Environmental Science and Technology

Introduction

The Environmental Science and Technology Program was structured based on the continuous growth of environmental activities on areas related to nuclear programs at IPEN. The program comprehends five main areas:

- Environmental analysis
- Chemical Technology
- Polymer technology nucleus
- Chemical and Isotope Characterization
- Analytical Chemistry for the Nuclear Fuel Cycle Samples

Recent activities are highlighted bellow:

- Development and use of modern analytical technologies for the characterization of pollutants and contaminated areas;
- Development of chemical fingerprint methodologies for the identification of materials for forensic purposes (cannabis origin, gunshot residues, cocaine origin and nuclear signatures);
- Studies of trace gases as part of LBA project (Large Scale Biosphere-Atmosphere Experiment) in the atmosphere of Amazonian region and greenhouse gases of urban areas;
- Cooperation with SABESP (Water and Sewage Company) and CETESB (State Environment Agency) in programs for the development of public policies, such as the critical revision to the guidelines of drinking water standards.
- Studies and development of recycling technologies reuse of materials, waste storage and decontamination;
- Studies and developments in biodegradable polymers, polyolefins and advanced methods for polymer and rubber destruction etc.;
- Studies on the production of Hydrogen from renewable sources for fuel cell purposes.
- Electrochemical techniques for the dissolution of metals and treatment of industrial and radioactive wastes
- Clean Technologies
- Synthesis and development of magnetic nanoparticles and participation on the RENAME (network on nanotechnology research) project.

These achievements were conducted with support from national and international funding agencies - FAPESP, CNPq, FINEP, CAPES, IAEA - as well as cooperation with partners and clients, such as SABESP, CETESB, Braskem, Biolab Sanus and Petrobras.

Environmental chemistry and water science

The global importance and vulnerability of our water supply, both in terms of quantity and quality has been well documented and, although water is a renewable resource, it is also a finite resource. Water, vital to both human health and ecosystem sustainability, is under increasing pressure as urbanization and agricultural intensification increase and, as such, it is essential that we improve our understanding of the types, and complexity and potential impacts of chemicals that are increasingly being released into the environment.

It is recognized that the pollution influences living organisms, humans included, both directly (by affecting their health) and indirectly (via contamination of food and abiotic compartments). Heavy metals and organic compounds, such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), volatile organic compounds (VOCs) and pesticides, have been the center of attention for a long time.

Environmental and Analytical Chemistry focus activities in these areas by bringing together academic staff with a common research interest in understanding a variety of aspects of natural and polluted present-day environments and ancient environments. Since these are complex systems, studies of both organic and inorganic species of natural and anthropogenic origin rely heavily on the use and development of modern analytical methods. Scientific Cooperation programs supporting by CNPq and FAPESP in partnership with Environmental Agency State (CETESB) and SABESP were developed:

Identification of the influence of sludge discharges from water treatment plants
The growing concern of environmental surveillance of the quality of hydric resources guides the development of research on management of residues generated in water treatment plants (WTP). Approximately 8.000 WTPs in Brazil operate without a treatment program of the residues, disposing these effluents in the environment. This work evaluated WTP discharges into watercourses by collecting superficial waters, sediments and benthic samples at the town of Registro, São Paulo State, Brazil. Even though superficial waters and benthic samples showed no further contamination, sediment analysis pointed out that aluminum deposits detected near sludge discharges may represent a potential risk to the environment.

Assessment of agriculture impact on environmental preservation areas of the Ribeira de Iguape River, São Paulo
In order to ascertain the impact of agricultural activities on water quality of the Ribeira de Iguape River Basin in the state of São Paulo, surface water areas for catchment and drinking water have been characterized. The sampling period covered March/2002 - February/2003 and January/2004 at 10 different catchment points. SPE-LC-UV/Vis was used to monitor various pesticide classes such as carbamates, triazines and nitro anilines. The results revealed that water quality is associated with seasonal variation. Of 152 samples analyzed, only 24% showed the presence of pesticides, particularly during the wet season. High variability in pH, turbidity and color were observed.

Environmental water quality in Pedroso Reservoir (Billings's watershed)
The present work aimed to evaluate the environmental water quality in Pedroso Reservoir (Billings watershed) situated in Santo André - Sao Paulo State. Sixty four water samples (41 drinking water samples and 23 surface water samples) Ag, Al, As, B, Ba, Be,Cd, Co, Cr, Ca, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, V, Zn, NO3-, SO42-, PO43-, F- and Cl- were evaluated. The sampling period covered June 2005 to December 2006. For the drinking water samples all elements analyzed were detected in concentrations below the limit established by the Brazilian Drinking Water Standard - Portaria N° 518/MS/04. For the surface water samples of all elements analyzed, only to Ag, Al, Fe and P were detected in concentrations, above the limit established by CONAMA 527/05.

Evaluation of water quality using physicochemical parameters and a modified water quality index
The Brazilian Federal Designation Nº 5440/05 establishes definitions and procedures for water quality control of supplying systems and defines mechanisms and instruments for transmitting information about human consumption water quality to general consumer. The current guidelines for drinking-water standards (Portaria Nº 518/04), in article 9º of section IV: charge the responsible of the operation of the water system to supply all the consumers' information about the quality of the distributed water, in the terms of the Code of Defense of the Consumer. A Water Quality Index (WQI) is a numeric expression used to evaluate the quality of a given water body and to be easily understood by managers. Therefore, the purpose of this paper is to identify, in some of the several water quality indices described in the literature, a dynamic index of water quality for supplying, which will be used as a tool to simplify the report of the water quality data.

Contribution of Taquaruçu Grande Basin to Luis Eduardo Magalhães Reservoir - TO
Many reservoirs have been found to receive significant pollutant loading from their upstream watersheds. Wide usage of agricultural pesticides and fertilizers, inappropriate landuse management

high intensity rainfall and steep-slope farming are major factors that contribute to the degradation of reservoir water quality. The sub-basin of Ribeirão Taquaruçu Grande located at Palmas city, has preserved sources, contains agricultural areas and by the end of their course receives influence the process of urbanization. This project aims to assess the physical, chemical and biological contribution of the Ribeirão Taquaruçu basin through the analysis of the limnological variables, metals and trace elements determination, and the identification of phytoplankton community.

Soil contamination

The metal partition coefficient (Kp) is ratio between the concentration of metal bond to the soil and metal concentration in soil solution. The Kp may vary by several orders of magnitude because of the different soil characteristics. For human health risk assessment it is important to determine the specific soil metal Kp. One study the metal Kp of soil samples were determined for the coal-fired Figueira (Figueira county, north of Parana State) power plant surrounding soil. Another study the Kp of benzo(a)pyrene was determined in tropical soil. Radionuclides of the natural series, such as ^{238}U, ^{228}Ra, ^{226}Ra, ^{210}Pb and ^{40}K, in raw material samples of coal used by the main power plants in Brazil (RS; SC; PR) were evaluated. The results showed that the uranium concentration in coal from (PR) was at least three times higher than concentration found in other coal samples in Brazil, RS and SC. The natural radionuclide contents in pulverized coal, furnace bottom ash and fly ash samples in Figueira coal-fired power plant were evaluated. High enrichment factor was observed for the last stage filter fly ash. The concentration of the uranium series found in the ashes is close to the limit adopted by the Brazilian guideline. Therefore, it is advisable to evaluate the environmental impact of the installation. Soil columns with batteries placed at the top were leaching with an acid-rainwater solution during one year. Zn and Mn showed a high tendency to be retained at the upper layer of the soil column.

Autochthnous species of invertebrates in aquatic toxicity test

Daphnia laevis, Ceriodaphnia silvestrii and Chironomus xanthus are among the autochthonous species whose biology has been studied and which have been used as test-organisms. However, routine actions are required to be introduced in assay labs, such as sensitivity evaluations and establishment of control-charts. Based on Daphnia laevis, Ceriodaphnia silvestrii and Chironomus xanthus continuos cultures in laboratories involving biology studies for methods standardization, this research shows species sensitivity based on tests with reference substances, a fundamental requirement for them to be considered eligible for toxicity evaluations within the specific sensitivity range for a reference substance. This requirement meets what is established in quality systems for assay laboratories, according to ABNT ISO/IEC 17025 (ABNT, 2001) and Good Laboratory Practices (OECD, 1998). Standardized cultivation procedures have been developed for Daphnia laevis, Ceriodaphnia silvestrii and Chironomus xanthus species, according to ABNT ISO/IEC 17025 (ABNT, 2001) and Good Laboratory Practices (OECD,1998), from biology studies of species based on existing literature and guidelines by ABNT (1993), CETESB (1991), ASTM (2000) and EPA (2002, 2004).

Occupational and environmental exposure assessment levels to emerging pollutants, metals, endocrine disruption and organic compounds

Pharmaceuticals, personal care products, and potential endocrine disrupters are part of a large and diverse group of organic compounds, labelled as emerging contaminants, which have received much attention in recent years. Many of these contaminants enter the environment by way of wastewater systems and their fate and the consequent environmental risks are only now being considered in detail through ecotoxicological studies. This is partly due to the improved sensitivity of analytical techniques but also because reuse of wastewater is becoming more common worldwide, driven by pressure on other sources of fresh water.

For endocrine disrupting chemicals in the environment, concerns arise primarily from the effects that may be induced in wildlife. A well studied example is estrogenic chemicals in the aquatic environment and their effects on fish. Directly measuring effects, in fieldwork studies, is an expensive and time-consuming approach that is fraught with many difficulties, ranging from study design right through to data analysis and interpretation. Several chemical substances suspected of endocrine disruption are currently being used in industrial and agricultural activities in Brazil. Virtually nothing is known about the related health effects, highlighting the need to implement a national program to evaluate such impacts. Scientific Cooperation programs supporting

by CNPq and FAPESP in partnership with SABESP were developed focus:

Determination of endocrine disrupters in public water supply on Paraiba do Sul River region, Brazil
This research line focuses on investigate the presence of some endocrine disrupters agents (EDs) and pharmaceuticals and personal care products (PPCPs) which may affect the quality of public water supply on Paraiba of the South River Basin. The study has been developed according to: (1) occurrence of EDs and PPCPS in surface and drinking waters; (2) optimization of the analytical procedures proposed to quantify a specific class of chemical contaminants; and (3) determination of EDs and PPCPs in surface and potable waters and effluents of a municipal sewage treatment plant (STP).

Geochemistry distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in sediments of Park Pedroso Reservoir, Santo Andre, Brazil
An environmental diagnosis identifying the presence of PAHs in sediment and surface water has been carried out. The methodology involves the identification of HPA's and the combination of other physical and chemical parameters.

Selenium in ground water of the Northwest Area of the State of São Paulo
In some districts of the Northwest Area of the State of São Paulo the public provisioning is made mainly by reception of underground water of the Guarani aquifers, through tubular wells. The monitoring of Se was realized in four wells of the Northwest Area of the State of São Paulo, to follow the variation of the concentration of that element for a hydrologic cycle.

Identification of pesticides on sludge discharges from water treatment plants
Sludge from water treatment plant (WTP) is analyzed in this study. Many compounds can be concentrated in this material as it is an end-residue generated in this purification process. A WTP in the Vale do Ribeira, SP, region of banana crops, was chosen. Using liquid chromatography, several pesticides are determined after liquid-liquid extraction. Methodology validation was performed.

Adsorbent studies based on zeolites and ceramics applied to environmental monitoring and wastewater treatment

The development of adsorbent material to monitoring the water quality by the measurements of physical, chemical and biological aspects for water quality evaluation of the urban stream and the development of an adsorbent material with remain fixed for an immersion period in polluted urban waters, when submitted to a series of analyzing procedures, presents toxic compound content equivalents to the waters existing ones with the information about the presence of toxic metals and organic composites with also the measurement of water eutrophic condition of rivers, streams, lakes and reservoirs with dense pollution as the urban streams Pirajuçara, Aricanduva, Tamanduateí and Sapateiro located in the Metropolitan area of Sao Paulo.

Application of zeolite materials for metals removal from aqueous solutions and soil

The combustion of high ash content coals promotes a serious environmental problem in southern Brazil. It is in the south, in the States of Rio Grande do Sul, Santa Catarina and Paraná, that the coal mines coal-fired power plants are located. The States of Rio Grande do Sul and Santa Catarina show areas that are already environmentally degraded with the resulting contamination of both surface and ground waters.

Brazilian coals are characterized, among others things, for very high ash content ranging between 45 and 60%. This represents 4.0 x 10^6 tons/year of ashes produced in 2005. Most of these ashes are deposited randomly in landfills and has contributed to the deterioration of the surrounding environment. Since just 30% of that total is commercialized for the production of building materials (bricks, blocks, cement), it is necessary to search for new alternative uses for this abundant residues and give a high added-value to coal ash.

The Brazilian coal ashes consist, basically, of aluminosilicate with high silicon and aluminium oxide contents. Depending on its origin, the iron oxide contents can vary over a wide range. Since coal ashes are composed of a large amount of silica e alumina and also due to a low ratio SiO_2/Al_2O_3, they can be converted into zeolite by alkaline hydrothermal activation. Various types of zeolites can be obtained by changing the source of ashes or activation parameters.

The zeolitic material obtained contains a non-converted part of coal ash and the zeolite content in the conversion product varies as a function of the coal ash properties and the conditions selected. Zeolites have uniform pore sizes and large surface area that make them very useful materials for a wide range of applications such as ion exchange, molecular sieves, adsorbents and catalysts. The coal ash samples were obtained from a coal-fired power plant located in Figueira county, in the North of Paraná State, Brazil.

The utilization of synthetic zeolites as adsorbent for the treatment of the electroplating effluents, immobilization of heavy metals in soil, decontamination of actual acid mine drainage and removal of dyes from aqueous solution has been

evaluated. The results obtained in the project showed a great reduction in the pollutant concentration in treated waters and soil and demonstrated the high potential of the zeolites synthesized from Brazilian coal ashes as low-cost adsorbent material.

Green House studies in Amazon Basin and ozone precursors in Sao Paulo cityvertical profiles of carbon dioxide and other trace gas species over the Amazon Basin using small aircraft

This project is part of the LBA project (Large-Scale Biosphere-Atmosphere Experiment in Amazônia). Since December 2000 vertical profiles of CO_2, CH_4, CO, H_2, N_2O and SF_6 have been measured above central Amazônia (Over Tapajós National Forest, a primary forest in Para State and over Cuieiras Biological Reserve, a primary forest in Amazonas State) and the Brazilian coast (Fortaleza over the ocean).

Samples are collected aboard light aircraft between the surface and either 4 km (Tapajós National Forest) or 5 km (Fortaleza) using the NOAA/CMDL semi-automatic portable flask package (PFP). The PFP consists of 17 glass flasks with 750 mL volume that are pressurized to about 3 bar to enable measurements of all the gases mentioned above. Until the end of 2003 the PFP's were sent from Boulder, Colorado to Brazil, where they are filled, and then sent back to Colorado for analysis. The strategy was changed to increase the frequency of measurements, which was severely hampered due to problems inherent in shipping samples between Brazil and the United States.

In order to accomplish this, a replica of the NOAA/CMDL trace gas analysis system was constructed and installed in IPEN/LQA starting in May 2004. The equipment set up in Brazil is capable of high-accuracy and high-precision measurements of CO_2, CH_4, CO, N_2O and SF_6 in the flask and PFP samples. All measurements are calibrated to internationally accepted scales. The fluxes determination using atmospheric measurements from aircraft profiles over Floresta Nacional do Tapajos (SAN - 02º51'S; 54º57'W, over tower 67km) and Reserva Biologica de Cuieiras (MAN 02º36'S, 60º12'W, over tower K34). SAN profiles started December 2000 and MAN started December 2004, both running until 2007. Samples are collected aboard light aircraft between the surface and 4 km using the NOAA/CMDL semi-automatic portable flask package (PFP), with 17 flasks samples. Using a column integration technique of CO_2 profile measured subtracted by CO_2 background, it was determinates the flux for each flight. The CO_2 background was determinates using a co-measured SF6 as a transport tracer. Two NOAA/CMDL background sites, Ascension Island (ASC) located in the Atlantic Ocean (8'S, 14'W) and Barbados (RPB) located in the Atlantic Ocean (12'S, 59'W) were used to calculate the fractions of air arriving at the sites studied. Back trajectories from HYSPLIT model were calculated for every profile each 500m height to determinate the time of the air mass between coast and the sites. Arembepe, Bahia Background station was start CO_2, CH_4, CO, H_2, N_2O and SF_6 measures since October 2006 in cooperation with INMET, NOAA and WMO. This is the first Brazilian station in global net work. This project opens the possibility to start others stations in others place in Brazil.

Ozone Precursors in São Paulo City
The pollution in the urban area of Sao Paulo city is mainly related with vehicular emissions and secondary with industrial emissions. The metropolitan area of Sao Paulo suffers from heavy air pollution, for both gases and aerosol particles. The vehicular emissions are responsible about 98% of CO, 97% of HC, 96% of NOX, 50% of aerosols, and 55% of SOX. Volatile organic compounds speciation and the contribution to the ozone formation have been investigated. The research has been carried out by means of an extensive sampling campaign between March 2005 to March 2006, using traditional methods of sampling (canisters) and analysis (CG/MS/FID) for VOCs. It was made 2 sampling campaigns to following trace gases measurements: CO, NOx and O_3 in winter and summer period. Meteorological data was collected to understand the transport process of these compounds. OZIPR mathematical model was used to determinate the principals VOCS in ozone formation. Financing by NASA, NOAA and CNPq.

X-Ray Fluorescence Techniques applied to environmental, geological and biological studies. Chemical characterization of the nuclear and non-nuclear materials

X-Ray Fluorescence Laboratory (LFX) (Fig. 1) has worked in geological, environmental and biological studies establishing new analytical methodologies for different samples such as soils, sediments, air filters, used lubrificating oils, domestic dust, metal

monitoring plants, Brazilian medicinal plants, diets, organic fluids like tissue, serum and whole bloods. The R&D activities have been supported by the IAEA, CNPq and FAPESP organisms. The main projects, carried out and ongoing, are listed bellow:

Food
The inorganic elements (Ca, Cl, Cu, Fe, K, Mg, Mn, Na, P, Se and Zn) in typical industrial Brazilian workers were determined for comparison with Neutron Activation Analysis data and participation in a network using analytical techniques, such as NAA, XRF, AAS, ICP-OES and HPLC, for certification of national in-house bovine liver reference material.

Environmental diagnostic
The inorganic elements (Na, Mg, Al, Si, Ca, Ti, Fe, P, S, V, Cr, Mn, Ni, Cu, Zn, As, Rb, Sr, Zr, Ba and Pb) in soil, ashes, coals and grasses were determined to study thermoelectric powder plant pollution.

Brazilian medicinal plants
The quantitative inorganic profile for Brazilian medicinal plants (Anadenathera macrocarpa, Schinus molle, Hymenaea courbaril, Cariniana legalis, solidago microglossa and Stryphnodendron barbatiman) were established by Na, Mg, P, S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, Rb and Sr determination.

Indoor pollution
The inorganic elements (Na, Mg. Al, Si, P, K, Ca, Ti, Cr, Fe, Ni, Cu. Zn, Se and Pb) and organic compounds (phthalate esters) in domestic dust in the metropolitan area of São Paulo city has been determined for urban and indoor pollution study.

Residue recovery
Reuse and recovery for used lubrificating oils using ionizing radiation (60-Co source) has been studied. The removal degree was determined for Mg, Al, Si, P, S, Cl, Ca, Cr, Mn, Fe, Ni, Zn and Pb elements using different absorbed doses. The organic compounds degradation, related with different absorbed doses, has also been studied.

Metrology
Uncertainty of measurements for P-10 plant steel and 302 and 304 series stainless steel samples analyzed by WDXRF and OES-spark techniques has been calculated.

Clinical studies
The analytical method for K, P, Cl, Na, Fe and Ca determination in serum and whole blood, has been developed for comparison with Neutron Activation Analysis data, aiming the Brazilian reference value determination.

Hazardous substances
Analytical method for Cr, Br, Cd, Hg and Pb determination has been developed, to meet general requirements of the RoHS (Restriction of the use of Hazardous Substances in electrical and electronic equipments), WEEE (Waste Electrical and Electronic Equipment) and ELV (End of Life Vehicles) directive.

Quality assurance
In the period, the LFX implanted de ISO IEC 17025, version 2005. The several topics of the Quality Manual were modified and adapted according to new requirements. The analytical methods validation and robustness were determined for 302 and 304 series stainless steels, sediments and igneous rocks chemical assays, calculating the uncertainty of measurements and the accuracy, using statistical tools. The annual internal audit by SGI/IPEN was carried out. The Laboratory participated in national and international inter-laboratory programs (steel and alloy samples: promoted by IPT/Brazilian Metrology on Chemistry Program, IPT/PBMQ ; bauxite by SGS-GEOSOL, MG, Brazil ; synthetic aqueous solution by Instituto Nacional de Tecnología Industrial, INTI, Argentina and biological and herbal samples by the International Atomic Energy Agency, IAEA, Austria. The Laboratory participated in the RILCA program (Red Iberoamericano de Laboratorios de Calidad del Agua) supported by CYTED (Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo). (http://www.cepis.oms.org/bvsala/E/taller-relac/RILCA.ppt). In 2007, the Laboratory participated in "I Taller Iberoamericano sobre Calidad de la Información Analítica en los Laboratorios de Calidad del Agua", as a Brazilian representantive, lecturing about the Brazilian Water Quality Laboratories. Inside the RILCA program, a course on laboratory accreditation, according to ISO/IEC 17025/2005, was given in Facultad de Ciencias Exactas y Naturales, Paraguay (5th - 9th November, 2007).

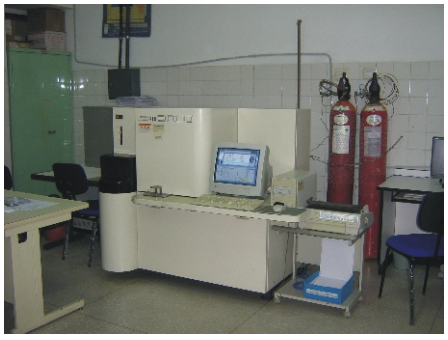

Figure 1. X-Ray Fluorescence Laboratory (LFX)

Analytical chemistry for environmental diagnosis and to assist the Nuclear Fuel Cycle samples

The Laboratories of Chemistry and Environmental Diagnosis Center - CQMA, were established methodologies for evaluation of physical-chemical, chemical and toxicological parameters to support several research projects in development for environmental diagnosis and to assist the Nuclear Fuel Cycle Program.

All methodologies adopted are established in the standard methods (ASTM, EPA) or specified by the clients. The classic methods and instrumental techniques analysis such as atomic absorption spectrometry (AAS), inductively coupled plasma emission spectrometry (ICP-OES), ion chromatography (IC), gas chromatography (GC), gas chromatography mass spectrometry (GCMS), high performance liquid chromatography (HPLC;), X-ray fluorescence (WD-XRFS), differential pulse anodic stripping voltammetry (DP-ASV) have been used.

The Center have been participated in several international interlaboratory programs sponsored by: CETAMA (Etablissement Comission des Analyse Méthods, France), IAEA (International Atomic Energy Agency), INTI (Instituto Nacional de Tecnologia Industrial, Argentina), SENAC (Brasil), ABACC (The Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials), SABESP (Basic Sanitation Company of the State of São Paulo, Brasil) and Rede Metrológica Rio Grande do Sul (Brasil). The Quality Handbook according to ISO GUIDE 17025 has been elaborated. The XRF Laboratory has been participated of Quality Control in Analytic Laboratories of the AIEA-ARCAL LVXXI Program - Test Aptitude. The Laboratory of Chemical and Isotopic Characterization - LCQ has been accorded the prestigious INMETRO Certificate of Accreditation in accordance with ISO/IEO 17025: 2005. Several methodologies were established to support research projects in development:

Environmental
- The specificity and sensitivity in the pesticides analyses were enhanced by a new methodology using solid-phase extraction followed by high performance liquid and gas chromatography mass spectrometry (GCMS). The impact of pesticides use in agriculture was verified.

- Evaluation of selenium in groundwater and sediments samples by Atomic Absorption Spectrometry (AAS, HGAAS, CVAAS) Selenium is associated to some human metabolic processes; however, they become toxic when present at high levels.

- Metal evaluation in top water and drinking water.

- Metal evaluation for industry wastewater.

Biomedicine
Hydroxide-apatite Ca/P relation in teeth for laser prevention studies has been determined by ICP-OES.

Nuclear fuel cycle
- Evaluation for quality control of metal and rare earth impurities of Nuclear Fuel Cycle Program (U_3Si_2; UF_4; U_3Si_2-Al,) using extraction chromatography and ICP-OES. The routine analyses related to nuclear materials by RFX (Si_3U_2, aluminum powder and alloys, AgInCd alloys, uranium and thorium compounds).

- Development of method for Si and U determination in U_3Si_2 system by X ray fluorescence and gravimetric/volumetric techniques. This method is applied to the assembled fuel elements.

IEA-R1 Reactor
Evaluation of IEA-R1 water quality.

Industrial Partnership
- An analytical methodology was established for the determination of Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu and Zn in adhesive materials, applied in the automotive manufacturing, for SABÓ IND. e COM. de AUTO-PEÇAS LTDA.

- A similar method was developed for Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu and Zn determination in adhesive ribbons, used in the electrical components isolation, for VOITH SIEMENS HYDROPOWER GENERATION.

Environmental Monitoring Programme (EMP-Q) to assist the no radioactive chemicals at IPEN

The environmental monitoring program of no radioactive chemicals compounds, is carried out by measuring samples of ground water and waste water discharge in the influence area of IPEN. The aim of this monitoring is to provide Ipen of technical documentation necessary for accomplish environmental laws force and accomplish the demands of the TAC IBAMA referring to

their facilities, to:

- Assess the environmental impact from activities of IPEN;

- Demonstrate compliance of the procedures adopted in the release of liquid effluents with the authorized limits and the appropriate legal requirements;

- Maintain a continuous recording of the effects of plants on the levels of natural chemical compounds, in the influence region under the campus of IPEN;

- Detect any weaknesses and plan corrective measures;

- Providing information to the general public.

Figure 2. Effluents monitoring plant

The mankind has faced challenges from energy needs and prices, resource shortages and global environmental problems. Therefore, there are new needs such as knowledge-based products or services that improve operational performance, productivity, or efficiency while reducing costs, inputs, energy consumption, waste or pollution. Nowadays, products, services or processes should use limited or zero non-renewable resources and creates significantly less waste. Such technologies are named Clean Technologies that use energy, water and raw materials more efficiently, create less waste or toxicity, deliver equal or superior performance, and promote cost reduction and/or increased revenues. Given the environmental benefits these technologies confer, Clean Technology is an intrinsic part of a Sustainable Economy. Some major clean technology sectors are energy, water, manufacturing, advanced materials and transportation. The pollution control and waste reduction are also some important fields, consequence of the public perception of problems like global warming and the impact from the burning of fossil fuels, besides the introduction of contaminants into the environment, as a result of industrial activities. Clean technologies are seen to be the next engine of economic growth and the CQMA has dedicated attention and research initiatives in accordance with this approach.

Biosorbents for the wastewater treatment

Adsorption techniques are recognised as effectiveness for the removal of heavy metal ions and dyes at trace quantities from wastewater. Activated carbon has undoubtedly been one of the most popular adsorbents employed in wastewater treatment throughout the world. But the process has not been used extensively due to high cost activated carbon. For that reason, non-conventional and low cost materials as sorbent to replace the costly activated carbon have been highlighted in recent years.

Biological resources, known as biomass, are available in large quantities and many theirs have been proven for its effectiveness for sorption. Different types of biomass have shown different levels of contaminant uptake so they have been considered biosorbents.

Biosorbents include by-products or waste materials from agriculture, food processing industries are abundant in nature and are classified as low-cost and non-conventional adsorbents. Sugarcane bagasse, coir pith, banana pith, coal fly ash and chitosan have been investigated as alternative biosorbents to commercial adsorbents for the removal of U, Th, Pb, Zn, Ni, Cr ions and dyeing wastewater. Their biosorption has been studied by means of batch equilibrium, isotherm equilibrium kinetic and thermodynamic. The equilibrium data have been analyzed using the Langmuir and Freundlich isotherm models. In the greater number of cases, the Langmuir model was found to best describe the data. Generally, the biosorption is favoured by an increase of pH and is directly related with the concentration of biomass in the suspension until to reach the equilibrium.

Kinetic and thermodynamic investigations of sorption process and sorption data were fitted to different sorption isotherms using pseudo first-order and pseudo second-order models and Vant´Hoff equation. In all cases, the pseudo second-order model was found to explain the rapid kinetic of biosorption of metal ions and dyes and Gibbs free energy indicated the spontaneous nature of the adsorption processes. The major interesting of the studied biosorbent materials are high tolerance for organics and regeneration possible. Futhermore, they are abundant and inexpensive natural resouces.

The dynamic sorption of Ni ions was verified using a column process with bagasse. Sorption breakthrough curve showed that bagasse is a good candidate for use in filters of the wastewater treatment containing trace amounts of Ni. The biomass allowed the reuse in three subsequent adsorption-desorption cycles. The research project of sugarcane bagasse and coir pith biosorbents was supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq in the period 2005-2007. The banana pith biosorbent work was awarded the Young Scientist Prize in 2007.

Among studied biosorbents, chitosan was largely comparable to that of the commercial adsorbent. Chitosan has demonstrated a versatility in its ability to bind both cations and anions. The experiments conducted in this research have shown the sugarcane bagasse, banana pith, coir pith and chitosan were efficients for removal of U, Th, Pb, Zn, Ni, Cr ions and reactive orange 16 dye. Therefore, they are potential biosorbents for the wastewater treatment. This is especially advantageous from environmental point of view because the biosorbents are wastes or subproducts available in large quantities that represent pollutants and hence theirs application to the treatment of wastewater is considered an economic sustainable activity.

Electrochemical techniques for the dissolution of metals and treatment of industrial and radioactive wastes

Electrochemistry is considered as an important partner in the treatment of wastes and other chemical processes due to its no pollutant characteristics.. For this reason, electrochemical processes have been under study for industrial and radioactive waste treatment at CQMA. The applied areas can be resumed as follows:

- Treatment of radioactive (Cs) and industrial (Cr) wastes using electrochemical ion exchange (Figure 3);

- Separation of rare earths (Eu, Sm, etc,) (Figure 4);

- Recovery of pure Pb from RETOTER (Rare earths and thorium waste);

- Electrodissolution (or anodic dissolution) of aluminum presents in irradiated uranium silicide fuels and incorporation of the radioactive material in a vitreous matrix for final storage;

- Electrochemical synthesis of rare earth chromates for application as corrosion inhibitors

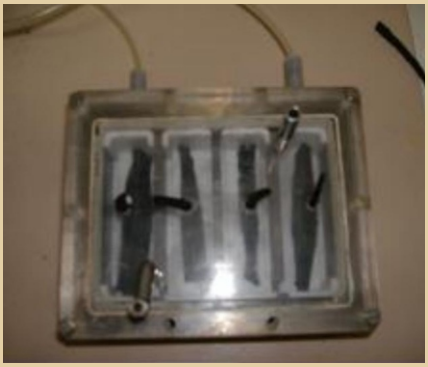

Figure 3. A 4-stage electrolytic cell with ion exchange electrodes used in the treatment of wastes containing Cs or Cr

Figure 4. Electro-reduction/Precipitation of Sm from a RE concentrate containing Eu, Gd, Y, Nd and Tb

The mass spectrometry technique is a well known analytical tool to characterize many physical chemical samples. The scope of this research is to characterize chemically, contaminants and constituents on environmental samples using mass spectrometry techniques. The task is divided into three specific activities, one is the specific scientific research plan, second is students training to do research and the last one has the target to publish the research and apply the methodology developed into the environmental agency. The first task, concern about projects on mass spectrometry link to characterization of environmental contaminants. The second task, concern about mass spectrometry courses, training students: undergraduate and graduate. The third task concern about publications, introducing the developed analytical methodology before the Brazilian environmental agency and do routine analysis to the IPEN costumers. The proliferation on hybrids analytical techniques develops parallels analytical techniques, such as Gas Chromatography, Liquid Chromatography and Infrared absorption techniques that are explored in this research as well. The following list shows each research work done and ongoing in the laboratory the years of 2005 to 2007.

- Multiresidue method of benzimidazoles, carbamates and triazines pesticides in corn by liquid chromatography/Tandem mass spectrometry with electrospray ionization.

- Determination of chloramphenicol residues in industrialized milk and honey samples using LC-MS/MS.

- Residues determination study of glyphosate and aminomethylphosphonic acid (AMPA) in soybean and water samples using liquid chromatography coupled electrospray ionization tandem mass spectrometry (LC-ESI/MS/MS).

- Characterization of acrylate and methachrilate cross linked copolymer attained by photopolymerization for waveguide employment.

- Determination of hexachlorcyclohexane residues on blood plasma of exposed employees of the historical achieves of Joinville on 80's decade.

- Hydrogen characterization from methanol cracking for fuel cells / melting silicium oxides.

- Evaluation of the composition of the açai oil submitted to different doses of ionizing radiation.

- Characterization of the saturated and unsaturated fatty acids in Amazones oils: copaiba, buriti, maracuja, açai, and Para nuts by GC/MS.

- Direct and sensitive analysis of phenol and trichlorophenol by GC/MS.

- Diesel emissions significantly influence composition and mutagenicity of ambient particles: a case study in São Paulo, Brazil.

Synthesis and characterization of new rare earths compounds and their application as electrocatalysts in proton exchange membrane fuel cells (PEMFC)

The separation and purification of rare earths (RE) it is still today a matter of utmost concern. The technology and the procedures for the separation of macroscopic amounts of RE are always welcome. Brazil has a long tradition in rare earth technology, from monazite ores mining until the industrial separation and production of RE concentrates. These RE concentrates were studied and some high grade pure oxides were produced, like lanthanum, cerium, neodymium, samarium and yttrium, to be used as standards. The dissolution of the RE concentrates with ammonium carbonate was also studied and the resultants complexes treated with hydrogen peroxide for the precipitation of the corresponding peroxicarbonates. The behavior of the solubility of the RE and complex formation toward ammonium carbonate and the differential precipitation of the corresponding peroxides were investigated. The carbonate chemistry is of relevant importance to the rare earths from both analytical and industrial aspects. The RE were precipitated and dissolved by alkaline carbonate as well. The RE catalysts precursors thermally stable were synthesized by sol-gel method and characterized. An electrochemical method for the separation of europium and samarium from RE concentrates were developed. Praseodymium has been separated by ion exchange method and its purification is the final step. The preparation of nanoparticles of RE from high pure acetates are under study. This research is of great importance, since these materials will be applied as co-electrocatalysts in PEM fuel cells. The use of RE as co-electrocatalysts has been studied since 2005 in a project supported by CNPq.

Molten salt processes for waste treatment

The suitable final disposal of hazardous organic wastes such as PCBs (polychlorinated biphenyls), pesticides, herbicides, some organic radioactive wastes and hospital residues constitutes a serious problem. In some point of its lifecycle, these wastes should be destroyed, in reason of the risk that they represent for the human being, animals and plants. The thermal decomposition has been used commercially in the waste disposal, mainly the incineration, whose most important characteristic is the combustion with flame. During the last three decades, incineration was usually a more practical and less expensive alternative. However, the conventional incineration, as way of destruction, presents some restrictions, due to the gaseous emissions eventually generated in the process. PCB-contaminated organic wastes are difficult to treat by incineration due to the formation of dioxins and furans, cancer-causing agents, at incineration temperatures, which are typically above 1200°C. An alternative to the incineration, for the treatment of a vast range of dangerous wastes, is the waste decomposition by molten salt oxidation. This process has several advantages over incineration. Molten salt oxidation is a thermal means of oxidizing (destroying) the organic constituents of mixed wastes while retaining inorganic and radioactive constituents in the salt. For this reason, molten salt oxidation of hazardous wastes is considered a promising alternative to incineration for the treatment of a variety of organic wastes. IPEN has constructed pilot-scale molten salt oxidation equipment in which tests are being performed under carefully experimental conditions.
In this process, organic wastes are injected with a stoichiometric excess of air (oxidant) beneath the surface of a pool of molten sodium carbonate at temperatures between 900-1000°C. A special injection lance is used to introduce the organic waste and air into the bottom of the molten salt bed that is contained in the reactor vessel. Therefore, the waste and the oxidizer are mixed in a turbulent bed of molten salt. The large thermal mass of the molten salt provides a stable heat-transfer medium and ensures temperature uniformity. Flameless oxidation takes place within the salt bath converting the organic components of the waste into CO2, and water. Due the flame absence, it is not considered an incineration process. Reactive species such as halogens (fluorine, chlorine, bromine, iodine), sulfur, phosphorous and arsenic, present in the organic waste, react with sodium of the molten salt to form the corresponding neutralized salts, such as, for instance, NaCl, NaF, NaBr, NaI, Na_2SO_4, Na_3PO_4, which are then trapped in the salt bath. Other non-oxidizable inorganic constituents, heavy metals, and radionuclides are captured in the salt, mainly as oxides, and most can be easily separated for disposal. The sodium carbonate can be reused after a dissolution-filtration recovery process and the salt can return to

the reactor vessel. In the figure 5, a schematic drawing of the molten salt process is presented.

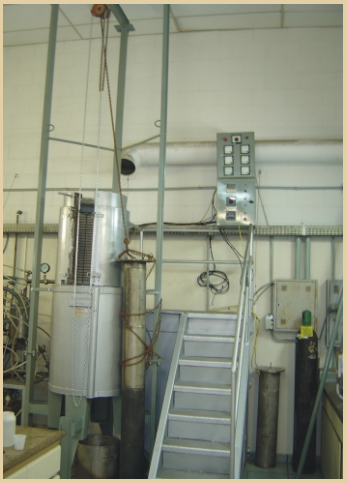

Figure 5. Equipment scale

Microwave technology

The microwave technique has been studied all over the world to identify (qualitatively and quantitatively) and define the mechanism of microwave-material interaction, in rubbers devulcanization and in several types of petroleum hydrocracking and hydrotreating processes. In Brazil, the application of this process is a very recent field and has been studied as a new tool in materials processing, which uses high temperatures. The knowledge of this technology is important to begin the development process in industrial scale and consequently in reducing the environmental pollution caused by these kinds of residues. Microwaves are a form of electromagnetic energy in the frequency band from 300MHz to 300GHz (not ionizing radiation). Industrial microwave processing is usually accomplished at a frequency of 2.45GHz (which corresponds to a wavelength of 12.24cm) to avoid interference with telecommunication and cellular phone frequencies. Microwave processing offers numerous advantages in relation to conventional heating methods (convection or conduction), where the material's surface heats first and then the heat moves inward. One of the most important characteristics is saving energy, because the material absorbs microwaves readily (the heat is generated from the inner parts to the surface of the material) reducing the processing time. Also the selective energy absorption allows heating in specific points of the material. This process is environmentally clean because it reduces pollutant emission. Finally, the microwave heating does not require an appreciable amount of time to effect temperature changes such as the conventional methods and when the microwave device is turned of the effect of these electromagnetic waves is instantaneously interrupted. Contracts between CENPES - Centro de Pesquisas da Petrobrás e IPEN:

- Project and Assembly of Microwave System Applied the Catalytic Reactors for Crude Oils Processing (Fev/2005-Fev/2007);
- Microwave Application in HDT and HCC Reactions: Batch studies and equipment construction for continuous operation (Jun/2007-Jun/2009);
- Project of Recovery of the Previously Laboratory for Zirconia Preparation at IPEN Amend building to attend Projects of PETROBRAS Interest in the future refinements Area (Set/2007- Ago/2008).

Petroleum or crude oil is a naturally occurring mixture of hydrocarbons and smaller amounts of organic compounds containing heteroatoms such as sulfur, oxygen, nitrogen, and metals. The petroleum products obtained from crude oil processing vary considerably, depending on market demand, crude oil quality and refinery objectives. In current industrial practices, crude oils are submitted to distillation under atmospheric pressure and under vacuum. The distillation fractions (including the residual fractions) undergo further catalytic refining processes so high-value products can be produced. The hydrogen content of petroleum products is an important index of their economic value. In conventional hydrocracking and hydrotreating processes, the hydrogenation reactions of aromatic compounds play a crucial role. Heavy residual compounds are normally aromatic in nature. The complete or partial saturation of these compounds by hydrogen addition is an important step in their cracking into smaller, more valuable compounds. Conventional heavy oil hydrocracking processes require relatively high temperature and very high pressure. In hydrotreating and hydroreforming processes, some catalysts become active only at the high temperature range. In order for reactions to take place at a favorable lower temperature range, metal catalysts are usually used to achieve good hydrogenation efficiency. Attempts have been made to find new classes of catalysts that would significantly lower the process parameters, while increasing the hydrogenation efficiency in terms of deep reduction of aromatic content. In another aspect, in Brazil microwave provides a new method of organic compound hydroprocessing. The method comprises the irradiation of hydrocarbons with a catalyst, by using high temperature and high pressure, having a reaction surface to produce a catalyst-organic compound mixture.

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Honor Mention and Awards

Prêmio Inventor 2007 Petrobras. Dispositivo de sistemas para processamento de cargas a altas temperaturas e pressão em presença de microondas. 30/11/2007 - Petrobras - RJ - Dra. Sumair G. Araujo e equipe.

3° lugar Prêmio Fernando Cerviño Lopes. Reciclagem de resíduos gerados em usina termelétrica para aplicação na remoção de corante em água. Sindicato dos Químicos, Químicos Industriais e Engenheiros Químicos do Estado de São Paulo - Dra. Denise Fungaro.

1° lugar categoria Graduado. Uso da casca de banana para o tratamento de efluentes radiotóxicos. XXII Prêmio Jovem Cientista - Gestão sustentável da biodiversidade: desafio do milênio - Boniolo, M.R.; Yamaura, M.

Prêmio Fernando Cerviño Lopes. Reciclagem de resíduos gerados em usina termelétrica para aplicação na remoção de corante em água. Sindicato dos Profissionais de Química do Estado de São Paulo - 2007.

Prêmio Internacional da Água e da Ciência. Simpósio de Água de Cannes, França, UNESCO; Universidade das Nações Unidas e Universidade de Nice Sophia Antipolis. Dra. Denise Fungaro.

Prêmio Polícia Cidadã da Fundação Sou da Paz, Governo do Estado de São Paulo e Rede Globo de Televisão. O residuográfico azul. Coordenado por Regina Branco e realizado em conjunto com pesquisadores do Centro de Química e Meio Ambiente do IPEN, Instituto de Química da USP e Unicamp. Dra.Vera Salvador.

3º lugar Prêmio Fernando Cervino Lopes - Novas técnicas de reciclagem. Sistema de tratamento de efluentes e resíduos sólidos oriundos da indústria hidroletalúrgica e baterias exauridas. Sindicato dos Profissionais da Química do Estado de São Paulo - junho/2005 - Dra. Denise Fungaro, Dr. Alcídio Abrão, Fátima Maria.

Prêmio Bramex Ambiental 2005 - categoria Inovação. Contribuição à preservação ambiental em região de complexo carboelétrico. Câmara da Indústria, Comércio e Turismo Brasil-México - Dra. Denise Fungaro.

Prêmio Polícia Cidadã do Instituto Sou da Paz. Desenvolvimento de pesquisa que resultou na possibilidade de verificação científica da origem da maconha - 2005 - Dr. Jorge Sarkis.