of São Paulo, according to the Environmental Protection Agency of the State of São Paulo guidelines. When

compared to similar studies in other cities around the world, São Paulo soils presented higher levels, probably due to its high density traffic and industrial activity. The concentrations obtained for As and Cr indicate anthropogenic origin. The high levels of the traffic-related elements Ba, Sb, and Zn in soils nearby high density traffic avenues indicate they may originate from vehicular exhausts. (Partnership: Environmental Institute of Scientific Networks, Germany).

Biomonitoring atmospheric pollution
Tillandsia usneoides

Tillandsia usneoides (L.) is an aerial epiphytic bromeliad that lives on trees or other kinds of inert substratum, absorbing water and nutrients directly from the environment. Due to this characteristic, this species also accumulates pollutants present in the atmosphere. In this study, *T. usneoides* was used as biomonitor aiming to verify if the construction of the western and southern parts of the peripheral highway Mario Covas (SP-21) in São Paulo city would alter the profile of atmospheric contamination by Ba, Cr and Zn in the region. These elements are often associated with traffic and can indicate contaminated urban areas. This knowledge is of great interest to the city, which has one of the biggest vehicle fleets in the world, with more than seven million circulating motor vehicles and serious environmental problems due to air pollution. Neutron Activation Analysis was employed as analytical technique. Samples of *T. usneoides* were irradiated at the IEA-R1 nuclear reactor at IPEN-CNEN/SP, and the induced activity was measured by high resolution gamma-ray spectrometry. Increasing concentrations of Ba, Cr and Zn were observed in the biomonitor after the inauguration of the highway, indicating that these elements originated from vehicular emissions. (Partnership: Instituto de Botânica de São Paulo; Instituto Oceanográfico-USP).

Lichens

Lichens have been widely used as trace element air monitors since they are widespread and capable of absorbing elements directly from the atmosphere and accumulating in their tissues. Besides this, the use of lichens as biomonitors presents advantages because of their easy sampling, their wide geographical distribution and the use of less expensive technical equipment for sample collecting.

In the last decades, several researchers have successfully used epiphytic lichens as indicators of pollutants in the atmosphere. Moreover, lichens are not used only to detect concentrations of chemical elements but also radionuclides and persistent organic compounds such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs. Consequently the studies of different lichen species are of interest since their choice for monitoring purposes depends on the biodiversity of the ecosystem under study. In trace element biomonitoring, factors such as occurrence, accumulation characteristics, ease sampling and sample treatment, tolerance to pollution and background concentrations of the elements should be considered for the selection of lichen species.

In the present study, comparisons were made between the elements accumulated by two epiphytic lichen species *Canoparmelia texana* (Tuck.) Elix & Hale and *Usnea amblyoclada* (Müll.Arg.) Zahlbr in order to evaluate the their suitability to monitor aerial pollutants. *C. texana* is an epiphytic lichen species of the Parmeliaceae family. It is one of the most widely spread lichenized fungi species in open spaces of the natural primary vegetable formations as well as inside cities all over the Brazilian territory except in the coastal cities. It is foliose lichen with large thallus (5 to 10 cm in diameter) with radial growth found on tree barks or, more rarely, on rocks. *Usnea amblyoclada* is also of the Parmeliaceae family. It is a fruticolous lichen and most abundant saxicolous species in Argentina. Its thallus is shrubby, compact with long branching and it is used in popular medicine and as biomarker of air quality.

Samples of both lichen species were collected on the same dates and same location of Parelheiros sub prefecture, located far from São Paulo downtown in a rural area near a region of native vegetation. Samples of each lichen species collected during the period from November 2010 to November 2012 were cleaned and analyzed by neutron activation analysis. Results obtained indicated that both lichen species can be

used to monitor air quality pollution. Various elements of interest from the environmental point of view were found in both species. However *C. texana* showed higher accumulation capacity of several elements than *Usnea amblyoclada*. The capacity of particle trapping of lichens can be influenced to a great extent by their morphology. From the laboratory work point of view it can be stated that *Usnea* that is fruticose lichen presents easier cleaning for the analysis when compared with foliose *C. texana*. The results obtained in different sampling periods showed that, in general, elements did not exhibit well defined trends, but rather showed fluctuations. These findings of this study suggest further research on the vitality of both species to be used as a transplant for trace element monitoring. (Partnership: FMUSP).

Tree barks

Tree bark is considered to be a promising indicator of air pollution monitoring, because of its accumulation of aerosol particles, simplicity of species identification and wide geographical distribution. However, there are no established protocols for its sampling as well as about its capabilities to be used as an alternative or complementary indicator of aerial pollution. Besides, there are contradictory opinions about the accumulation capability of bark as and its adequacy as a bioindicator of atmospheric pollution. In this study barks from very common and dominant arboreal species in urban areas were analyzed in order to define adequate conditions for their use in the pollution monitoring. In this study barks from very common and dominant arboreal species in urban areas of São Paulo city were analyzed in order to define adequate conditions for their use.

Tree bark samples collected from Sibipiruna (*Caesalpina peltophoroides*) and Tipuana (*Tipuana tipu*) species at a height of 1.5 m from the soil were cleaned using a nylon brush. Then bark surface layer were removed using a Ti grater and ground for element determination by neutron activation analysis (NAA). Preliminary results demonstrated that the nuclear technique of NAA provides reliable data for element concentrations (|Zscore| < 2) and the characteristics such as arboreal species or bark porosity, bark surface layer taken for analysis as well as tree trunk diameter or age of tree should be considered in bark sampling ant treatment for use in air pollution monitoring. (Partnership: FMUSP).

Birds

Egrets belonging to the Ardeidae family are wading water birds and are top consumers in the food chain with potential to accumulate contaminants through bioaccumulation and biomagnification. These characteristics become the egrets as a suitable biomonitor of aquatic environmental pollution to assess the fate of inorganic compounds and as species of concern for ecological risk assessments. Moreover, these species are more susceptible to the deleterious effects of environmental contamination, which brings up the need for their conservation. Aiming to verify the possibility of using *Ardea alba* (Great Egret) in the evaluation of environmental contamination, the livers of these adult birds found unable to survive in the São Paulo Metropolitan Region (SPMR) and in other locations of the state of São Paulo, were analyzed by the methods of neutron activation analysis (NAA) and by atomic absorption spectrometry (AAS). Permission to acquire bird liver samples was obtained from the Brazilian Institute of Environment and Renewable Resources (IBAMA). Elements Br, Cd, Co, Cs, Cu, Fe, Hg, K, Mg, Mn, Na, Rb, Se and Zn were determined in livers of egrets found in SPMR and a wide variability in their concentrations was verified. These variations indicated different levels of contamination throughout the SPMR. Comparisons of our results with those literature reported values showed that the concentrations of most elements found in livers of egrets from the SPMR are higher or of the same magnitude as those of polluted areas. Comparisons made between element concentrations of different genders of egrets by applying appropriate statistical test indicated that females present lower concentrations of Cs, Hg, Se and Zn than males, probably due to physiological and ecological differences between genders. Pearson correlation coefficients between elements concentrations showed significant positive correlations between the elements Cd, Cu, Hg, Mn, Se and Zn suggesting that anthropogenic activities may be contamination sources of these elements in the SPMR. The findings demonstrated the viability of using egret livers to evaluate environmental contamination as well

as these results constitute important informations for conservation studies of the egret species. (Partnerships: Technical Division of Veterinary Medicine and Wildlife Management DEPAVE-3/SVMA, Municipal Prefecture of São Paulo; Municipal Zoo "Quinzinho de Barros", Sorocaba, SP and Screening Center for Wild Animals - CETAS - of São Sebastião, SP).

Biomonitoring of marine pollution

Biomonitoring of coastal areas using marine organisms is an attractive approach for the study of pollution caused by anthropic discharges. There are two main types of experiments that are generally used for this purpose: *passive biomonitoring*, in which the native organisms are collected and analyzed and *active biomonitoring*, in which organisms from a pristine area (like a mussel farm) are collected and transplanted to polluted sites. In the first phase of this work, the *active biomonitoring* approach was used and the marine bivalve *Perna perna*, very abundant in the coast of the State of São Paulo, Brazil, was transplanted from a mussel farm and used for biomonitoring of four sites (Itaipu and Ilha das Palmas, in Santos and TEBAR oil terminal and Ilha Bela, in São Sebastião), situated in coastal regions close to domestic and/or industrial discharges. Hg, Cd and Pb were determined in the transplanted organisms by AAS and As, Ca, Co, Cr, Fe, Na, Se and Zn were determined by INAA. After the transplant experiments of the organisms to the sites of study, a rise in concentrations was observed for all elements, depending on the season and site of study thus indicating the applicability of the *Perna perna* mussel as biomonitor. It could be observed that the concentrations of As and Se were always above the tolerance limits of the Brazilian legislation (1.0 µg g-1 for As and 0.30 µg g-1 for Se), in all sites of study, including the control site. For the potentially toxic elements Cd, Hg, Pb and Zn, the concentrations obtained were always below the maximum limits established by the legislation (1.0 µg g^{-1} for Cd, 2.0 µg g^{-1} for Pb, 0.5 µg g^{-1} for Hg and 50 µg g^{-1} for Zn). In the second phase of this work, a *passive biomonitoring* approach is being applied, and two types of organisms have been chosen for the study: the *Perna perna* mussel, collected in a mussel farm at the Cocanha beach (clean area) and in two sites at Santos Bay (Itaipu and Palmas) and the *Crassostrea brasiliana* oyster, collected at Cananeia (oyster farm) and at Bertioga and Santos Estuary. Inorganic trace elements were determined: As, Br, Co, Cr, Fe, K, Mg, Mn, Zn and V, by INAA and Cd, Pb and Hg by AAS. Also ecotoxicological tests with the neutral red reagent were made, in order to evaluate the level of stress of the organisms in the polluted regions. In the period from 2009 to 2013, this work with *passive biomonitoring* of marine organisms became part of the IAEA/ARCAL Project: *"Regional Programme for the biomonitoring of contaminants in molluscs and fish to ensure seafood safety in Latin America and the Caribbean using nuclear analytical techniques"* and also the analysis of fish consumed by the population of the city of São Paulo was included in the project. Samples of some of the most consumed fish species by the population (*robalo*, *sardinha*, *pescada*, *salmão*, *corvina*, *tainha* and *anchova*) were acquired at the CEAGESP, the main food distributor of São Paulo and are being analyzed for inorganic trace elements, also by the methods of INAA and AAS. The results obtained will be compared to the values of the Brazilian legislation for food contaminants.

In the second part of the work, using *the passive biomonitoring* approach, short irradiations, of about 10 s, were used to determine the group of elements: Br, Cl, K, Mg, Mn and V in the *Perna perna* mussel. It was verified that, contrary to expected, the bioaccumulation of the elements was high in the mussel farm, especially in springtime. The concentrations of Br found were in general higher than the bromophenol amounts normally found in mussels. In the case of V, which is a marker for petroleum contamination, the concentrations were higher in the mussel farm and in the other sites of the Santos Bay, in springtime.

As to the fish study, samples of *corvina*, *robalo* and *pescada* were analyzed up to now. It was verified that in *corvina* the concentrations, of 6.86 µg g^{-1} were much higher than the limit of the Brazilian legislation, of 1.0 µg g^{-1}. On the other hand, it must be pointed out that it would be necessary to make the speciation of As, since the organic forms generally present normally do not represent a health hazard. In

the case of *robalo* and *pescada*, the elements As, Br, Co, Cs, Fe, K, Na, Rb, Se and Zn were determined. It was verified that, for Se determinations, *robalo* presented 0.30 µg g^{-1}, which is exactly in the limit of the Brazilian legislation and *pescada* presented concentrations somewhat higher, of 0.43 µg^{-1}. These analyses and interpretations are underway and additional conclusions will be presented in the future. (Partnership: São Paulo University Oceanographic Institute).

Figure 8. Collection of the haemolymph of oysters for the ecotoxicological test.

Assessment of the content of mercury, methylmercury and other elements of interest in fish and school children hair from Iguape and Cananéia coastal cities, São Paulo State, Brazil

The Cananéia-Iguape estuarine-lagoon complex, located in the southern coastal region of Sao Paulo State, is part of the Biosphere Natural Reserve (UNESCO) due to its environmental-cultural importance. It is a region of overall low pollution impact in the southern part of the hydrological system (Cananéia estuary) and is an Environment Protected Area. The present study assessed total Hg content and micronutrients (Ca, Fe, K, Na, Se and Zn) in the fish most consumed by the population from Cananéia and Iguape coastal cities. Furthermore, total and MeHg levels were also determined in hair samples of children from both cities in order to verify bioaccumulation of Hg in this populational group. From these results it was possible to evaluate the nutritional content of the fish consumed and the exposure of the children to Hg and MeHg in these coastal cities. (Partnership: IOUSP).

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.

The International Atomic Energy Agency (IAEA) has been supporting several projects with the objective of laboratory capability improvement in Latin America. In this context, CRPq participated in the IAEA project "Improvement of analytical quality through proficiency testing and certification of matrix reference materials using nuclear and related analytical techniques in the Latin American nuclear analytical techniques network" (IAEA ARCAL RLA 0214). In this project, the Neutron Activation Laboratory was responsible for the preparation of a new fish reference material. Whitemouth croake (*Micropogonias furnieri*), also known as *corvina*, was chosen as it is the second fish in production in Brazil and it is widely distributed and consumed in the Latin American countries.

All the steps for the production of the Brazilian fish reference material were developed, including sampling, sample pretreatments, freeze-drying, grinding, sieving, homogenization and gamma ray sterilization. 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. With IAEA support, an international interlaboratory program was performed for assignment of element certified values and associated expanded uncertainties. Certified values for As, Cd, Cu, Fe, K, Mn, Na, Se and Zn in the fish tissue CRM were established, while information value was established for Hg and indicative value for I. (Partnership: IRD-CNEN/RJ).

Figure 9. Whitemouth croake - *corvina*.

Figure 10. Bottling process and bottles of the fish reference material.

Nuclear and non-nuclear analytical techniques applied to archaeological studies

The artifacts found in archaeological sites are related to ancient people who lived there long ago. The more abundant and important artifacts found in many areas worldwide are ceramics which combine, in the most part, durability with ubiquity. Several analytical methods including the nuclear and non-nuclear analytical methods are used for the study of the characterization and the manufacturing of the artefacts. 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.

The Archaeometric Studies Group of the IPEN-CNEN/SP from 1996 is working with a research program as a means of physical and chemical characterization of ceramic from Amazon and other regions using several analytical techniques, like instrumental neutron activation analysis, INAA, X-ray diffraction, XRD, thermoluminescence dating, TL, among other. During the period 2011 to 2013 years, the Group analyzed hundreds of archaeological ceramics specimens in sites from Manaus in collaboration with various archaeologists and geologists.

With the elements determined by INAA special attention is paid in establishing inter-sample similarity by means of advanced statistical methods like Mahalanobis distance, cluster analysis , principal components analysis, Kernel density, and other as Procrustes analysis, neural network to cite just a few of the statistical method used.

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 material NIST-SRM-1633b, and IAEA-Soil-7 are weighed in polyethylene bags and wrapped in aluminum foil. Groups of 8 to 10 samples and the references materials 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 8.92×10^{12} cm^{-2} .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 is possible to determine the mineralogical composition in the ceramics, i.e., 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.

Thermoluminescence dating is being used in our Group as a means of obtaining the firing 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 are 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 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 (D_e) which is the absorbed dose, generally expressed in Gy (1Gy = 1J) and is measured in a Luminescence reader. While that the annual dose (D_{an}), which is the received dose of ionizing radiation rate, expressed in mGy/year or Gy/ka. The ratio between both doses, D_e / D_{an}, provides the age. A typical ceramic from Amazon is presented in the Figure 11.
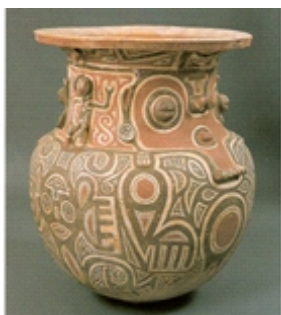

Figure 11. Funerary urn.

The Fig. shows a funerary urn which contained skeletal remains possibly a young adult. The designs have a symbolic significance of a social or religious character with highly complex ceremonial wares in form and decoration. Decorative techniques involve slip, painting, incision, excision and scraping. The ceramics are tempered with ground potsherds (grog) and two plain types that also define two different types of paste that can be found in all decorative types. Some pottery tempered with crushed ashes of a tree bark known as caraipé (*Licania scabra*) are also found. The use of caraipé as temper material was introduced in the Amazon Basin towards the end of the first millennium and it is associated with Polychrome Tradition.

Using nuclear and non-nuclear analytical techniques, our Research Group, three main objectives guide the examination of compositional variability in raw material and in finished products: 1) to explore whether it is possible to detect chemical compositional differences between two or more closely situated archaeological sites in a single geological region 2) to evaluate the closeness of fit between clay compositions from specific sources and products manufacturing and finally 3) to seek explanation for aspects of observed compositional variability.

Determination of rare earth elements, U, Th, and other trace elements in geological samples by neutron activation analysis for geochemical studies

Trace elements, including U, Th, Ba, Rb, Ta, Cs, Co, Hf and rare earth elements (REE), have been widely used in geochemical and petrogenetic studies due to the information they can provide about the formation and weathering of rocks. Instrumental neutron activation analysis (INAA) has been used as a powerful tool in these studies due to the high sensitivity, precision and accuracy in these trace elements determination. INAA provides multielemental analysis in concentrations of about mg kg^{-1} to ng kg^{-1}, without the sample chemical attack. The Neutron Activation Analysis Laboratory at IPEN (LAN-IPEN) has been analyzing trace elements in different kinds of rocks by INAA.

The analytical procedure consisted of weighing aliquots of about 100 mg of the powdered rock and of geological reference materials used as standard in polyethylene bags. Samples and reference materials were submitted to a neutron flux of about 10^{12} n cm^{-2} s^{-1} for 8 hours at the IEA-R1 nuclear reactor at IPEN. The measurements of the induced gamma-ray activity were carried out in a GX20190 hyperpure Ge detector (Canberra). The multi-channel analyser was a 8192 channel Canberra S-100 plug-in-card in a PC computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma-ray of ^{60}Co. The gamma-ray spectra were processed by using the VISPECT gamma-ray software which locates peak positions and calculates the energies and net areas.

The geochemical and isotopic compositions of tholeiites of the Northern region from the Paraná Continental Flood Basalts (PCFB), one of the largest continental provinces of the world, were studied. In order to examine the mantle sources involved in the high-Ti (Pitanga and Paranapanema) basalt genesis, Sr, Nd, and Pb isotopic systematics, and major, minor and incompatible trace element abundances were studied. The REE patterns of the investigated samples (Pitanga and Paranapanema magma type) are similar (parallel to) to those of Island Arc Basalts' REE patterns. The incompatible trace element ratios and Sr-Nd-Pb isotopic compositions of the PCFB tholeiites are different to those found in Tristan da Cunha ocean island rocks, showing that this plume did not play a substantial role in the PCFB genesis. The geochemical composition of the northern PCFB may be explained through the involvement of fluids and/or small volume melts related to meta-somatic processes. In this context, we propose that the source of these magmas is a mixture of sublithospheric peridotite veined and/or interlayered with mafic components (e.g., pyroxenites or eclogites). The sublithospheric mantle (dominating the osmium isotopic compositions) was very probably enriched by fluids and/or magmas related to the Neoproterozoic subduction processes. This sublithospheric mantle region may have been frozen and coupled to the base of the Parana basin lithospheric plate above which the Paleozoic subsidence and subsequent Early Cretaceous magmatism occurred. (Partnership: Astronomy, Geophysics and Atmospheric Sciences Institute of the University of São Paulo - IAG-USP).

The collision of oceanic arcs with continents is a common plate tectonic process in the Phanerozoic, but its recognition in the Precambrian is hampered by deformation and metamorphism. The Rio Capim volcanic-plutonic-sedimentary belt lies in sharp tectonic contact with Archaean rocks of the Uauá block in the northern part of the São Francisco craton. Field relationships and high-precision geochronology indicated that the Rio Capim basalts, gabbros, diorites, and dacites were emplaced approximately at 2148-2143 Ma, and later intruded by 2128 Ma-old diorite to tonalite plutons. All rocks were metamorphosed under amphibolite to granulite facies conditions mainly between 2080 Ma and 2070 Ma, but deformation may have lasted until about 2040 Ma as estimated from syn-deformation zircon and titanite grains. The association of basalt, andesite, dacite, and their plutonic counterparts, combined with their positive εNd(t) values and incompatible trace element geochemical signatures similar to island arc magmas, support the proposition that the Rio Capim belt was a Palaeoproteorozoic intra-oceanic arc sequence that collided with a continent, of which the

Mesoarchaean Uauá block is a remnant. (Partnership: Geosciences Institute, University of Campinas - UNICAMP).

Soils developed from different volcanic rocks from the Fernando de Noronha island: rare-earth element patterns and isotopic lead composition: this study examines how pedogenesis influences the distribution of rare earth elements in soils derived from different rock types, formed under tropical humid climate, and the possible contribution of airborne transported Pb in soils. Five soil profiles developed from different volcanic rocks cropping out in the Fernando de Noronha island were studied. Results show that in the course of weathering REE accumulated. The REE patterns in soils are similar to those of the parent material, except for a slight preferential HREE enrichment. Pb data indicate the presence of a non-radiogenic anthropogenic component in the upper horizon of the soil profiles. (Partnership: Geosciences Institute, University of São Paulo - USP).

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 deposed in the sample along the years. The accumulated dose of radiation, called Archeologial Dose (AD), is produced by the exposition to environmental radiation provided by U, Th, K and cosmic rays. If the environmental dose rate (D_{an}) 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: 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) spectroscopy was applied to date megafauna fossil teeth of *Stegomastodon waringi* and Toxodontinae (two teeth) found in Baixa Grande, Bahia, Brazil. The additive method was employed to construct the dose response curve and to calculate the Equivalent Dose (D_e). Neutron Activation Analysis of enamel, dentine and soil where the samples were buried was used to determine the main radioisotopes concentration. These data were used in the conversion of D_e into age, using the ROSY ESR dating software. The results of age obtained were 50 ± 10 ka for *S. waringi*, and 43 ± 8 ka and 9 ± 2 ka for Toxodontinae teeth. Although Late Quaternary fossils from the extinct South American megafauna are relatively common in Brazilian's Northeast region, few geochronological studies were conducted. Thus dating samples found in this region will allow a better time and space understanding of that fauna.

Another study was performed to place the Quaternary Águas de Araxá's Notiomastodon platensis population in a chronological context through ESR dating and to investigate its paleoenvironmental context and extinction causes. The ESR analysis was made on both crushed tooth enamel and sediment from the study area. They were subjected to Neutron Activation Analysis to determine the concentration of U, Th and K. The ESR dating indicated an age somewhere between 60,000 and 55,000 a for this *N. platensis* population (Lujanian, the last age of the Late Pleistocene South American Land Mammal Ages - SALMA). The date found for these gomphotheres is included in the Middle Pleniglacial, which is characterized by a cold and arid climate. Previous paleodiet studies suggest that the feeding habits of those individuals were basically opportunistic/generalist herbivores (C3 grasses and woody plants). Taphonomically, it was observed that the gomphotheres carcasses were transported by a high-energy water stream, typical of fluvial systems, and that the large amount of

individuals in the fossil record is due to a mass death event related to a dry period. Based on taphonomical, paleoecological and chronological evidence, it is possible to assume that the gomphothere population from the Quaternary of Águas de Araxá is probably an example of individuals that suffered from climate changes during the Late Pleistocene in South America. (Partnership: Universidade Sagrado Coração; Departamento de Física, Faculdade de Filosofia Ciências e Letras, USP).

Clay composition studies by Neutron Activation Analysis

About 150 applications are known for clay and clay minerals, among them oil and water adsorbent, catalyzer, bactericide, ceramics, beverage whitening, filters production, porcelain, waste treatment, cosmetics, and so on. In the pharmaceutical industry, clays are used as excipients, lubricants, diluents, binders, desiccants, emulsifiers, thickeners, masking flavors, isotonic agents and chargers of active substances.

The use of minerals for therapeutic purposes is an ancient practice, especially clay minerals such as smectite, kaolinite and palygorskita. The clays were used in wound healing, skin irritation relief, skin cleaning and also for anti-inflammatory purposes. In cosmetic, the topical application is recommended due to the clay ability to adsorb substances such as fats and toxins.

In the period from 2010 to 2013 neutron activation analysis was applied to determine the elemental concentrations in clay and clay minerals used as cosmetic and medicine in the following projects.

Chemical, mineralogical and radiological Peruíbe Black Mud characterization and clinical evaluation of the effects of mud therapy in patients with knee osteoarthritis

The use of Black Mud of Peruíbe is traditionally done, and also currently, through applications of peloid in its natural form, preserving the rich bacterial flora present, and it is believed that it can just be used this way. Currently peloid undergoes a beneficiation process, which uses sea water, which is aimed to decontaminate the mud in a process called maturation. Although widely used worldwide, the mechanisms of action of mud therapeutic application (mud therapy) are not yet well understood, especially considering the different origins and composition of the used muds. In this sense several hypotheses have been considered in an attempt to clarify these mechanisms.

However there is an old discussion about whether this is the only adequate preparation for the Black Mud use and if it is possible to submit it to a sterilization process, without loose its therapeutic properties currently observed in its use non-sterile form.

Inside a large universe of conditions that respond positively to the use of Black Mud, certainly the chronic arthritis are one of those that respond faster and efficiently, is also a disease that affects a large number of people so that it is possible to compose two observation groups. Thus, this pathology was chosen for this study to verify the effectiveness of the application of the mud in patients with osteoarthritis of the knees, and a comparison of the therapeutic effect of mature Black Mud and black mud matured and sterilized by radiation gamma.

The study will be conducted by the method of double-blind observation, where neither the investor nor the patient know who is receiving the Black Mud sterilized and unsterilized. The groups will be formed by 25 people each and patients will be followed by a period of nine weeks, and the method of observation based on subjective information gathered by the table modified Lequesne and SF36. The effectiveness of the treatment will be evaluated by measuring levels of pro-inflammatory mediators, cytokines (IL-1, IL-6, IL-18, PGE2 and TNF-alpha) and will also be collected demographic, clinical, and physical and radiographic examinations.

Simultaneously, the Peruíbe Black Mud will be analyzed in order to better understand its mineralogical, chemical and radioactive composition and its microbiological content, ruling out the possibility

that the use of this material can somehow come to cause any negative effect on human health. X-ray diffraction, X-rays fluorescence, neutron activation analysis, atomic absorption, content of organic matter determination and sequential extraction will be used to characterize these mud aspects.

For the realization of these characterizations X-ray diffraction will be applied to determine the mineralogical composition of the mud; X-ray fluorescence, to determine the major components SiO_2, Al_2O_3, MnO, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, Fe_2O_3, and trace elements Cu, Ga, Nb, Ni, Sr, V, Y and Zr; neutron activation analysis for determining the elements As, Ba, Br, Ce, Cl, Co, Cr, Cs, Eu, Fe , Hf, K, La, Lu, in, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb, and Zn; atomic absorption to determine Ca, Pb and Hg; gamma spectrometry to determine the radionulídeos ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K, determination of organic matter, nitrogen and sulfur and the study of speciation by sequential extraction.

Chemical and radiological composition of Peruíbe Black Mud cosmetics

In Brazil, an example used as cosmetic is the Peruibe Black Mud of São Paulo State. This material is characterized by large amounts of fine particles, high organic matter content, high sulfate reducing bacteria content and consequently high reduction potential. The Peruíbe Black Mud is commonly used to treat psoriasis, dermatitis peripheral acne and seborrhea, in addition to its use in myalgia, arthritis and rheumatic diseases such as arthrosis and rheumatism sciatic. This mud also has application in healing skin disorders, allergies and chronic eczema. This study aimed to evaluate the elementary composition (As, Ba, Br, Cs, Co, Cr, Fe, Hf, Na, Rb, Sb, Sc, Se, Ta, Th, U, Zn, Zr, Sc, Ce, Eu, La, Lu, Nd, Sm, Tb and Yb, by neutron activation analysis, Pb, Cd and Hg, by atomic absorption spectrometry) and activity concentration of radioactive nuclides (^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K) in the Peruíbe Black Mud and in cosmetics made with it: conditioner, moisturizer, soap, liquid soap, shampoo, facial mask and sterilized mud. For the radionuclides analysis, the results showed that only the face mask cosmetic and sterilized mud possess measurable activity concentration. In all the other cases, the activity concentration was below the detection limit. Elementary concentrations indicate that the face mask and the sterilized mud are also the type of cosmetic with closer values to the mud. Liquid soap and shampoo were the cosmetics with the lowest values compared to the mud.

Evaluation of the elemental composition of clays in Campos Gerais (MG)

There are numerous applications given to clays. Over 140 applications only for bentonite clay are found in literature such as oil and water adsorbent, catalyst, bactericide, ceramics, whitening of beverages, cosmetics, manufacture of filters, porcelain, waste disposal, etc. Generally the clays are used as adsorbents in bleaching processes in the textile and food processes, in remediation of soil and landfills, to adjust the rheological properties of drilling fluid oils and in paints, as carrier of organic molecules in cosmetics and pharmaceuticals and as support for catalysts. In the pharmaceutical industry, clays are used as excipients, lubricants, diluents, binders, desiccants, emulsifiers, thickeners, masking flavors, isotonic agent, as charger and delivery of active substances. The objective of this study is to determine the elemental composition of clays from Campos Gerais, Minas Gerais, with a view to their applicability in the production of cosmetics. It will be determined the elements As, Ba, Br, Ce, Cl, Co, Cr, Cs, I, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb, Zn, Pb, Cd and Hg and radionuclides ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K .

Multielemental determination by Neutron Activation Analysis applied to medicinal plants and their extracts

In recent decades, with the increase of the interest in the drugs developed from plants more attention has been paid to their macro, micro and trace elements constitution, the correlation of the plant elemental composition with its therapeutic applications and the influence of the increasing environmental pollution. The presence of stable and radioactive elements in plants constitutes one of the main pathways for their migration to the human, via uptake of tea or

remedies made with medicinal herbs. In the period from 2010 to 2013 neutron activation analysis was applied to determine the elemental concentrations in medicinal plants and their extracts in the four following projects.

Determination of inorganic constituents in medicinal plants

Different types of therapies have been introduced as an alternative treatment to combat different human disorders. Among them, the use of herbal teas has been highlighted due to their cost/benefit, easiness of acquisition and administration. Inorganic constituents and the concentration of As, Ba, Br, Ca, Cl, Co, Cr, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, Sb, Sc, Se, Ta, Th, Ti, U, V, Zn and Zr, by were determined by neutron activation analysis; Cd, Cu, Ni and Pb, by atomic emission spectrometry, with inductively coupled plasma and Hg, by atomic absorption spectrometry, with cold vapor generation in medicinal plants and their extracts, whose marketing was regulated in 2010 by ANVISA. The relevance of these analyzes is justified by the need of contributing to the recommendation of such plants as sources of minerals in the diet and, also, verifying if their concentrations can pose some harm to the body.

Inorganic composition study and evalutaion of biological activity of *Peperomia pellucida* in the growth of *Aspergillus flavus*

In recent decades, there has been a great advancement in research in developing drugs from plants. Nevertheless, few care deeply exist in literature about stable elements concentration, as well as, the activity concentration of ^{238}U and ^{232}Th decay products in plants used for this purpose. In this study, the elemental composition of *Peperomia pellucida* and surrounding soil samples collected in Botanical Garden in Rio de Janeiro was determined; it also was determined the elemental concentration in alcoholic extract and infusion processes of dry plants. *Peperomia pellucida*, whose popular name is "erva de jabuti", is a plant known by its medicinal properties like healing property, analgesic activity, antibacterial activity and antifungal activity against food fungi. The elemental concentration of As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn was determined in different plant parts and in their extracts obtained by maceration and infusions and in the surrounding soil by Instrumental Neutron Activation Analysis (INAA). The analytical methodology used to determine the elements Cd, Hg and Pb was Atomic Absorption Spectrometry (AAS) and the activities of ^{226}Ra, ^{228}Ra and ^{210}Pb were carried out by gross alpha and beta counting after radiochemical separation. The essential oil, ethanolic and hexane extracts of *Peperomia pellucida* were tested for antifungal activity against *Aspergillus flavus* in vitro on Petri plates. The antifungal activity was based on the inhibition zone and IC50 values against the pathogen on Petri plates assays. Also essential oil chemical composition was determined by GC-MS.

Influence of the soil elemental composition in the production of volatile oil by Melissa officinalis

The expansion of interest in medicinal plants has required the standardization of the sector with implementation and constant review of technical standards for production and marketing of these medicines in order to ensure the safe use, therapeutic efficacy and quality of the products. According to data from the World Health Organization, approximately 80% of world population has resorted to the benefits of certain herbs with therapeutic action popularly recognized. Despite the vast flora and the extensive use of medicinal plants by the population, it is a consensus that scientific studies on the subject are insufficiency. Therefore, the objectives of this project are to determine the content of inorganic constituents in herbal medicine (As, Ba, Br, Ca, Cl, Cs, Co, Cr, Fe, Hf, K, Mg , Mn, Na, Rb, Sb, Sc, Se, Ta, Th, U, Zn and Zr) by neutron activation analysis and Pb, Cd and Hg by atomic absorption and the main secondary metabolites of Melissa officinalis specie in order to establish a protocol of volatile oil production by this species.

Micronutrients evaluation in medicinal plants used for diabetes treatment

Studies show that more than two thousand Brazilian plants are used as natural medicines by the population for various ailments such as inflammation, blood pressure, throat infection, ulcer, thrush, worms, diarrhea, osteoporosis, menopausal problems, diabetes, etc. Diabetes

mellitus is a disease that affects the metabolism of carbohydrates, greases and protein. Among its most characteristic aspects are the hyperglycemia due to defective or deficient secretion of insulin and glucose excretion in the urine. World Health Organization has estimated that the number of diabetes cases would arrive in 2030 at 366 million with the most occurrences in people with age varying from 45 to 64 ages. Medicinal herbs are widely required for the treatment of diabetes and more than 1200 species are employed around the world for this purpose. In Brazil the use of this natural resource is also widespread and more than 50 species of plants are intended to treat patients with diabetes. Among the plant species used, both in Brazil and other parts of world, can be found *Bindens pilosa* and *Salvia officinalis* that show themselves effective in improving symptoms related to diabetes. Another parameter that recently has been discussed is the role played by trace elements in the metabolism of people with diabetes. Recent studies show that there is a correlation between the concentration of these elements with the presence and the development of the disease. Therefore it becomes important to study medicinal plants used in the diabetes treatment and the correlation between trace element concentrations and secondary metabolites production by these plants. This project proposes to study of elements Cr, Fe, Mg, Mn, V and Zn by Instrumental Neutron Activation Analyses method in samples of *Salvia officinalis* and *Bindens pilosa* cultivated with normal treatment (commercial substrate) and with the addition of the above mentioned elements. Besides the analyses of inorganic constituents, this work will evaluate by gas chromatograph if there is any correlation between the content of these elements with the production of secondary metabolites produced by these plants.

Nuclear data

Uranium fission product interference factors
Instrumental neutron activation analysis (INAA) is a very suitable technique for the determination of several elements in different kinds of matrices. Due to its high sensitivity and accuracy, this method has been extensively applied to environmental sciences, nutritional and health studies, geological, geochemical and material sciences, archaeological studies and nuclear data measurements. Despite the advantages and applications of INAA, when the sample contains high uranium concentrations this method presents interference problems of uranium fission products. The same radioisotopes used in INAA are formed in uranium fission. The radioisotopes ^{141}Ce, ^{143}Ce, ^{140}La, ^{99}Mo, ^{147}Nd, ^{153}Sm and ^{95}Zr are among interfering U fission products. The extension of this interference may affect the accuracy of the results depending on the ratio of concentration of each element to be determined and that of uranium in the sample, as well as the decay time and irradiation conditions. So, in order to obtain reliable analytical results in samples containing high level of uranium, it is necessary to determine uranium fission interference factors (F) to correct this interference due to U in the determination. In this study uranium fission interference factors were determined experimentally irradiating the synthetic standards of U and of elements Ce, La, Mo, Nd, Sm and Zr and also theoretically calculating by use of reported nuclear parameters and the ratio of thermal and epithermal neutron fluxes. These determinations of F were carried out at the IEA-R1 nuclear research reactor in the position 14b. The results obtained in this study showed that accurate determination of elements in samples containing U requires a very careful correction for U fission interference. Comparison made between F values obtained experimentally and theoretically showed, in general, a good agreement. On other hand when compared with literature values, F values of some radioisotopes indicated differences due to the ratio of thermal and epithermal neutron fluxes at the facility used.

Half-life determination for short-lived nuclides of interest for NAA
Nuclear applications require a good degree of knowledge on parameters of the nuclei involved; for instance, in Nuclear Activation Analysis (NAA), nuclear parameters as the decay half-life have to be well known in order to compute the results, and the uncertainties in these parameters frequently undermine the results obtained in the analyzes; also, as the values usually employed come from data compilations as the *Nuclear Data Sheets*, new measurements of these half-lives can always contribute to reaching a better, more accurate and precise, compiled value. In this sense, the half-lives of ^{52}V, ^{66}Cu, ^{28}Al, ^{108}Ag and ^{110}Ag, ranging from 23.47s to 303.66s, were determined. The resulting values had uncertainties comparable to or lower than the literature values, and proved that the compiled values of some of these half-lives, most notably ^{28}Al, ^{66}Cu and ^{110}Ag, must be reassessed.

Research and development

Application of LSC for the determination of gross alpha and beta activity in drinking water

A methodology was established for the determination of gross alpha and beta activity in drinking water by liquid scintillation counting - LSC. The determination was performed using a 1220 Quantulus™ Ultra Low Level Liquid Scintillation Spectrometer. The 1220 Quantulus™ has the advantages of having an extremely low background for performing radioactivity measurements and very good alpha/beta-separation/discrimination capabilities to determine gross alpha and beta activities in water samples, simultaneously. Sample preparation is very rapid and simple, involves concentration of the sample and transfer to a scintillating vial and homogenization with the scintillator solution. The counting efficiency obtained was 0.77 ± 0.04 cps dps^{-1} for alpha emitters and 0.55 ± 0.05 cps dps^{-1} for beta emitters. The detection limits achieved were 0.016 Bq L^{-1} and 0.109 Bq L^{-1} for gross alpha and beta activity, respectively; after a 1:20 concentration process by simple evaporation and a counting time of only 300 min. The proposed technique is adequate for the determination of gross alpha and beta activities in drinking water, since it presents detection limits below the limits adopted by the Brazilian Regulatory Agency and World Health Organization (WHO).

Assessment of natural radioactivity in sands, rocks, granites and marbles of some Brazilian regions

Natural terrestrial radionuclides contribute to a major portion to the background radiation exposure to humankind. The natural radioactivity in rocks and sands mainly comes from the ^{238}U and ^{232}Th decay series and potassium and varies widely from place to place. Measurements of radiation levels in granites, marbles and sands samples has been carried out in selected regions of Brazil, to establish a data base. All activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K were determined by high resolution gamma spectrometry. Fifty commercially used granite samples from Paraná state and twenty (including marbles) from Espírito Santo state, Brazil were assessed. Also a scan of near 150 superficial sand samples over the coast of Espirito Santo state, including Camburi beach (Figs. 12 and 13), in the metropolitan region of "Grande Vitória was performed. For Paraná state samples, the activities concentrations varied from 20 Bq kg^{-1} to 90 Bq kg^{-1} for ^{226}Ra, 10 Bq kg^{-1} to 150 Bq kg^{-1} for ^{232}Th and 800 Bq kg^{-1} to 1600 Bq kg^{-1} for ^{40}K. All results are within the range of literature values for similar rocks. For Espírito Santo state samples, preliminary results show concentrations varying from 20 Bq.kg^{-1} to 270 Bq.kg^{-1} for ^{226}Ra, from 30 Bq.kg^{-1} to 200 Bq.kg^{-1} for ^{232}Th, and from 500 Bq.kg^{-1} to 1500 $\pm$ 60Bq.kg^{-1} for ^{40}K. The southern region of Espírito Santo State shows the highest concentrations for ^{226}Ra, ^{232}Th and ^{40}K and the northern region, the lowest ones. For Espírito Santo sands, activities concentrations varied from 4 Bq kg^{-1} to 1400 Bq kg^{-1} for ^{226}Ra, with the highest values for point 5, Camburi beach (Fig. 13); 10 Bq kg^{-1} to 7500 Bq kg^{-1} for ^{232}Th, with the highest values for Areia Preta beach (Guarapari) and point 5, Camburi beach and from 10 Bq kg^{-1} to 900 Bq kg^{-1} for ^{40}K, with the highest values for Areia Preta beach.

Figure 12. Camburi beach with the 11 locations of the collected samples.

Figure 13. Camburi Beach *in situ* with visible black spots due to ilmenite content.

Natural and anthropogenic radionuclides in Brazilian commercial pet food

In recent decades, the exposure of non-human species to ionizing radiation, as well as its effects, has been given a different focus; on the one hand due to the increasing knowledge on different exposure situations that these species are subjected to and on the other hand, due to the concern regarding biodiversity and its protection. There is, however, no specific representative for domestic animals, like dogs and cats. Brazil holds the second largest dog and cat population in the world, consuming over 2 million tons of feed every year. The present study will evaluate absorbed doses for domestic animals (i.e. dogs and cats) due to ingestion of food designed for them, by determining the radioactivity content of natural and anthropogenic cause. Initially, the activity concentrations in different brands of dry dog and cat food will be assessed by high resolution gamma spectrometry. Several brands usually consumed in Brazil were selected for the study. Preliminary results for eighteen dog food show no concentrations of artificial nuclides, such as ^{137}Cs, ^{60}Co, ^{106}Ru, ^{103}Ru, ^{131}I and ^{241}Am, whilst the concentrations of natural radionuclides varied from 1.17 ± 0.31 Bq kg^{-1} to 5.01 ± 0.38 Bq kg^{-1} for ^{226}Ra; from 1.20 ± 0.50 Bq kg^{-1} up to 8.07 ± 0.96 Bq kg^{-1} for ^{232}Th and from 212.90 ± 10.80 Bq kg^{-1} up to 377.00 ± 17.78 Bq kg^{-1} for ^{40}K. Further, the study will be extended to a larger number of dog food brands and to cat food brands available in Brazil and eventual radiological consequences of absorbed dose will be assessed.

Radon dosimetry with activated charcoal adsorption technique and nuclear tracks detectors

Radon produced by the radioactive decay of ^{226}Ra, is a natural radioactive noble gas that can be found in soil, water and air. Exposure to radon accounts for more than half of the annual effective dose from natural radioactivity.

Radon levels can be assessed by several techniques, as activated charcoal adsorption technique and nuclear tracks detectors. The radon exhalation rate from soil around IPEN nuclear facilities was determined through the activated charcoal adsorption technique (Fig. 14), by measuring the concentration of ^{214}Pb and ^{214}Bi descendants by gamma-ray spectrometry. The radon exhalation rates from soil varied from 0.008 ± 0.001 Bq m^{-2} s^{-1} to 0.052 ± 0.002 Bq m^{-2} s^{-1}.

The radon levels at the Radioactive Waste Storage Facility of the Waste Management Department of IPEN was carried out through the passive method with CR-39 nuclear tracks detectors over a period of twelve months, changing detectors every month in order to determine the long-term average levels of indoor radon concentrations. The radon concentration results, covering the period from June 2012 to June 2013, varied from 0.55 ± 0.05 kBq m^{-3} to 5.19 ± 0.45 kBq m^{-3}.

Radon exhalation rate of granitic rocks commercialized as inner coating material (Fig. 15) was evaluated to estimate, for a model room, the internal radon concentration increase due only this coating. Radon exhalation rates from 34 rock samples with dimensions 15 cm x 15 cm x 2 cm (length, width and height, respectively) were assessed by the "sealed-can" technique and CR-39 nuclear tracks detectors. The indoor radon concentrations were estimated considering the measured radon exhalation and the indoor covered area for a building room model. The superficial radon exhalation rates values are in the range from (0.011 ± 0.001) Bq.m^{-2}.h^{-1} to (1.9 ± 0.1) Bq.m^{-2}.h^{-1}. The radon concentration estimates ranged from (0.019 ± 0.002) Bq.m^{-3} to (3.5 ± 0.2) Bq.m^{-3}, in agreement with similar literature concentrations values of ^{222}Rn in residences due to building materials.

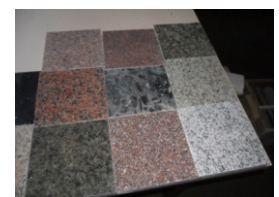Figure 14. PVC pipes with activated charcoal filters inside, placed in the soil at IPEN.

Figure 15. Granitic tiles commercialized in construction stores, Paraná state, Brazil.

Lixiviation of natural radionuclides in columns of tropical soil amended with phosphogypsum

The main phosphate industries in Brazil are responsible for the production of 5.5×10^6 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}Ra and ^{228}Ra does not exceed 1 Bq g^{-1}. In Brazil, PG has been widely used as soil amendment, to improve the soil fertility. To assure a safe utilization in agriculture, it is important to estimate the lixiviation of the radionuclides in PG. For this purpose, an experiment was carried out, in which columns filled with sandy and clayish Brazilian typical soils and PG were percolated with water, to achieve a mild extraction of these elements. The results obtained for the activity concentrations of ^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po in the clay soil are approximately four times higher than the sandy soil. The results obtained for the radionuclides concentration in the PG varied from 144 ± 11 to 294 ± 5 Bq kg^{-1} for ^{226}Ra, from 149 ± 4 to 352 ± 23 Bq kg^{-1} for ^{210}Pb, from 86 ± 8 to 210 ± 6 Bq kg^{-1} for ^{232}Th and from 116 ± 1 to 228 ± 6 Bq kg^{-1} for ^{228}Ra. However, the addition of PG to the soils studied did not represent any increase in the final activity concentration. The final concentrations observed are of the same order of magnitude of the values reported by UNSCEAR for the soil world average values. The maximum ^{226}Ra and ^{228}Ra activity concentration observed in the PG samples, 294 ± 5 Bq kg^{-1} and 228 ± 6 Bq kg^{-1}, are below the limits adopted by CNEN, therefore its use is allowed for agricultural purposes. The results obtained for the activity concentration of all the radionuclides 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 for the intake by plants. This project had financial support from CNPq and FAPESP and was conducted in partnership with Vale Fertilizantes.

Inorganic chemical and radiological characterization of *Nicotiana tabacum* L. cultivated in Brazil and derived products

The tobacco products are extensively used throughout the world and the most consumed are cigarette, cigar and narghile. The damaging effects that these products cause to human health are worldwide discussed and many researches are performed with the aim of relating the use of these products with various diseases. Brazil is the second largest producer and exporter of tobacco worldwide, according to the production of the crop year 2009/2010, with 95% of agricultural production concentrated in the southern region of Brazil. The tobacco plant (*Nicotiana tabacum* L.) (Fig. 16) is used to manufacture all derivatives and chemical composition resulting smoke varies with the type of tobacco leaves as they are grown, the origin region, the characteristics of preparation of their derivatives (compression, and filter paper) and temperature variations resulting from the incomplete combustion of tobacco. The existing national and international literature on the chemical and radiological characterization of the cigarette is vast, but scarce on this same characterization of *Nicotiana tabacum* L. plants growing around the world and especially in the Brazilian varieties and other products besides cigarettes. The objectives of this project are to perform the inorganic chemical and radiological characterization of the varieties of *Nicotiana tabacum* L. most cultivated in Brazil and the main and most consumed tobacco Brazilian products. To achieve these objectives the trace elements As, Ba, Br, Cd, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, K, Na, Nd, Rb, Sb, Se, Sm, Ta, Tb, Th, U, Zn and Yb will be determined as well as the natural radionuclides ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po. With these results, the equivalent dose absorbed due to of their use will be evaluated.

Among all the radionuclides studied, ^{210}Pb presented the highest results; by comparing these results with values from international literature, it can be observed that the Brazilian tobacco has higher

Figure 16. *Nicotiana tabacum* L., Burley variety.

values, but they are in agreement with a previous work that analyzed ^{210}Pb in Brazilian cigarette. The preliminary results obtained for all radionuclides can contribute with the better knowledge and understanding of ^{210}Pb behavior found in *Nicotiana tabacum* L., cultivated in Brazil, since Brazil is the largest exporter of tobacco in the world.

Dating of lacustrine and marine recent sediments using ^{210}Pb method

The use of natural radionuclides from the U and Th decay series in environmental studies has increased since the middle of 20th century. Natural decay series studies have contributed to the development of a better understanding of the physical, geochemical and biological processes that occur in the environment. One good example is the determination of sedimentation rates in lacustrine and marine environments. The study of recent sediments is important for tracing man's activities in the environment; which has been mostly impacted in the last 150 years. Lake and estuarine sediments provide a basis for reconstructing many aspects of this impact, estimating rates of change. The knowledge of the rate at which sediments have been accumulating over the past several hundred years has fundamental importance in understanding aquatic and sedimentary geochemical processes. ^{210}Pb is a naturally occurring radioactive element; it is used in these studies to determine the accumulation rate of recent sediments in lakes, estuaries and oceans. The ^{210}Pb dating method was applied to determine sedimentation rates in lakes located in Pantanal, Brasil and Laguna Melincué, Argentina and an estuary located in Recife, Pernambuco (Fig. 17). The results obtained of sedimentation rates and age of the sediments for all environments studied were in agreement with the local history showing that for these cases the ^{210}Pb method can be used as a tool to understand aquatic and sedimentary geochemical processes.

Figure 17. Lakes from: A) Pantanal, B) Laguna Melincué, and C) Estuary in Pernambuco.

Flux of ^{7}Be and ^{210}Pb measured at ground air level and rainfall in the city of São Paulo

The cosmogenic radionuclide ^{7}Be ($T_{1/2} = 53.3$ d), is produced in the upper atmosphere by cosmic ray spallation of oxygen and nitrogen. ^{210}Pb ($T_{1/2} = 22.3$ y), a natural radionuclide from ^{238}U series can be found in the atmosphere, as a product of ^{222}Rn decay that emanates from the ground, where its atoms become rapidly fixed to aerosols and return to the earth as dry fallout or are washed out in the rain. These natural radionuclides has been widely used as an atmospheric tracer of metals, pollutants and soil erosion, to determine the aerosol residence time as well as chronometers in the environment. Their subsequent deposition to the land surface occurs as both wet and dry fallout, although it was observed that ^{7}Be fallout is primarily associated with precipitation Both radionuclides were measured, from March 2011 to December 2013, in samples of air at ground level, every fifteen days, and rainfall in all the rainy events that occurred at IPEN (Fig. 18). IPEN campus (23°32'S - 46°37'W at 760 m above sea level) is located in the city of São Paulo, state of São Paulo, Brazil. The concentrations of ^{7}Be were measured, by non-destructive gamma-ray spectrometry using a coaxial Be-layer HPGe detector with 25% relative efficiency, live counting time varying from 150,000 s to 300,000 s. ^{210}Pb concentration was measured by beta gross counting in a low background gas flow proportional detector, after radiochemistry procedure. The results obtained, for both radionuclides, were correlated to seasons, rainfall, temperature and sunspot number. For ^{7}Be the higher values obtained were in spring and summer time presenting good correlations with the amount of precipitation and sunspot number and a clearly seasonal variations was observed. For ^{210}Pb the highest concentrations were obtained in the months of winter and the lowest in summer presenting a strong correlation with the amount of precipitation and hence

showing seasonal trends.

Figure 18. A) Air sampler B) Rain gauge.

Open source code for gamma-ray spectrometry

Radioactivity quantification of gamma-ray emitter radionuclides in samples measured by HPGe gamma spectrometers relies on the analysis of the photopeaks present in the spectra, especially on the accurate determination of their net areas. A methodology and an algorithm description for the peak search and analysis in order to obtain the relevant peaks parameters and their uncertainties were developed. The procedure is performed on a three-step approach: a) a preliminary search is done by using the second-difference method; b) experimental peaks widths are assessed in order to obtain a width vs. channel relationship and to define regions with single or overlapping peaks; c) a non-linear fit is applied to each region of the spectrum with candidate peaks.

The computational implementation is released entirely in open-source license. The code was developed in C++ language and the interface was developed with Qt GUI software toolkit (Fig. 19). GNU scientific library, GSL, was employed to perform linear and non-linear fitting procedures as needed. Previously acquired spectra were analyzed with the presented methodology and with the commercial software package WinnerGamma. Results obtained are consistent with those obtained with the latter package, suggesting that the developed code could be safely used in general-purpose gamma-ray spectrometry.
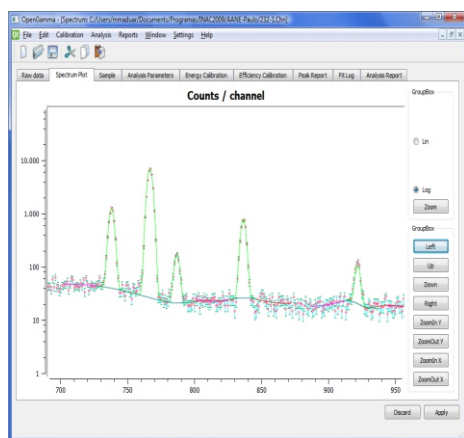

Figure 19. Snapshot of the gamma-ray spectra analysis code.

Natural gamma-ray emitters in clays used for therapeutic purposes

The use of minerals for therapeutic purposes is an ancient practice, especially clay minerals topically employed in the therapy of skin disorders and rheumatic processes. In Brazil, an example of such application is the use of a clay-based mineral extracted from a deposit in Peruíbe, a resort town in the country's southeast. Such mineral has been used both in raw form, after a washing process or as an active component of cosmetics.

A comprehensive characterization of samples from this deposit is underway. Results of the determination of natural radionuclides in samples of this clay and its derived preparations, along with the assessment of the effective dose due to beta and gamma radiation on the skin, showed that the dose increment arising from this practice is of the order of 0.8 µSv for a whole therapeutic treatment.

Temporal evolution of natural radionuclides distributions in the Bransfield Strait, Antarctica Peninsula

Research on the distribution of natural radionuclides in Antartica is rare and thus, there is a great interest in knowing their occurrence and factors related to its mobilization, transference and accumulation in this extremely fragile environment. This study evaluated the distribution of natural radionuclides ^{238}U, ^{234}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po in the Bransfield Strait during 2 samplings carried out in the 2011 Austral Summer (OPERANTAR XXIX and XXX) (Fig. 20). ^{234}Th (24.1 days) is a particle-reactive radionuclide produced continuously in seawater by decay of its soluble precursor, conservative with salinity, ^{238}U (4.5 10^9 years). Since ^{234}Th presents relatively short half-life, it is used to quantify processes that occur in temporal scale varying from days to weeks. The disequilibrium ^{234}Th / ^{238}U in the surface ocean has been applied to estimate carbon fluxes exported via sinking material. The flux of biologically productive out of the euphotic zone in the Southern Ocean has special attention due to its importance in the control of CO_2 atmospheric concentrations. The radionuclides ^{210}Pb (22.3 years) and ^{210}Po (138 days) are also particle reactive. The disequilibrium ^{210}Po / ^{210}Pb has been used to estimate fluxes of particles exported in the ocean in time scale of weeks. The long-lived Ra isotopes, ^{226}Ra (1,600 years) and ^{228}Ra (5.75 years) are soluble in seawater, presenting unique properties that make them excellent tracers of water masses. ^{234}Th activity concentrations varied from 1.3 to 3.7 dpm L^{-1}. Activity ratios of ^{234}Th / ^{238}U ranging from 0.6 to 1.6 were observed in OPERANTAR XXX. ^{210}Po activities in surface waters of Bransfield Strait varied from 0.3 to 6.5 dpm L^{-1}. In OPERANTAR XXIX expedition, activity concentrations of ^{226}Ra ranged from 0.1 to 2.8 dpm 100 L^{-1}, while ^{228}Ra varied from 0.3 to 2.2 dpm 100L^{-1}. Activity ratios of ^{210}Pb / ^{226}Ra in surface waters during OPERANTAR XXX ranged from 20.6 to 103. ^{228}Ra presented a conservative behavior in the region. However, the ^{226}Ra distribution was influenced by volcanic fumes, discharge of groundwater and upwelling water sources.

Figure 20. Research Vessel Ary Rongel (Brazilian Navy) during water sampling on Aldmirant Bay (OPERANTAR XXX).

Determination of long-lived natural Ra isotopes, ^{226}Ra and ^{228}Ra, in mineral and spring waters from Caxambu (MG) and Águas de Lindóia (SP) Spas

The aim of this work was to study the long-lived Ra isotopes, ^{226}Ra and ^{228}Ra, natural distribution in mineral and spring waters from Caxambu (MG) and Águas de Lindóia (SP) waterparks (Fig. 21). In Caxambu mineral water, it was observed ^{228}Ra activity concentrations slightly higher than those of ^{226}Ra. The elevated content of carbonates and bicarbonates of these waters can result in an increased solubility of the both Ra isotopes and may play an important role for the fate of ^{228}Ra and its equilibrium distribution between solid and liquid phases. In Caxambu Thermal Spa, arithmetic mean activities ranged from 83 mBq L^{-1} to 3599 mBq L^{-1} and from 60 mBq L^{-1} to 4481 mBq L^{-1} for ^{226}Ra and ^{228}Ra, respectively. The highest ^{226}Ra activity was found in Venâncio Spring, while the maximum ^{228}Ra activity value was determined in Ernestina Guedes. ^{228}Ra / ^{226}Ra activity ratios varied from 0.079 (Conde D'Eau and Princesa Isabel Spring) to 4.2 (Mairink II

Spring). In Águas de Lindóia, arithmetic mean activities ranged from 4.8 mBq L^{-1} to 41 mBq L^{-1} and from 30 mBq L^{-1} to 54 mBq L^{-1} for ^{226}Ra and ^{228}Ra, respectively. The maximum ^{226}Ra activity concentration was found in bottled mineral water São Jorge, while the higher ^{228}Ra activity concentration was determined in Santa Filomena Spring (public station 2). ^{228}Ra / ^{226}Ra activity ratios varied from 1.2 (bottled mineral water São Jorge) to 9.1 (bottled mineral water Jatobá 1). This work also performed the dose assessment due to the ingestion of ^{226}Ra and ^{228}Ra in Caxambu and Águas de Lindóia mineral and spring waters. The committed effective doses were estimated by using a conservative dosimetric model and taking into account the results over a lifetime (70 years) following intake of both long-lived Ra isotopes. The results from this radiological evaluation showed that the guidance committed effected dose level of 0.1 mSv y^{-1} recommended by World Health Organization (WHO) was exceeded in all samples studied in Caxambu, except for Viotti Spring. In Águas de Lindóia and Lindóia, the highest committed effective doses estimated were 8.4 10^{-3} mSv y^{-1} for ^{226}Ra (Santa Filomena spring - station 2). Both values were below the limit recommended by WHO. The maximum committed effective doses per year obtained in this work were 7.4 10^{-1} mSv y^{-1} for ^{226}Ra (Venâncio Spring) and 2.2 mSv y^{-1} for ^{228}Ra (Ernestina Guedes Spring). Considering the case of ^{226}Ra intake via mineral water, the dose obtained represents less than 31% of the average effective dose attributable annually from natural background radiation. However, in the case of ^{228}Ra the annual committed effective dose limit recommended by ICRP (considering all sources of radiation exposure for the world population) was exceeded not only in Ernestina Guedes Spring, but also in Beleza Spring.

Figure 21. Mineral spring analyzed in Caxambú waterpark.

Distribution of natural Ra isotopes in Paranaguá Estuarine Complex

Four Ra isotopes occur naturally in the marine environment: ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra. The determination of these isotopes in the field of oceanography is an important tool to demonstrate the coast apart surface and groundwater, which in turn subsidize information to determinations of mass balances and biogeochemical fluxes to the ocean. In this study, the distribution of activity concentrations of Ra isotopes in Paranaguá Estuarine Complex (CEP) was investigated. Surface water samples and sediment samples were collected in the estuary, as well as surface water and sediments in some major rivers that flow into the study area, and a sample of groundwater from an artesian well located around the estuary. The higher activities of the isotopes analyzed in surface water were observed in the inner part of the estuary, where there is influence of river inflow and presence of port activities. In sediment samples, activity concentrations of Ra isotopes were lower in the mouth of the east-west axis and elevated in the outermost part of the north-south axis. Apparent ages calculated indicate that the surface water in the east-west axis takes about 8 days to travel a distance of 47 km, while in the north-south axis a distance of 21 km is achieved in 2 days.

Metrology in diagnostic radiology

In order to achieve the X radiation calibration process optimization, a software was developed providing the best calibration results with lowest external interferences (from the operator, for instance) to decrease the possibilities of error occurrences. A semi-automated LabVIEW-based calibration software has been developed at LCI and it has been subjected to constant testing and improvements so far. The software is divided into two basic modules: one is responsible for calibration of the monitor chamber with a reference standard dosimeter, while the other is used to perform instrument calibrations using the monitor chamber as reference.

The use of a Product Kerma-Area (PKA) meter is essential to evaluate the radiation dose in radiological procedures and it is a good indicator to make sure that the dose limit to the patient's skin does not exceed the limits. In this work, a methodology was developed for calibration in situ of PKA meters using a Patient Dose Calibrator (PDC) as reference. The tests were performed with portable PKA meters and in interventional radiology equipment that has a fixed PKA meter. The results were good and the need for calibration of these meters and the importance of in situ calibration with a reference meter were proved. A device was developed and validated to perform the tests established by ABNT NBR IEC 60601-1 standard with the purpose of determine the HVL and filtration with equivalent filtration quality in mmAl, materials that intercept the X-ray beam from their emission to the X-ray image receiving device. The device was validated with respect to the effect of positioning and distribution of the filters in the filter changer device and the influence of purity of the aluminum filter used in the device.

Metrology in radiation protection

The development and implementation of a system was carried out for adequacy of the process of gamma radiation monitors calibration. It is constituted by (i) a pneumatic dispositive to exchange the attenuators and (ii) a positioning table, both activated by a control panel. A Caesa-Gammatron Irradiator System was also implemented, increasing the range of the air kerma rates, due to its higher activity than the current system of gamma radiation in use.

A study of thirty Geiger-Müller detectors, separated into three groups of ten detectors from different manufactures and models, was conducted in relation of energy dependence in standard fields of gamma radiation. The results obtained agree with national and international standard recommendations.

A study of the whole calibration process in the Instrument Calibration Laboratory of IPEN was performed focusing the gamma calibration procedures of the Gamma Laboratory in radioprotection level. The data sheets and all information in relation of that procedure were integrated in a few data sheets and in one data bank. That improved new process reduces mistakes in each step of that process and reduces the time spent in each calibration performed.

In the Instrument Calibration Laboratory a program of tests was developed to be applied to portable survey meters before the calibration in gamma radiation fields. About 20% of the equipments calibrated in gamma radiation fields have problems that appear during the procedures. However, if some tests are applied to the equipments like: check of the battery voltage, display right operation, etc. many troubles in the equipment operation can be found before the calibration procedures, reducing the costs and time spent in the whole calibration process.

Metrology in radiotherapy

The improvement of a quality control program of the clinical dosimeter calibration laboratory was developed using gamma radiation. The behavior of 167 dosimeters was analyzed and in this study 62 of them have been tested with respect to their response repeatability, reproducibility and current leakage. The main problem detected during calibration tests was current leakage, i.e., electronic noise.

The applicability of Fricke xylenol gel (FXG) phantoms, developed at IPEN (produced with national gelatin), in clinical radiation beams three-dimensional dosimetry for the quality control of the radiotherapy and radiosurgery treatments, employing magnetic resonance imaging (MRI) technique was evaluated. The FXG solution studied using optical absorption spectrophotometry (AO) (Fig. 22) and MRI

techniques for clinical electron and photon beams was characterized. Anthropomorphic FXG phantoms (brain and head) were also developed and characterized for clinical photon beams using the MRI technique. Isodose curves were determined and three-dimensional dose reconstructions for FXG phantoms employing three-dimensional conformal radiotherapy (3DCRT) and linear accelerator (LINAC) based radiosurgery were obtained. In addition, the system of location using frameless stereotactic radiosurgery technique for image guided radiotherapy (IGRT) using a FXG brain phantom was validated. The obtained results were compared with data of the planning treatments. Finally, a protocol for the preparation, irradiation and MRI measurement of FXG phantoms for a possible application in quality control in 3DCRT, LINAC based radiosurgery and frameless stereotactic radiosurgery with IGRT was established.
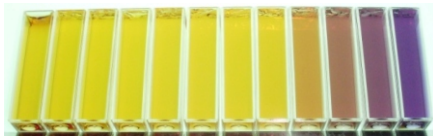
Figure 22. Optical dose responses to electron clinical beams of FXG solution.

The performance of a head phantom filled with FXG solution (Fig. 23) was also evaluated using RMI technique to 3DCRT with multiple radiation fields and clinical photon beams. The obtained results indicates that the target volume can be clearly observed for all MR images of the FXG phantom irradiated with 6 MV clinical photon beam and, in the case of coronal image, the radiation beam projection and the overlap of different radiation fields used can also be observed (Figures 24 and 25). These results encourage additional tests using complex treatment techniques and they indicate the viability of applying the studied phantom for routine quality control measurements and in A3DCRT and IMRT treatment planning.
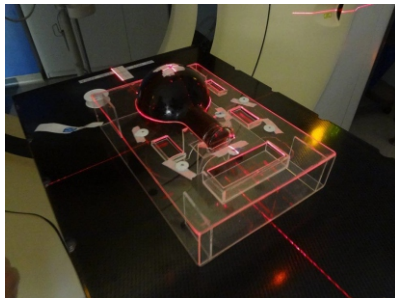

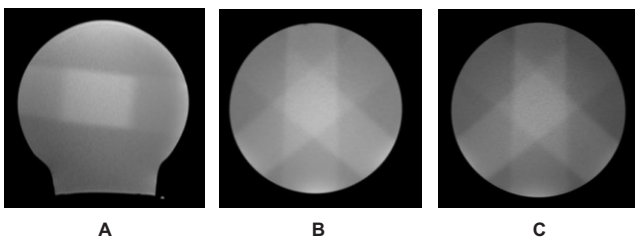Figure 23. PMMA support and head phantom filled with FXG solution.

Figure 24. MR Images of FXG head phantom (3DCRT, 6 MV photons and 20 Gy in the target volume): sagital (A) and axial (B, C) views.
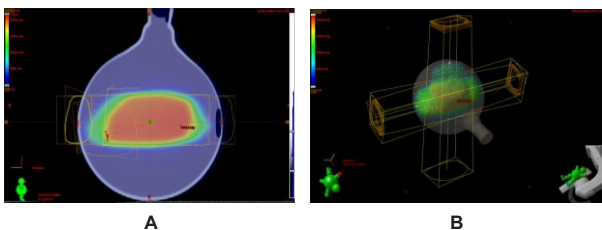

Figure 25. Isodose curves of FXG head phantom obtained from (A) 3DCRT, 6 MV photons and 20 Gy in the target volume and (B) 3D reconstruction of target volume with projection of radiation fields using Eclipse® planning system .

Dosimetric materials

The main objective of this research area is the development of new dosimetric materials with high sensitivity, low cost and easy obtaining. Single crystals of $CaSO_4$:RE (rare earth) were obtained aiming to improve the TL sensitivity of the crystals and investigate its dosimetric properties in order to evaluate the applicability of this material to clinical dosimetry. The results show that $CaSO_4$:Tm presents high sensitivity and reproducibility and may be applied to clinical radiation dosimetry. Other Rare Earth elements, namely, Ce and Eu, were also assessed as $CaSO_4$ activators. Both $CaSO_4$:Ce and $CaSO_4$:Eu present high sensitivity, good reproducibility, linear dose-response in the range of 0.01 to 10 Gy and energy independence to clinical photon beams. Aluminum oxide composes the modern TL and OSL radiation dosimeters. The TL and OSL phenomena are related to chemical elements present in the crystalline structure of the α-Al_2O_3. The purpose of this work was to study the TL and OSL dosimetric properties of white electrofused alumina commercially available as abrasive material to be applied as dosimetric material. Sintered pellets of electrofused alumina were obtained using soda-lime glass, a relatively inexpensive, chemically stable, reasonably hard, and extremely workable material, capable of being re-softened and re-melted numerous times. The fracture micrographs of the EAG pellets were also obtained and presented at Figure 26. The electrofused alumina-glass pellets (EAG) showed significant TL and OSL signals. Results on TL glow curves, OSL decay curves and dosimetric properties such as repeatability, dose response curves and useful dose range were evaluated.
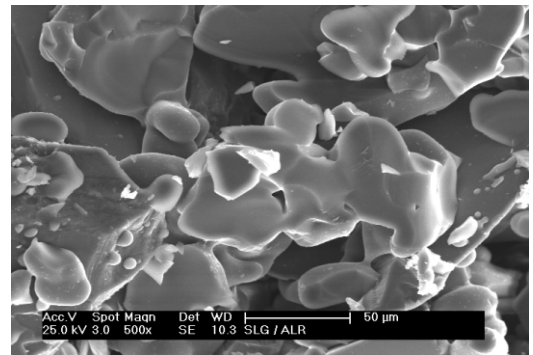

Figure 26. Fracture surface electron microscopy image of the EAG sintered pellet.

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 spectrophotometry evaluation technique can be used comparing the two spectrum wavelengths bands: 457 nm band that corresponds to ferrous ions and 588 nm band that corresponds to ferric ions concentration to evaluate the dosimetric properties of this material.

The performance of the Alanine gel solution developed at IPEN was studied using spectrophotometry technique. The obtained results indicate that signal response dependence for clinical photons (4, 6, 9, 12 and 15 MV) and electrons (4, 6, 8, 12 and 16 MeV) beams of alanine gel dosimeter is better than 3.6 % (1σ) and the energy dependence response is better 3% (1σ) for both beams. These results indicate that the optical response is energy independent in the studied dose range and clinical photons and electrons beams energies.

Internal dosimetry

The workers that carry out activities in areas where unsealed sources are handled are routinely monitored to demonstrate that they are receiving adequate protection from 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 internal 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. The air is conditioned and the temperature maintained at 25ºC. The measurement system is calibrated in energy and efficiency, with sources of ^{152}Eu, ^{241}Am and ^{60}Co with gamma emissions between 59.54 and 1,408.08 keV, positioned within Alderson Research Labs anthropomorphic phantom. The background measurements spectrum are obtained from worker's that was 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. The dose distribution studies, during operational tasks and maintenances in restricted areas of radiopharmaceutical production plant, have been carried out taking the survey data from 2005 to 2011. It was done using a methodology which aims to identify and determine the key variables that impact on the worker's dose. The results were presented for variables individual occupationally exposed, operation variable, task type variable, duration of operation variable and the dose variable. This research have contributed to operational improvements in restricted areas that may result in lower individual doses without causing significant changes in routinely work.

External dosimetry
The intrinsic efficiency of CaSO$_4$:Dy TL dosimeters, developed and commercialized by IPEN to be applied in individual, area and environmental dosimetry, was evaluated for 4, 6, 8, 12 and 16 MeV clinical electron beams at their depth of maximum ionization in polymethyl methacrylate (PMMA), Solid Water (SW) and standard liquid water phantoms aiming to use this material in personal and radiotherapy dosimetry. The reproducibility of the TL response is better than 2.4% and the TL response as a function of the dose, linear between 0.01 and 3.25 Gy. The obtained intrinsic efficiency indicates that CaSO$_4$:Dy dosimeters can be applied to the radiation protection for high energy electron beams generated by linear accelerators. The TL performance of CaSO$_4$:Dy and LiF:Mg,Ti dosimeters to clinical photon beams applied to radiotherapy was also investigated. The TL response of these dosimeters was studied for 6 and 15 MV photons beams using PMMA, liquid water and Solid Water (SW) phantoms, using a Varian linear accelerator Clinac 2100C. The TL dose-response of both dosimeter and three phantoms types present linear behavior on the photon dose range from 0.1 to 5 Gy. The obtained results indicate that the performance of CaSO$_4$:Dy dosimeter is similar to LiF:Mg,Ti dosimeters and this material can be an alternative in clinical electron beams dosimetry.

Aiming to evaluate the dose range that animals submitted to pulmonary radiographic exams are exposed and the relationship with the individual doses of owners and clinical staff, the entrance surface skin dose of dogs of different breed and sizes with cancer and with suspected pulmonary metastasis were evaluated. TL dosimeters of CaSO$_4$:Dy were used to entrance surface skin dose evaluation of 27 dogs. Simulations of dog's irradiation were also carried out using a water phantom. Each procedure was carried out by the acquisition of three chest radiographic images, two latero-lateral and one ventro-dorsal of dogs with suspect of pulmonary metastasis. The obtained results has shown to be extremely important the assessment of doses involved in veterinary diagnostic radiology procedures both to protect the occupationally exposed workers and to optimize the delivered doses to the animals.

Blood irradiation is routinely performed as a process of inhibiting the proliferative capacity of lymphocytes and reduces the risk of transfusion-associated graft-vs-host disease (GVHD). The conventional irradiator used for blood sterilization comprises a ^{137}Cs radiation source and a rotation system. A review of dose distribution at different points inside the irradiator is critical to the quality control of the irradiation process. The Fricke Gel dosimeter allows obtaining phantoms tissue equivalent, which enables three-dimensional - 3D scanning of the dose distribution when measured by Magnetic Resonance Imaging - MRI technique. This work intended to evaluate the 3D dose distribution of a Gamma-cell Elan irradiator employing Fricke Gel dosimeter and Radiochomic Film. To evaluate the dose distribution in the blood bags four distinct regions of the sagittal, coronal and axial plane image were delimited. The average value of the signal intensity and its standard deviation of each region were compared (Fig. 27).
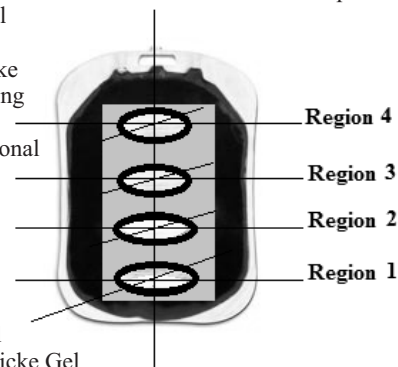

Figure 27. Regions selected in the irradiated blood bag for dose distribution evaluation.

The obtained results indicate that the irradiator Gammacell Elan showed no homogeneity in the dose distribution. The region 4 is out of the lower limit according to the standards required by ANVISA and the Council Europe although the average dose is higher than 25 Gy. The film GafChromic MD-55, despite being built for double-sided irradiation did not show satisfactory results for application in routine dosimetry in Gammacell Elan irradiator.

High doses and accident dosimetry
Ultraviolet (UV) radiation is produced naturally (by the sun light) or artificially (by passing an electric current through a gas or vapor), this radiation type is used in several human activities areas (medicine, industry, etc.). All types of UV (*UVA* 320-400 nm; *UVB* 280-320 nm and *UVC* 100-280 nm) can cause a photochemical effect within the polymer structure. Changes in the characteristics of UV irradiated polymeric films characteristics can be evaluated by the spectrophotometric technique and used to monitor this processes. Polymers, such as *polycarbonate*, *fluoropolymer* and *polymethylmethacrylate* available commercially were analyzed before and after exposed to UV artificial source (HBO 200 W - OSRAM mercury lamp) to evaluate the changes occurring in their properties. These polymeric films are UV sensitive and changes were detected in their spectra; optical measures of absorbance (Fig. 28) can be correlated with the absorbed doses of UV radiation. The UV exposure parameters studied were exposure time (20 minutes - 7 hours); sample-source distance (5-20 cm) and wavelength (280 - 400 nm). The irradiated dosimeters were measured using a Shimadzu UV-2101PC spectrophotometer. The UV radiation exposure leads to the color and brightness instability, and, absorption spectrum changes significantly were observed. Polycarbonates proved to be the most sensitive material.

Figure 28. Equipment Cary5000_Agilent for optical measures of absorbance.

Preliminary evaluation of a neutron calibration laboratory
In the past few years, Brazil and several other countries in Latin America have had experimented a great demand for the calibration of neutron detectors, mainly due to the increase in oil prospection and extraction. The only laboratory for calibration of neutron detectors in Brazil is localized at the Institute for Radioprotection and Dosimetry (IRD/CNEN), Rio de Janeiro, which is part of the IAEA SSDL network. This laboratory is the national standard laboratory in Brazil.

With the increase in the demand for the calibration of neutron detectors, there is a need for another calibration services. In this context, the Calibration Laboratory of IPEN, which already offers calibration services of radiation detectors with standard X, gamma, beta and alpha beams, has recently projected a new calibration laboratory for neutron detectors. The laboratory was completed with a ^{241}Am(Be) source and an adequate detector positioning system. The laboratory was evaluated using Monte Carlo simulation (MCNP5 code), in order to verify the adequateness of the room shielding. The obtained results showed that the shielding is effective, and that this is a low-cost methodology to improve the safety of the workers and evaluate the total staff workload. The frontal view of the laboratory is presented in Figure 29 (A), and the geometry employed during the simulations in Figure 30 (B). All results were within the CNEN regulations. After this study, the neutron beam characterization is in development.
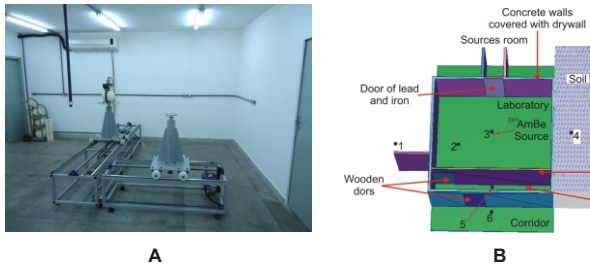

Figure 29. (A) Frontal view of the LCN where it is possible to observe the irradiation system and (B) the geometry employed during the simulations.

Development and establishment of reference systems for radiation dosimetry
During the period 2011-2013, several new dosimeters were developed at the GMR, employing new materials and national components, which proved to be robust and with low cost. Comparing the different dosimeters employed in radiation dosimetry, ionization chambers present the most precise measurements. There are several different ionization chambers, employed for different applications, such as pencil ionization chambers, used in computed tomography (CT) dosimetry, parallel plate ionization chambers used for mammography and linacs dosimetry, and some ionization chambers employed as primary standards, as a Böhm extrapolation ion chamber used for beta dosimetry and cavity ionization chambers, used for the air kerma determination for gamma radiation.

The main dosimeters developed at the LCI were a new set of pencil ionization chambers, with three different sensitive volumes (0.34 cm^3, 1.06 cm^3 and 3.4 cm^3) (Fig. 30(A)) for dosimetry in CT, a new type of parallel plate ionization chamber for mammography (Fig. 30(B)) and one for high energy photon dosimetry (Fig. 30(C)) and a set of graphite ionization chambers developed as a primary standard system for ^{60}Co gamma beams, composed of a parallel plate and a cylindrical ionization chambers (Fig. 30(D)). A primary standard system for beta dosimetry (Böhm extrapolation chamber) was characterized (Fig. 30(E)). A new postal system for the calibration of ^{90}Sr+^{90}Y clinical applicators was also developed (Fig. 30(F)). This new postal system has the advantage to avoid the transport of the clinical applicators to the Calibration Laboratory.
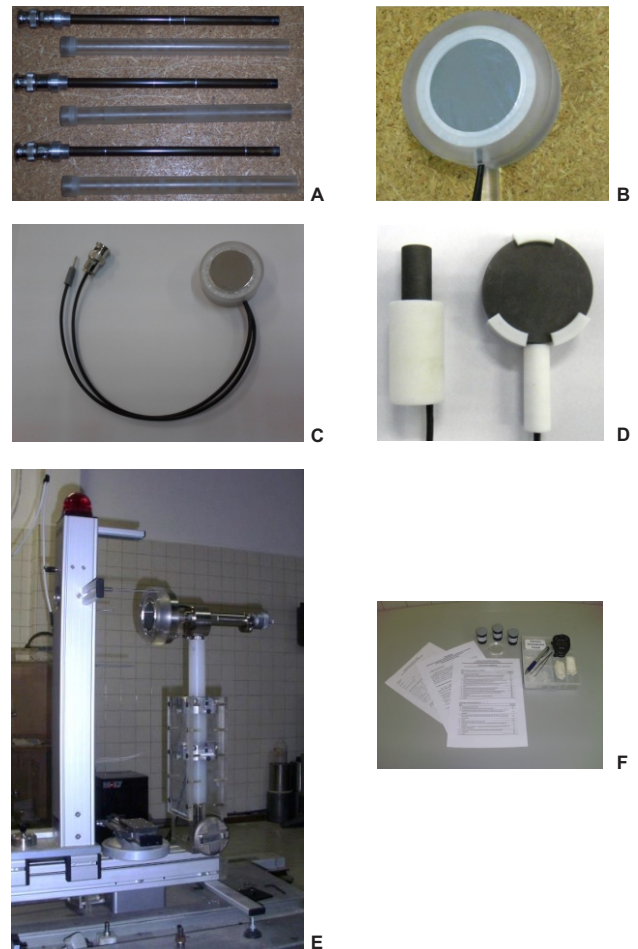

Figure 30. (A) New set of pencil ionization chambers, (B) New prototype of parallel plate ionization chamber for mammography, (C) New prototype of parallel plate ionization chamber for linacs dosimetry, (D) New primary standard system for ^{60}Co gamma beams, (E) Böhm extrapolation chamber as the beta radiation standard, and (F) Postal dosimetric system for the calibration of ^{90}Sr-^{90}Y clinical applicators.

Activities at the Nuclear Metrology Laboratory

Since 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 $4\pi\beta$-γ 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 4π geometry, called 4π(PS)β-γ. The disintegration rate is obtained by the application of the efficiency extrapolation technique. During the period from 2011 to 2013, the following radionuclides have been standardized by this technique: ^{67}Ga, ^{68}Ga, ^{99m}Tc, ^{111}In, ^{123}I and ^{152}Eu.

These systems can run by means of conventional electronics for data acquisition or by applying a recently developed 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.

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 $4\pi\beta$-γ coincidence technique. For this purpose the response functions of beta and gamma detectors

have been calculated by means of the transport code MCNP, version 5, and MCNPX. These response functions are used as input data for another code developed at the LMN, called ESQUEMA. 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.

The LMN has also been involved in the determination of gamma ray emission probabilities per decay of ^{67}Ga, ^{68}Ga and ^{123}I. In addition, the total internal conversion coefficients for the two main transitions of ^{111}In, and the half-life of ^{67}Ga metastable transition have been determined experimentally. The measurements of gamma ray emission probabilities per decay were carried out by means of a REGe spectrometer with a Be window.

The development of radioactive water-equivalent solid sources prepared from an aqueous solution of acrylamide has been continued, by using bisacrylamide and ammonium persulphate for its polymerization. The sources have been prepared in cylindrical geometry with ^{133}Ba radioactive solutions with density similar to water as well as good uniformity.

Another field where the LMN has been involved is neutron measurements. Since 2007 research is being developed on covariance analysis of *ko* Nuclear Activation Analysis (NAA) methodology. During the period from 2011 to 2013, the neutron spectral parameter α and the neutron flux ratio *f* were determined at the 24A irradiation position near the IEA-R1 research reactor core. In addition, parameters *ko* an *Qo* were determined experimentally for reactions ^{64}Zn(n,γ)^{65}Zn and ^{68}Zn(n,γ)^{69}Zn.

An additional research area has been thermal and resonance neutron cross section measurements using the IEA-R1 as the neutron source. This work has been performed in collaboration with the Institute of Physics at the University of São Paulo. During the period from 2011 to 2013, the experimental determination of the cross section and resonance integral for the ^{41}K (n,γ) ^{42}K nuclear reaction has been completed.

Products and services

Determination of radionuclides in environmental samples
Radioactivity is measured on a routine basis, by using alpha and gamma spectrometry, gross alpha and beta counting and neutron activation analysis, in order to determine the contents of artificial and natural radionuclides in environmental samples. The following analyses are available: Determination of gross alpha and beta activities; Determination of natural and artificial gamma emitters; Determination of uranium, thorium and radium isotopes; Determination of ^{210}Pb and ^{222}Rn; Determination of radionuclides in foodstuffs and food commodities imported and exported by Brazil; Determination of ^{90}Sr in foodstuffs and food commodities; Determination of ^{3}H in water.

Calibration of radiation monitors and dosemeters
The Calibration Laboratory has since 1980 been calibrating instruments used in radiation protection and therapy measurements, belonging to hospitals, industries, clinics and other users located in São Paulo and in other parts of Brazil. Since 2000, the calibration service is being offered to users of diagnostic radiology instruments too, with the establishment of standard radiation qualities at this level (Fig. 31). At the radiation protection level there are special set-ups with gamma (^{60}Co and ^{137}Cs), beta (^{90}Sr + ^{90}Y, ^{204}Tl and ^{147}Pm), alpha (^{241}Am, ^{233}U, ^{238}Pu, ^{244}Cm, etc.) and low energy X radiations (60 kV).

Clinical dosemeters (radiotherapy level) can be calibrated, using gamma (^{60}Co) or low energy X radiations. As 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. For 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.

The types of instruments that were calibrated are: several kinds of ionization chambers, pen dosemeters, survey meters (including superficial contamination detectors), alarm dosemeters, activimeters, clinical dosemeters and others. Besides this service, samples including thermoluminescent dosimeters, alanina and others, using beta, gamma and X radiation were irradiated.

Figure 31. General view of the gamma radiation calibration room.

High dose dosimetry
The High Dose Dosimetry Laboratory of IPEN developed a dosimetric system based on alanina/ESR (Fig. 32) that presents good characteristics for use in gamma fields such as: wide dose range from 10 to 10^5 Gy, low fading, low uncertainty (<3%), no dose rate dependence and non-destructive ESR signal readout. 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. The dosimetric system was validated by IDAS program from IAEA and is available to high doses measurements.
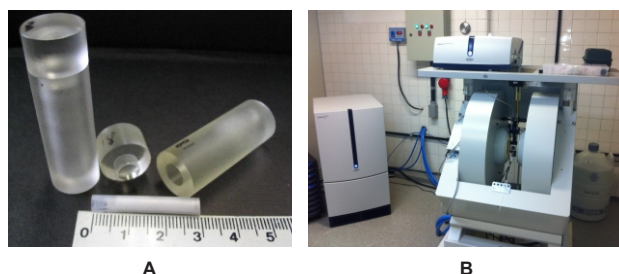

Figure 32. Alanine/EPR dosimetric system: (A) alanine encapsulated in polyethylene tube and build-up cap in polymethylmethacrylate; (B) Bruker ESR spectrometer (X-band).

Dosimetric pellets of CaSO$_4$:Dy
The Dosimetric Materials Laboratory developed and patented the CaSO$_4$:Dy crystals growth system and the method to produce the Teflon® sintered pellets. The CaSO$_4$:Dy crystals are growth in the sealed system and they are cold pressed with the binding material to making the 6 mm diameter pellets (Fig. 33). The CaSO$_4$: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 to the clinical dosimetry. They are utilized to solid state dosimetry research too. The pellets of several materials such as quartz, topaz and jade could be also produced by means of the same referred method. The requests of CaSO$_4$:Dy crystals and pellets from many institutions have been attended by the laboratory.

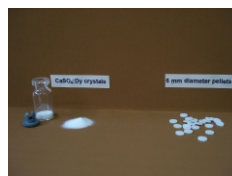Figure 33. CaSO$_4$:Dy crystals and sintered pellets.

Routine external dosimetry

The external dosimetry applies the thermoluminescent (TL) technique and $CaSO_4$:Dy based dosimeters completely developed at IPEN to carry out individual external exposure, area and environmental monitoring. The individual monitoring service for external exposure is accredited by CNEN (Brazilian Nuclear Energy Commission) regulatory committee, CASEC (Essays and Calibration Services Evaluation Committee) and 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, which are not under the scope of any regulatory office, are also performed in different society sectors, such as research institutes, universities and private foundations and companies. Aiming to improve individual external exposure, area and environmental monitoring services and give society a return of the budges invested in them, papers based on the results obtained by the services have been present in the most relevant scientific reunions over the triennial period of 2011-2013.

Internal dosimetry

During the period from January 2011 to December 2013, approximately 2,700 direct measurements of both whole-body and thyroid contents had been carried 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 participated in an AIEA international intercomparison for in vivo thyroid measurements and the obtained results were considered satisfactory according to the ANSI criteria.

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Honor Mention and Awards

The study developed in the LEER: "Determination of Inorganic Elements in Blood of Golden Retriever Muscular Dystrophy Dogs using Neutron Activation Analysis" was awarded with financial support from Women in Physics Travel Grant Award, IUPAP (International Union of Pure and Applied Physics) to be presented in the 5 International Congress of the FESTEM of the European Societies for Trace Elements and Minerals, Avignon, France, 2013.

Tatiane da Silva Nascimento - melhor pôster pelo trabalho: "Standardization of Y-90 in Liquid Scintillation Counting System by Means of the Ciemat/Nist Method" no XXXVI Reunião de Trabalho sobre Física Nuclear no Brasil, 2013.

The study "Concentrations of Ions in Blood of Amateur and Elite Runners using NAA" was awarded with the Young Scientis, Bangkok, Thailand, 2012.

Two studies developed in the LEER: "Concentration of Ca in Blood of Amateur Runners using NAA" and "The Half Life of Te131g,m" were awarded in the XXXV Reunião de Trabalho sobre Física Nuclear no Brasil, 2012.