

## Chemistry Sector



*Outside view of Building for Cryogenic Techniques*

# Chemistry

Maria de Fátima Araújo

Fundamental and applied research are conducted in specific areas of expertise, consisting on the development on the **synthesis of inactive and radioactive compounds** dedicated to the progress of **health, materials sciences and catalysis**, and the use of **nuclear based and related methods** to **environment, earth sciences and cultural heritage**. Research activities are grouped in five areas:

**Solid State** – the group centre its research activity on selected new materials with unconventional electrical and magnetic properties. Strong skills combining preparative chemistry expertise with specialized solid state physics enable the team to deal with different problems of modern materials science. Activities were centred in selected materials namely: molecular based conducting and magnetic materials and intermetallic compounds with *f*-elements.

**Inorganic and Organometallic Chemistry** – Research activities are focuses on the synthesis, characterization, chemical reactivity and energetics of 4f and 5f element compounds and in gas-phase ion chemistry studies of highly radioactive actinides by FTICR/MS. IOC team has been involved in environmental studies, particularly the vitrification of radioactive wastes containing actinides and, in collaboration with the Radiation Technologies group (Physics), in gamma radiation effects on waste water sources. Of importance is also a new collaboration with OMNIDEA, Lda., a start-up company dedicated to R&D of aerospace technology and energy systems.

**Inorganic and Radiopharmaceutical Chemistry** – Research in modern Radiopharmaceutical Chemistry is dedicated to find innovative radioactive tools for molecular imaging and/or targeted radiotherapy with interest for Nuclear Medicine. To achieve this goal IRC team develops and implements expertise on organic, inorganic and organometallic chemistry of d- and f-elements, radiochemistry, radiopharmacy, cell and animal studies and biochemistry. IRC expertise and infrastructures justify the support of an international pharmaceutical company and funding from CIMAGO/FLAD.

**Environment and Analytical Chemistry** – multidisciplinary team supported by high specialized

methodologies - EDXRF, Mass-Spectrometry for Light Isotopes, and Radiocarbon and Tritium dating – applied to Environmental Geochemistry, Isotope Hydrology, Oceanography and Archaeometry. Research aims at the understanding of the recent and palaeo-evolution of natural coastal environments: ground water systems, rivers, lagoons, estuaries and continental shelf. Archaeometallurgical studies aim at the characterization of Pre and Protohistoric metal production, circulation and consumption in Portugal.

**Cultural Heritage and Sciences** – The group is especially devoted to the study of cultural assets and corresponding environment contexts, through the application of nuclear methods of chemical analysis and absolute dating. The main research domains comprise luminescence dating of archaeological and geological contexts, archaeometry of ceramic, metal and lithic materials, and geochemistry and mineralogy of the earth surface. Development of luminescence techniques has been done for ceramic art objects authenticity and production technologies

National and international projects with the scientific coordination and/or participation of Chemistry researchers have been running. Some laboratories were moved into a recently renovated building allowing new laboratories to be installed including a clean and a gamma-spectrometer laboratories under the program for new infrastructures and equipment financed by the National Scientific Infrastructure Programme were implemented (an INAA gamma-spectrometer with sample changer, a single grain luminescence reader, a SQUID magnetometer), an ICP-MS, and an ESI-QITMS are being acquired.

Education and training of Undergraduate, MSc, PhD and Post-doc students is one of the most important achievements at Chemistry, as well as an active participation of Researchers in advanced training activities in collaboration with Universities and in the framework of international networks.

Research has been financed by Projects supported by the FCT and the EC, also by Protocols, Contracts and Services with different Institutions and Industry.

## Chemistry Staff

### Researchers

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# Cultural Heritage and Sciences

*M. Isabel Prudêncio*

The Cultural Heritage and Sciences (CHS) group is especially devoted to the **study of the Portuguese cultural assets and corresponding environment contexts**, through the **application of nuclear methods**, including chemical characterisation and absolute dating.

Absolute dating, geochemistry and mineralogy are the main research domains, applied to archaeometry, environmental geology and paleoenvironmental reconstruction.

The principal research domains of CHS group include:

- Luminescence dating of archaeological contexts and artefacts.
- Optically stimulated luminescence applied to dating geological contexts.
- Thermoluminescence applied to archaeological / museum artefacts: authenticity of ceramic art objects.
- Chemical and mineralogical characterization and technological properties of Portuguese clays.
- Archaeometry of ceramic, metal and lithic materials.
- Environmental geochemistry: natural background and evaluation of anthropogenic inputs.
- Development and application of luminescence techniques and neutron activation analysis.

The analytical methods associated to the CHS group, include the instrumental neutron activation analysis (INAA) - comparative method, for chemical characterization, and luminescence dating (TL-OSL). Other methods, such as X-ray diffraction, SEM-EDS and Mössbauer are commonly used.

The application of ITN methodologies, unique in Portugal, is fundamental for solving problems of archaeological and geological nature. The research is

developed through collaboration protocols, financed projects, collaboration with national and international laboratories and universities, and contracts/services with private and public institutions.

This group is specialized in trace-element analysis and geochemistry (i.e., geochemical fingerprinting) and mineralogical phases assembly of archaeological specimens and raw materials (namely clays and silex) for the purpose of determining their provenance by using the above mentioned analytical techniques as tools. We are an archaeometrically oriented lab in Portugal with powerful analytical techniques in a single location. We also support geochemical research on the petrogenesis of various igneous, metamorphic, and sedimentary rocks, as well as environmental studies.

Research of CHS group also comprises luminescence techniques applied to various fields, archaeological and geological, including the study of natural radioactivity. New fields of application are in progress with the development of luminescence techniques, like a better knowledge of technological production of archaeological artefacts, allowing a better identification of post-burial phenomena. The Luminescence laboratory has incremented the variety of end users, supporting not only research projects, but also services to the community, like the authenticity of public and private ceramic art objects.

One of the CHS group most important activities involves the education and training of students from national and international universities. Our students participate in the entire research work, including field work, sample preparation, irradiation, and measurement and continuing through the statistical analysis and data interpretation, thus becoming well prepared to conduct research in academic and industrial environments.

## Research Team

### Researchers

M. I. PRUDÊNCIO, Princ. (Agregação), Group Leader  
M. I. DIAS, Invited Aux.

### Students

M. J. TRINDADE, PhD student, FCT grant  
A. JORGE, PhD student, U. Sheffield grant  
C. CAPITÃO-MOR, MSc student  
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L. PENG, MSc student  
P. FRANCISCO, graduation student  
F. GEIRINHAS, graduation student  
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### Technical Personnel

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### Collaborators

M. A. GOUVEIA, Princ. Researcher  
(Retired)

## Luminescence dating of archaeological contexts and artefacts.

M. I. Dias, M. I. Prudêncio, D. Franco, G. Cardoso, J. C. Waerenborgh<sup>1</sup>  
A. Zink<sup>2</sup>, A. C. Valera<sup>3</sup>, C. Odriozola<sup>4</sup>, V. Hurtado<sup>5</sup>, L. Osterbeek<sup>6</sup>

The TL-OSL absolute dating of archaeological contexts and related artefacts (ceramics and lithics) contributes to a better definition of the chrono-stratigraphic sequence of human occupation. The main goal of several running projects in this research area is to establish chronological references of human occupation levels. Beyond luminescence technique, the use of nuclear methods of analysis, namely INAA, using the RPI as neutron source is done, allowing a more accurate paleodose in the luminescence absolute dating determination. These methods are complemented with XRD for mineralogical control.

The main steps evolved in this research domain include: (i) field work - sampling collection and in situ measurements of environmental radioactivity (gamma measurements); (ii) laboratory preparation of samples according to specific protocols; (iii) natural radioactive elements (K; U; Th) contents determination, by INAA, using the RPI as neutron source; (iv) OSL (Optically Stimulated Luminescence) dating of sediments and paleosoils; (v) TL (Thermoluminescence) dating of lithic materials (silex) and ceramics.

A relevant work developed in this research area was done in an urban context stratigraphy occurred along the Lisbon hill slope of Bairro Alto, at Lumiares Palace. A chronological stratigraphic differentiation by luminescence dating (TL-OSL) was performed, with special attention to the preserved paleosoil identified in the archaeological excavations. Several stratigraphic units were identified in the archaeological excavation, also differentiating geological formations. Chemical (INAA) and mineralogical composition (XRD), granulometry, calcimetry and organic matter content were obtained for the sediments of the identified units, as well as luminescence dating of sediments, soils and heated silex. In a geochemical point of view, the occupation levels developed above Miocene deposits present affinities with them, even with higher contents of organic matter and of chemical elements related with ferromagnesian minerals. The colluvium above paleosoil is detachable from other deposits by a more heterogeneous mineralogical composition and with higher amounts of heavy minerals and plagioclases. A better definition of the chrono-stratigraphic sequence was obtained by TL-OSL of both human occupation levels and geological deposits (Fig. 1), by establishing a chronological reference of the human occupation level in a late phase of early Neolithic (B-OSL of paleosoil samples and TL for related artifacts - silex were consistent: 6.000 years; error:  $\pm 3\%$ ).

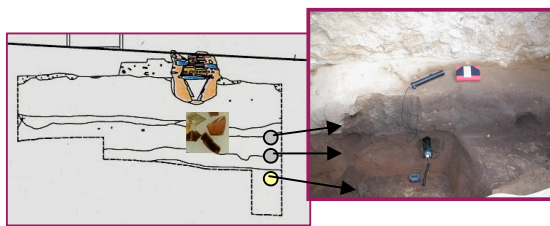


Fig. 1 – Luminescence dating of stratigraphic units identified in P. Lumiares Lisbon urban context.

A new application of luminescence techniques was undertaken in order to better estimate firing temperatures of archaeological ceramics. The identification of clay minerals in some ceramics (XRD), as well as the significant presence of iron oxides (essentially hematite) with nanometre granulometry (Mössbauer), suggests that pottery was not fired at temperatures above 500°C, or had had post-burial alterations. The already obtained TL results have been more enlightening: (i) reflecting maximum firing temperatures lower than 550°C (Fig. 2); (ii) pointing to the same firing temperature (550°C), but with modifications in the crystalline net that could reflect post-burial alterations.

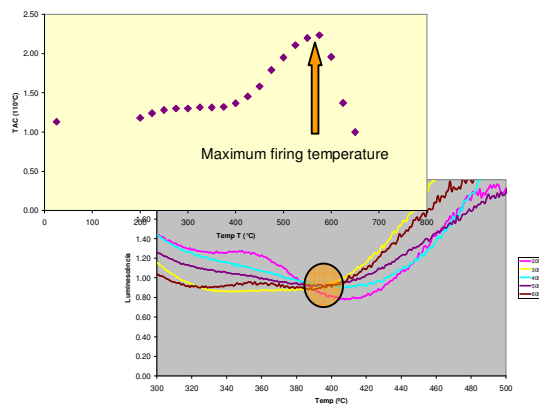


Fig. 2 – Glow-curves (TAC and annealing) for archaeological ceramic.

### Published or in press work:

G.O. Cardoso, M.I. Prudêncio, A. Zink, M.I. Dias, J.C. Waerenborgh, Determinação da temperatura de cozedura de cerâmicas arqueológicas: Luminescência – potencialidades e limitações. *Proc. Congresso Ibérico de Arqueometria*. Girona, Espanha (in press).

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**Optically stimulated luminescence applied to dating geological contexts**

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Research undertaken in this field by the CHS group involves the analysis of geological contexts, namely former coastal environments. Research is mainly devoted to palaeosol and sediment studies by absolute dating (OSL), chemical (INAA) and mineralogical (XRD) characterization. Recent and current projects have included working with other national and international laboratories and universities. Also services to private and public institutions were done. The application of OSL method to geological investigation has a huge contribution to the palaeoenvironmental reconstruction, investigating and explaining environmental change on different spatial and temporal scales. Our contribution assists landscape evolution, particularly the Portuguese coast line, in order to determine the geological processes that control the evolution of the beach and the effects that this evolution has in the shoreline displacement. Thus, these research fields aim to contribute to a better knowledge of the Portuguese Quaternary climate change scenario, based on multi-proxy investigations of paleosols, sediments and dunes. These investigations constitute the research component into long-term environmental change of climate and shoreline.

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**Thermoluminescence applied to archaeological / museum artefacts: authenticity of ceramic art objects**

*M.I. Dias, M.I. Prudêncio, D. Franco, G. Cardoso, A. Zink<sup>1</sup>, M O. Figueiredo<sup>2</sup>, T. Silva<sup>2</sup>*

Authenticity testing by thermoluminescence have been implemented and applied to art objects in ITN laboratory. This technique provides a very powerful independent judgment of what is genuine and what imitative. Research work has been performed in order to optimize the laboratory protocols for ceramics and porcelains. Services to private collectors were done to art objects of various chronologies and provenances. Recent collaboration with other laboratories and museums was established, specially aiming a better chronology precision, identification and differentiation of national production centres and technologies of ceramic production, and characterization of surface coatings (glazes and pigments).

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**Chemical and mineralogical characterization and technological properties of Portuguese clays**

*M.I. Dias, M.I. Prudêncio, M.J. Trindade<sup>1</sup>, R. Marques, D. Franco, M.A. Gouveia, F. Rocha<sup>2</sup>, J. Coroado<sup>3</sup>, M.A. Sequeira Braga<sup>4</sup>,*

Detailed studies of Portuguese clays of different geological contexts are in course, including geochemical, mineralogical and technological characterization for two main fields of application, namely ceramic production (ancient and present-day) and waste-fills liners. In Portugal ceramic handicraft has a long tradition. Detailed studies of raw materials will benefit this economic sector. An inventory of availability of potential raw materials for ceramic production is running in the southern and occidental Portuguese borders, followed by an evaluation of chemical (INAA) and mineralogical (XRD) transformations of clay materials of different nature, during ceramics production processes, and its implications on provenance and technological procedures studies of ancient and present-day ceramics. In Portugal, due to the replacement of old traditional waste-fills by new ones for domestic and other common wastes, according to EU norms, we need to find in each region of the country appropriate clay deposits for exploitation in order to use them as liners. The mineral and chemical composition and other relevant properties required for clay liners, such as: heat diffusion, cooling rate, fluid-rock interaction, hydromechanical behaviour and permeability are studied. Smectite is considered as the more adequate clay mineral for this kind of application. In Portugal, heavy clays utilized for structural ceramics are quite common. These clays containing smectite-illite-kaolinite assemblages and being considered, from the hydrogeologic point of view, as presenting extremely low permeability, will be our main target.

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**Archaeometry of ceramic, metal and lithic materials**

*M.I. Dias, M.I. Prudêncio, M.A. Gouveia, D. Franco, R. Marques, A. Jorge<sup>1</sup>, P. Day<sup>1</sup>, C. Capitão-Mor<sup>2</sup>, F. Rocha<sup>2</sup>, S. Rovira<sup>3</sup>*

Archaeometry is one of the main research fields of CHS group, mainly applied to archaeological ceramics. The application of nuclear methods of analyses to archaeometry was extended to other types of materials, like lithic and metal artifacts. The main goals include: (i) establishment of the technological procedures during the manufacture process of making ancient pots, and its provenance, in order to contribute to the establishment of continuities or innovations in ceramic production; (ii) ceramic raw materials resources exploitation strategies at local/regional scale; (iii) characterization and provenance of lithics; (iv) metalworking process including ore samples, crucible fragments and slag production; (v) ore sources of archaeological artifacts; (vi) to reconstruct the smelting process based upon qualitative and quantitative analysis of the materials; (vii) geological reappraisal of regional metal sources, contributing for the knowledge of geographical sources of raw materials and metal alloys used.

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**Environmental geochemistry: natural background and evaluation of anthropogenic inputs**

*M.I. Prudêncio, M.I. Dias, R. Marques, D. Franco, J.C. Waerenborgh<sup>1</sup>, F. Ruiz<sup>2</sup>, E. Galan<sup>3</sup>*

Geochemistry, crystal chemistry and mineralogy studies are applied to environmental projects, with a view of the preservation of classified natural environments and valorization of natural resources. The expertise on geochemistry of the earth surface of CHS group researchers enables a detailed and complete overview in this kind of studies. The characterization of the natural background is a main goal which is essential for the evaluation of the anthropogenic input in the geological environment. The CHS running projects, concerning the quality control and identification of pollutants of geological environments, refer mainly to lagoon environments focused in the study of the geochemistry of the earth surface, particularly the behavior of trace and major elements in secondary natural systems, and the alterations due to pollution actions.

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**Development and application of luminescence techniques and neutron activation analysis**

*M.I. Prudêncio, M.I. Dias, R. Marques, M.A. Gouveia, D. Franco, G. Cardoso*

The main objective of the Luminescence Dating Laboratory is the development and application of luminescence dating techniques (TL, G-OSL, IRSL, B-OSL) in collaboration with archaeologists and geologists, and assisting curators and private collectors in establishing chronologies. In addition, fundamental studies on the luminescence properties of minerals, which could be exploited for dating application, has been an important part of the work. In order to assure the quality of dating results and to optimize lab and measurements protocols, the ITN luminescence dating laboratory participates in international comparisons, particularly with the Musée du Louvre (CNRS), France and IUX, Spain. Instrumental neutron activation analysis is a well-established method within this group since the seventies. Based on the use of the nuclear research reactor (unique in the Iberian Peninsula), this analytical method (complemented with other methods) supports most of the research activities of the CHS group and is also used by other ITN researchers. Public and private institutions often requested CHS group for services, considering the high performance of the chemical analysis. Most of the activities concern archaeometry and environmental monitoring studies. The INAA is fundamental for the research activities of the group, allowing determine trace elements, especially Rare Earth Elements, which are excellent geochemical fingerprints. The quality of the analytical procedures of INAA is periodically controlled through the analyses of international standards and inter-calibrations with other laboratories, in order to maintain and increment the good performance of the laboratories.

Both laboratories (TL-OSL and INAA) were reinforced with new equipment on behalf of the national Re-equipment Program by FCT (CONC-REEQ/590/2001).



# Environment and Analytical Chemistry

Maria de Fátima Araújo

The activities within the Environment and Analytical Chemistry Research Group involve the study of the Biogeochemical Cycles of Chemical Elements and Light Isotopes in the Environment. Our main skills are in the fields of Instrumental Analytical Chemistry, Environmental Geochemistry, Isotope Hydrology, Oceanography,  $^{14}\text{C}$  Dating and Archaeometallurgy.

Instrumental Analytical Chemistry is based on the implementation of Energy Dispersive X-Ray Fluorescence Spectrometry, Mass-Spectrometry for Light Isotopes, Elemental Analysis coupled to Mass Spectrometry,  $^{14}\text{C}$  and  $^3\text{H}$  Dating techniques. These are being utilised in studies involving quantitative elemental analysis, isotopic determinations and dating of environmental and archaeological samples.

During the current year we have implemented a clean laboratory to install an ICP-MS (Inductively Coupled Plasma Mass Spectrometer) for isotopic and trace element research, financed by the “*Programa Nacional de Re-Equipamento Científico*”. Also, the operation of the Elemental Analyser coupled to mass spectrometer unit allowed the development and expansion of specific working domains in Isotope Hydrology and Isotope Geochemistry, with particular emphasis the use of isotopic techniques in the assessment of aquatic resources pollution related to agricultural practises.

Environmental Geochemistry and Oceanographic research was developed under a multidisciplinary approach, including sedimentology, geochronology, absolute dating, meteorology and paleoecology. Research was focused in Sedimentary Geochemistry to evaluate: 1. consequences caused by the changes that took place during the last centuries in the main Iberian river basins, and 2. environmental changes occurred during the Late Quaternary in lagoons and

interdune depressions of the SW Portuguese coast. Moreover, studies concerning the marine reservoir effect off the W margin of Iberian Peninsula, based on  $^{14}\text{C}$  dating of marine shells and charred wood or bones closely associated, have enabled the clarification of the variability of the coastal upwelling off Atlantic Iberia and the identification of episodes of abrupt shifts in oceanic circulation.

Isotope Hydrology was extended in order to achieve the comprehension of different environments, namely: Urban Areas; High Mountain Areas; Arid and Semi Arid Zones and Gas Geochemistry in  $\text{CO}_2$ -rich Thermomineral Waters. The characterisation of these systems is being addressed in the exploitation and future development of regional water resources and the delimitation of protection areas.

Research projects have been of a particular relevance in given support to political decisions, taking into account the sustainable regional development and the appropriate use of the water resources and coastal management on the basis of several European and national directives.

The Archaeometallurgical field was strengthened via the study of pre-historical important artefact collections to characterize the technological and social conditions of Copper and Bronze Age metal production and circulation in Portugal. New studies including corrosion process in archaeological Cu-based materials and surface enrichment processes were developed by using optical metallography, micro-fluorescence and scanning electron microprobe.

Due to the specificity of the available equipment and expertise within the group, technical services are provided to Universities, Public and Private Institutions

## Research Team

### Researchers

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J. MARTINS, Graduate student, PEPAP grant  
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M. CORREIA, Laboratory technician  
O. MARGO, Laboratory technician

### Collaborators

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## Environmental Geochemistry – Elemental and Isotopical Research

*M. Fátima Araújo, P. Carreira, A.M. Monge Soares, P.G. Fernandes, C. Corredeira, D. Nunes, P. Valério, R. Cardoso, J. Martins, O. Margo, A. Amaro, M. Correia*

### Objectives

This project aims at the development and promotion of coordinate research on Earth and Environmental Sciences by implementing analytical and absolute dating techniques:

1. Multielemental characterization ( $Z > 10$ ) using X-Ray Fluorescence spectrometry in solid samples;
2. Light isotope ( $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) determination in liquid and solid samples, including organic matter;
3. Radiocarbon dating;
4. Tritium dating of water samples.

The elemental, isotopic and dating techniques are being dedicated to the understanding and management of natural environments, particularly aquifers, rivers, lagoons, estuaries, coastal waters and continental shelf. Our main goals are:

- 1) to establish the evolutionary patterns of these environments since the Last Glacial Maximum; define geochemical signatures for different marine and terrestrial contributions; evaluate changes in sediment sources; delineate local fossil background values;
- 2) to determine the origin of different groundwater systems; assess the vulnerability of groundwater to surface pollution; understand and determine the origin of pollution in hydric systems;
- 3) to assess the variability of the W Iberian coastal upwelling; identify episodes of abrupt shifts in oceanic circulation, probably coupled with abrupt climatic changes.

### Results

Geochemistry and dating studies carried out in shelf, estuarine and lagoonal sediments revealed to be an important tool in the study of transitional and marine environments, giving particular indications in the marine/terrestrial origin of the deposited materials and allowing to recognise and evaluate some temporal changes occurred during the Holocene. During this year, studies were mainly focused on: the SW Iberian shelf sediments (Gulf of Cadiz); the southwestern coastal lagoons and in estuarine region of the drainage basins of Lima, Tagus and Sado rivers.

Guadiana shelf sediments exhibit an important continental contribution. The main sources of pollution are the mineral wastes of mining activities resulting from the ore exploitation along the Iberian Pyrite Belt. Heavy metal (Cu, Zn and Pb) enrichment determined for the upper layers (from the surface down to 20 - 80cm) of sediment cores collected along the mid and out shelf indicate a continental contaminated source. Spatial distribution of the enrichment factors (using as a reference the

concentration values of the deepest fractions of the cores) shows a similar behaviour in the heavy metal distribution patterns along this area of the continental shelf. Heavy metal contents and excess  $^{210}\text{Pb}$  along core sediments indicate a clear record of the beginning of “pollution” in shelf sediments coincident with the mining exploitation reactivation during the XIX century. Geochemistry of lagoonal and estuarine sediments has permitted the establishment of background levels to derive the enrichment caused by anthropogenic factors. Lagoonal sediments were classified according the concentration thresholds published in the Portuguese legislation that regulates the degree of contamination for dredged materials (DR II, nº. 141, 21/6/1995).

Besides, environmental isotope techniques applied to surface waters have identified and characterised sources of pollution: natural, industrial, agricultural, and domestic. Isotope techniques have allowed recognising incipient pollution, providing an early warning although the chemical and biological indicators did not point to any mixture of systems or pollutants contribution (Sado/Sines basins). Agricultural practices and high industrial areas with over exploitation of the systems were identified as sources of pollution to the environment: sediment and hydrological domains (Porto region and Sado basin).



Radiocarbon dating has been used as a tool to set up chronological frameworks for the past environmental changes identified in our research. Besides this, the regional marine reservoir effect,  $\Delta R$ , for the western Iberian coastal waters during the 4<sup>th</sup> and 3<sup>rd</sup> Millenium BC, a badly sampled time interval in previous research, was determined. The results enable a better clarification of the variability of the coastal upwelling off Atlantic Iberia. Radiocarbon dating was also applied to identify the possibility of occurrence of different age episodes of sand accumulation during aeolianite formation at the coastal region of Lisbon.



**Elemental and Isotopical geochemistry of fine sediments deposited along the Iberian continental shelf***M. Fátima Araújo, C. Corredeira, D. Burdloff, R. Cardoso, R. Calisto*

The geochemical characterisation (elemental and isotopical) of fine sediments collected along the Portuguese Continental Shelf adjacent to the main Iberian river estuaries (Minho, Douro, Tagus and Guadiana), was used to assess the influence of each specific river sediment load into the coastal marine environment. The variability on the sedimentary organic matter supply results from differences in the transported sediment load, hydrodynamism and morphological environment along the continental shelf. Sediments rates determined in sediment cores demonstrate the varying sediment supply and the influence of each drainage basin (Guadiana: 0.12-0.13 cm.yr<sup>-1</sup>; Tagus: 0.20-0.24 cm.yr<sup>-1</sup>; and Douro 0.45 cm.yr<sup>-1</sup>). Elemental distribution of lithogenic/biogenic elements indicates that Douro is the main source of the shelf fine sediments deposited northwards. At the northwestern shelf sediments, heavy metal contents suggest depletion by geochemical processes, probably due to a long transport and resuspension before deposition. Anthropogenic contamination detected at the shelf adjacent to Tagus is the result of urban wastes and industrial effluents from industries settled for decades in a high-populated region. Guadiana shelf sediment composition shows a significant continental contribution and the influence of the mineral wastes of mining activities. Particularly, the reactivation of the mining exploitation promoted by a British Company during the XIX century – construction of the “Pomarão” fluvial mining port (~50 km upstream) and railway connecting the mines to the ports has induced a clear metal enrichment in shelf sediments.

**Geochemistry of lagoonal and interdune depressions sediments from SW Portuguese Coastal lagoons***M. F. Araújo, A. Cruces, S. Moreira, M.C. Freitas<sup>1</sup>, C. Andrade<sup>1</sup>*

The Albufeira, Melides, Santo André and Sancha lagoons are located in the south western coast of Portugal, the first one in the Trafaria-Espichel stretch and the others in the southern half of the Tróia-Sines bay. In spite of their geographic proximity, specific features and internal dynamics of each unit result in distinct sedimentological and geochemical patterns/signatures. The presence of sand barrier hinders the lagoon-ocean contact in all cases, although in Albufeira, Melides and Santo André, the annual artificial opening of the inlet in spring allows exchange between the lagoonal and marine environments during several days, weeks or even months.

The textural and compositional variability, as well as the concentration values of 21 chemical elements of the lagoonal superficial sediments, were determined. The heavy metals concentration was normalized using the Al as the conservative element and compared with published international reference values (RV). The heavy metals content determined in the superficial sediments was compared and classified according to the concentration thresholds published in the Portuguese legislation that regulates the degree of contamination for dredged materials (DR II, n.º. 141, 21/6/1995): Class: 1 – clean; 2 - slightly contaminated, 3 - moderately contaminated, 4 – contaminated, 5 – very contaminated.

**Geochemistry of sediments from Portuguese estuaries***M. F. Araújo, R. Cardoso, F. Fatela<sup>1</sup>, M.C. Freitas<sup>1</sup>, C. Andrade<sup>1</sup>*

Estuaries are important transitional zones of sediment transfer between fluvial and marine systems, often acting as a sink for sediments. Therefore they may function as archives of Historical contamination and geochemical weathering. Several important rivers with many tributaries, flow across the Portuguese territory and develop estuaries with different typologies along the western coast. Drainage basins have striking differences, either natural: run-off, outcropping lithologies, climate, geomorphology and vegetation cover; and/or due to human occupation: urban centres, agricultural practises, industries, mining and dredging. Fluvial sediments, travelling throughout the Iberian Peninsula and being affected by many factors, are trapped in estuarine environments and/or exported towards the shelf. To establish the background composition it is necessary to separate anthropogenic contamination from elemental concentrations with a lithogenic origin, which varies according to the geology/geochemistry of estuarine catchment's and must be determined individually in each estuary. The geochemical study of several transects collected at different locations in the estuarine regions of Lima, Tagus and Sado rivers was carried out. Geochemical results combined with physico-chemical parameters and sedimentological features allow the establishment of reference values and assessment of heavy metal contamination.

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**Groundwater Resources as Indicators and Archives of Palaeoclimatic Changes***P.M. Carreira, P.G. Fernandes, J.M. Marques<sup>1</sup>, F. Monteiro Santos<sup>2</sup>, D. Nunes*

The regional geomorphology of the region seems to favours a conceptual circulation model for Caldas de Monção thermomineral system where the recharge area is located at south of Caldas de Monção, up hill between 300 and 600 m a.s.l (based on  $\delta^{18}\text{O}$  values). The underground flow paths are associated with the NNE-SSW fault systems and their NW-SE associated systems, issuing these waters when appropriate conditions are found. The geophysical models suggest that those tectonic systems may be deep and filled with mineralized water. The low  $^{14}\text{C}$  content (between  $4.82 \pm 1.00$  pmc and  $7.43 \pm 0.34$  pmc) of Caldas de Monção thermomineral waters (TDIC) together with the absence of  $^3\text{H}$  support the hypothesis of a long circulation path through the subsurface rocks. This hypothesis is corroborated by the minimum depth reached by the Caldas de Monção thermomineral water system (2.2 km) estimated by the geothermometric approach. The  $\delta^{13}\text{C}$  determinations give values in the range of -7 to -6 ‰, indicating a “complex” origin for the  $\text{CO}_2$  in these waters (mixture between atmospheric  $\text{CO}_2$ , decay of organic matter and upper mantle  $\text{CO}_2$ ). Geophysical, isotopic and geochemical studies performed at Caldas de Monção region have increase knowledge on the interaction between local shallow cold groundwater systems and the low-temperature geothermal waters.

This important environmental issue should be addressed either in the exploitation and future development of these low-temperature geothermal resources or/and in the delimitation of well-head protection areas.

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**Groundwater Resources Assessment by Anthropogenic and Natural Contamination Sources***P.M. Carreira, P.A. Fernandes, O. Margo, D. Nunes, L. Ribeiro<sup>1</sup>, E. Peralta<sup>2</sup>*

The work is being focused on the study of the quality of groundwater sources for Human supply and groundwater resources protection and management, through the identification and quantification of pollution sources traced by environmental isotopes ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $^3\text{H}$ ). Isotope techniques can assess the vulnerability of groundwater to pollution from the surface by determining how rapidly it moves and where it is being recharged. Surface waters of pollution can then be determined, e.g. natural, industrial, agricultural, or domestic. Isotope techniques can also identify incipient pollution, providing an early warning when the chemical or biological indicators do not give cause for concern. Some of the projects developed under this aim have to consider the agricultural practices and high industrial areas must be seen as new inputs of pollution in the environment (sediments and hydrological domains) through demographic density increase and growing of organics and toxic contamination. In the particular case of nitrogen isotopes, this tool can offer a direct means of source identification, since the two major sources of nitrate in agricultural areas, fertilizer and manure, have an isotopically distinct  $\delta^{15}\text{N}$  values. The relative contribution of these two sources to groundwater or surface water can be estimated by mass balance. The analysis of  $\delta^{18}\text{O}$  of nitrate in conjunction with  $\delta^{15}\text{N}$  improves the ability to trace nitrate sources and cycling. Preliminary results confirm that major source of nitrate-N in groundwater comes from agriculture and small percentage from natural N cycle and biochemistry origin.

The projects carried out by QAA research group will give scientific proves to support political decisions, taking into account the sustainable development of the region and the appropriate use of Nitrogen fertilizers on the basis of several European and national directives, namely vulnerable regions and EC Water Framework Directive.

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**High Mountain Areas in Catchment Water Resources***P.M. Carreira, D. Nunes, J.M. Marques<sup>1</sup>, J. Espinha Marques<sup>2</sup>, H. Chaminé<sup>3</sup>*

Mountainous areas are usually the source of most of the larger river systems all over the world, and represent some of the “black boxes” in the hydrological cycle. The seasonality and spatial variability of local groundwaters and the complex role of soils, geomorphology, geology, climate, land use and Human activities on the hydrology of mountain areas are rather particular. Special emphasis is dedicated on high mountains and their role and impact on surface water/groundwater interaction at Serra da Estrela region - Central Portugal in order to i) increase knowledge on recharge and discharge processes in this high mountain area and ii) assess snow as a source of thermal water resources, with the aid of isotopic techniques.

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**National Network for Isotopes in Precipitation***P.M. Carreira, M. Fátima Araújo, D. Nunes, P. Valério, M. Correia, L. Araguas-Araguas<sup>1</sup>*

Interpretation of the isotopic composition in terrestrial water (groundwater resources and superficial waters) requires knowledge about the meteoric water that feeds them: rain and snow. Their isotopic composition is quite variable in time and space, and depends on climate, geography, nuclear fallout and other factors. In the follow up of these for more than a decade we are participating in the Global Network for Isotopes in Precipitation (GNIP) in a close collaboration with the Isotope Hydrology Section of the IAEA. The work carried out aims to provide basic isotope data (<sup>2</sup>H, <sup>3</sup>H and <sup>18</sup>O), for hydrological investigations, by determining the temporal and spatial variations of environmental isotopes. The correlation between the water vapour samples and precipitation events in most cases is not clear probably due to the different characteristics of the sampling periods, although a similar evolution can be observed. The large depletion in the isotopic composition found in vapour and rain event samples are associated to the depressions over Atlantic (in front of the Portuguese coast – Mid North Atlantic) or over the British Islands, crossing Portugal mainland from W to E. The atmospheric weather depressions induce a progressive depletion both in rain and water vapour. Regional variations in the <sup>3</sup>H content (monthly data) between littoral and interior stations are probably a result of the oceanic dilution of the tritium content in the atmospheric water vapour. The Isotopic results are compiled and gathered in the IAEA Data Base and disseminated via IAEA publications ([www.iaea.org/programs/ri/gnip/gnipmain.htm](http://www.iaea.org/programs/ri/gnip/gnipmain.htm)), to be used in international hydrogeological and climatologic studies.

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**Hydrology in Urban Areas***P.M. Carreira, D. Nunes, H. Chaminé<sup>1,2</sup>; M.J. Afonso<sup>1,2</sup>, J.M. Marques<sup>3</sup>*

One of the most crucial water-related research issues at the turn of the millennium “Water and Society” with special emphasis dedicated on “Land habitat hydrology in urban areas” and their role and environmental impact on surface water/groundwater recharge and circulation. In urban regions the application of environmental isotope geochemistry includes the assessment of recharge from leaking water mains and sewers, from in situ sanitation, from waste water and from influent surface watercourses. The isotopic techniques most commonly employed are <sup>2</sup>H and <sup>18</sup>O in water and <sup>15</sup>N and <sup>18</sup>O in nitrate (in liquid and solid samples), in combination with major and trace hydrogeochemical indicators.

Rainfall, surface water systems, rivers and lagoons are possible sources of recharge related to groundwater systems. Thus, one question may arise: what is the relative importance of these several potential sources of recharge? To assess the quality/quantity based in hydrogeochemical, isotopic and ecotoxicological parameters and relate them with the underground circulation with the main goal to provide information to support water management and land use planning. A better understanding of urban hydrological cycle will contribute to a proactive management of urban groundwater resources.

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**Gas Geochemistry in CO<sub>2</sub>-rich Thermomineral Waters**

*P.M. Carreira, D. Nunes, M.R. Carvalho, J.M. Marques<sup>1</sup>, G. Capasso<sup>2</sup>, F. Grassa<sup>2</sup>*

In the Portuguese mainland, the greatest number of hot ( $\approx 76^\circ\text{C}$ ) and cold ( $17^\circ\text{C}$ ) CO<sub>2</sub>-rich thermomineral waters are situated in the Northern part of the country, occurring along or near major faults. Such faults should be considered important targets for geothermal exploration in Portugal. A new geochemical approach on the study of the nature of these thermomineral waters will be focused on the geochemistry of the gas associated with those waters. Gas chemical and isotope analyses Gas geochemistry will be used to improve knowledge on subsurface reservoir temperatures using several gas geothermometers. Gas isotopes will give new insights on the sources of gas constituents (crustal rocks, mantle, etc.). Chemical and isotopic signatures of the waters, together with the gas characteristics, will be used to confirm and/or update the preliminary conceptual models of the local and regional fluid circulation, producing new data on the geothermal potential of the northern part of Portuguese mainland. Trace elements in waters will expand the possibilities of quantitative interpretation of specific mineral-solution equilibrium conditions.

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**Arid /Semi Arid Zones Hydrology**

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Geophysical studies when combined with isotope techniques and geochemical data can provide comprehensive information on groundwater dynamics and recharge history, in order to assess arid zones hydrology. On the following up of Research Projects started in 2005 at Santiago Island (Cabo Verde) and in Esssaouira Basin (Morocco) such a multidisciplinary approach has been applied to evaluate the hydrogeological potential of arid zones and environmental / climatic changes. The combination of these different methodologies have been applied in this island with the goal of monitoring fresh-water – salt water interface. The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  data will be used to i) the identification and characterization of the recharge areas and ii) the quantification of amount (%) of mixture between seawater and fresh water. Besides, tritium content measurements will allow obtaining the mean residence time of the water system. <sup>3</sup>H and stable isotope data, together with the accumulation of chloride in the unsaturated zone, can be applied (under piston flow conditions) to provide a record of past recharge and help to reconstruct the antecedent climatic conditions. The obtained data may act as an additional climatic archive of the region. It is important to have in mind that the hydrological balance shows that the rainfall that falls on the islands is distributed in medium periods like following: 67% is evaporated, 20% is drained away as superficial drainage and only 13% recharges the aquifers.

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**Archaeometallurgy – Provenance, technology and use of metallic artefacts**

*M. Fátima Araújo, P. Valério, E. Figueiredo, A.M.M. Soares, J.C. Senna-Martinez<sup>1</sup>, A. Ávila de Melo<sup>2</sup>*

This field combines analytical and archaeological studies concerning the metallurgical activities of the Copper and Bronze Ages in the Portuguese territory. The relationship between archaeometallurgy research with historical, cultural and economical contexts will ultimately enhance our knowledge of those prehistoric societies. The research conducted in Late Bronze Age sites from *Beira Alta* (*Castro da Senhora da Guia*, *Castro de Santa Luzia*, *Castro do Outeiro dos Castelos de Beijós*, *Canedotes* e *Castro da Senhora das Necessidades*) establishes the preponderance of artefacts with an Atlantic typology although constituted by copper-tin alloys instead of the typical Atlantic leaded bronzes. The latter alloy is particularly scarce in this region, probably due to the fact that this is an area exceptionally rich in tin ores, namely cassiterite (SnO<sub>2</sub>). The absence of leaded bronze artefacts in Late Bronze Age *Beira Alta* is also a proof of the reduced exchange system of metallic commodities with the Atlantic world. Contacts with Oriental Mediterranean Cultures are also established by the presence of a few characteristic copper-tin artefacts, namely from the *Castro da Senhora da Guia* (*Baiões*).

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**Non invasive elemental characterization of pre-historic copper-based artefacts***P. Valério, M. Fátima Araújo, A.M.M. Soares, I. Silva*

Research concerning archaeological items requires the use of non invasive techniques in order to protect this significant part of our collective History. Energy Dispersive X-Ray Fluorescence spectrometry is therefore being used in the Archaeometallurgy field. Our work involves the elemental characterization of copper-based artefacts and related materials (e.g. crucibles, slags, etc.) from the Portuguese territory dated from the end of the IV millennium BC until the first half of I millennium BC. Several metallic artefacts from *Castro de Palheiros (Vila Real)* were analysed in order to establish the type of alloy, as well as its major impurities. Chalcolithic materials could be divided into copper with low and high arsenic content, as well as copper with different impurities of tin. Artefacts from the Iron Age occupation of the site are made from copper-tin alloys with low and high lead contents. In a different study, Copper Age materials from *Porto das Carretas (Évora)* provide significant results regarding the arsenical copper metallurgy of this period – artefacts are made from copper with high arsenic content, whereas analysed ore fragments from the same period, are constituted by copper without any traces of arsenic. The slag composition from *Castelo Velho de Safara (Moura)* point out to the local smelting of lead ores.

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**The reservoir effect of coastal waters off the western margin of the Iberian Peninsula***A.M.M. Soares, J. Martins, A. Amaro, J.A. Alveirinho Dias<sup>1</sup>*

Marine shells have not been used as extensively as charcoal or bone samples in absolute chronologies due to the unknown variability of past oceanographic conditions. At present, along the western coasts of Europe active upwelling is restricted to the western margin of the Iberian Peninsula. <sup>14</sup>C content of marine shells can be used a proxy of the upwelling intensity. However, present and past oceanographic conditions must be known in order to use radiocarbon dating of marine shells accurately. Sample pairs (marine shell – charred wood or bone) collected at the same stratigraphic level (and closely associated) from several western Iberian archaeological sites, representing different periods of time, were dated and the regional reservoir effect ( $\Delta R$ ) calculated:  $940 \pm 50$  to  $-160 \pm 40$  <sup>14</sup>C years. This considerable variation suggests a significant fluctuation in the strength of the Iberian coastal upwelling, which may be the result of fluctuations in the latitudinal migration of the subtropical front or of the North Atlantic Oscillation – the strength of northerly and northwesterly winds depends on these factors – or on the summer insulation – higher summer insulation results in increased sea breezes that strengthen the northerly component of the wind. Those data also enable, not only a clarification of the eventual variability of the coastal upwelling off Atlantic Iberia, but also the identification of episodes of abrupt shifts in oceanic circulation, probably coupled with sudden climatic changes. On the other hand, the viability of using radiocarbon dating of marine shells in order to get reliable chronologies was consequently tested out in this research.

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# Inorganic and Organometallic Chemistry

Noémia Marques

The activities of the group comprise the synthesis, characterisation and chemical reactivity studies of inorganic, organometallic and intermetallic compounds of actinides and lanthanides in order to understand the influence of the electronic structure and of the size of these elements in the chemical behaviour of their compounds. Chemical reactivity is assessed by stoichiometric reactions and by homogeneous and heterogeneous catalytic studies. Gas-phase ion chemistry studies with the same elements and the study of the energetic of *f*-element compounds are also made with the same objective.

Relevant facilities maintained in the group are a Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR/MS) laboratory, a laboratory for catalytic studies including work with CO, a laboratory for calorimetric studies and a laboratory for handling macroscopic quantities of the most toxic actinides.

Work on uranium chemistry with the nitrogen donor ligands  $\text{Tp}^{\text{Me}_2}$  and  $(\{\text{SiMe}_2\text{NPh}\}_3\text{-tacn})$  was completed. The results are included in several publications and are part of a PhD Thesis submitted to Faculdade de Ciências da Universidade de Lisboa. Studies on the reactivity of mono- functionalized tacn ligands and bis(phenolate)diamine ligands are now under investigation. Alkyl derivatives of the complexes based on these two type of ligands,  $[\text{MCl}_2\{\text{O}(3,5\text{-}^t\text{Bu}_2\text{Ph})\}_2\text{-tacn}(\text{Pr}_2)]$  ( $\text{M}=\text{Ti}, \text{Y}, \text{Sm}$ ) and  $[\text{MCl}(\text{O}_2^{\text{tBu}_2}\text{NN})(\text{L})]$  ( $\text{M}=\text{Ti}, \text{Y}$ ) are being tested in the polymerization of olefins.

Gas-phase ion chemistry studies of the actinides ( $\text{An}=\text{Th}$  through  $\text{Cm}$ ) by FTICR/MS were continued. The reactions of bare and oxo-ligated  $\text{An}$  cations with hydrocarbons were investigated and revealed a significant 5f-electron participation in organoactinide bond formation for  $\text{Pa}^+$  and  $\text{PaO}^+$ . New  $\text{AnPt}^+$  species were synthesized and the chemistries of  $\text{Uir}^+$ ,  $\text{UPt}^+$

and  $\text{UAu}^+$  examined in the context of the theoretical prediction of strong actinide-transition metal bonds.

Pursuing previous work, we have applied the urea-nitrate combustion method to the synthesis of  $\text{BaO-La}_2\text{O}_3$  and  $\text{MO-CeO}_2$  ( $\text{M}=\text{Ba}, \text{Ca}$ ) nanoparticles, promising candidate catalytic systems for  $\text{CO}_2$  valorization as C1 feedstock, namely through the selective oxidation of methane (OCM reaction).

A collaboration study with Faculdade de Ciências da Universidade de Lisboa and ITQB using the FTICR/MS facility showed that ionic liquids in the gas-phase behave as neutral ion-pairs and proved that it is possible to fractionally distill ionic liquids.

We are also applying our knowledge to environmental studies, particularly in the study of vitrification of radioactive wastes containing actinides and, in collaboration with the Radiation Technologies: Processes and Products group (Physics Sector), in a study of the gamma radiation effect on several waste water sources. Of importance is also a new collaboration with OMNIDEA, Lda., a start-up company dedicated to R&D of aerospace technology and energy systems.

Joint projects with the Faculdade de Belas Artes da Universidade de Lisboa on new lanthanide based fluorescent glasses and with the Glass Museum of Marinha Grande on provenance studies of Portuguese glasses continued.

An important part of the output of the Group has been the training of young research students. Some of the group members have been involved in undergraduate and post-graduate university courses. The work made was financially supported by several projects of FCT, four FCT PhD grants and one Post-doc FCT grant. A ESI mass spectrometer was acquired with support of FCT.

## Research Team

### Researchers

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## *f*-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

M. A. Antunes, B. Vieira, J. Cui, J. M. Carretas, A. M. Martins<sup>1</sup>, N. Marques

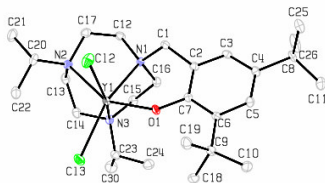
### Objectives

This project aims at to develop new coordination environments for *f*-elements with two main purposes: 1. To create new reactive centres with unusual reactivity patterns. 2. To explore the ability of new ligands in An/Ln separation.

### Results

Work on uranium chemistry with the nitrogen donor ligands  $\text{Tp}^{\text{Me}_2}$  and  $\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}$  (POCTI/QUI/46179/2002) was completed [1]. The results are included in several publications and are part of a PhD Thesis submitted to Faculdade de Ciências da Universidade de Lisboa.

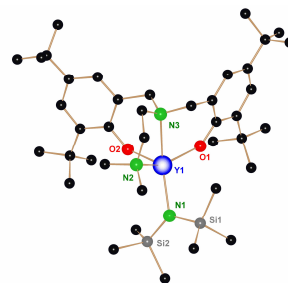
Studies on the reactivity of complexes based on mono-functionalized tacn ligands has proceeded (POCTI/QUI/46202/2002). The ligand  $[(\text{SiMe}_2\text{NPh})\text{-tacn}^{(\text{iPr})_2}]$  allowed the isolation of  $[\text{MCl}_2\{(\text{SiMe}_2\text{NPh})\text{-tacn}^{(\text{iPr})_2}\}]$  ( $\text{M} = \text{Ti}, \text{Y}$ ), but the system was not further explored since the reactions always gave secondary products due to nucleophilic attack on the Si of the  $\text{SiMe}_2\text{NPh}$  arm [2]. Hence, we decided to functionalize the tacn ring with an aryloxy group, due to the more robust character of the M-O bond. The synthesis of  $[\text{OH}(3,5\text{-}^t\text{Bu}_2\text{Ph})\text{-tacn}^{(\text{iPr})_2}]$  has been achieved. As admitted, this ligand gave rise to well characterized  $[\text{MCl}_2\{\text{O}(3,5\text{-}^t\text{Bu}_2\text{Ph})\text{-tacn}^{(\text{iPr})_2}\}]$  ( $\text{M} = \text{Ti}, \text{Y}, \text{Sm}$ ) complexes. These compounds could be derivatized to give alkyl complexes that are being checked in the polymerization of olefins.



Molecular structure of  $[\text{YCl}\{\text{O}(^t\text{Bu}_2\text{Ph})\}\text{-tacn}^{(\text{iPr})_2}]$

Metal complexes,  $[\text{TiCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')(\text{py})]$  and  $[\text{YCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')(\text{DME})]$ , supported by bis(phenolate)diamine ligands  $\text{}^t\text{Bu}_2\text{O}_2\text{NN}'$  ( $[\text{Me}_2\text{N}(\text{CH}_2)_2\text{N}\{\text{CH}_2\text{-(2-OC}_6\text{H}_2\text{-}^t\text{Bu}_2\text{-3,5)}_2\}]$ ), are also under investigation. Attempts to prepare a Ti(IV) cationic complex through reaction of  $[\text{TiCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')(\text{py})]$  with  $[\text{FeCp}_2]\text{PF}_6$  led to the isolation of  $[\text{TiFCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')]^+$ , attesting for the high electrophilicity of the transient titanium cation that is able to abstract a fluoride from the counter-ion. The

synthesis of the amide  $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')]^+$  and the alkyls  $[\text{YR}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')]^+$  ( $\text{R} = \text{CH}_2\text{SiMe}_3$ ,  $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2$ ) by halide metathesis of  $[\text{YCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')(\text{DME})]$  shows that this compound is susceptible to further derivatization. The reactivity of the alkyls towards unsaturated substrates is under investigation. In contrast with the above, formation of a polymeric compound,  $[\text{SmCl}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')]_x$ , was obtained in the reaction of samarium trichloride with the potassium salt of the diamino-bis(phenolate). Metathesis of the chloride led to formation of compounds containing the anion  $[\text{Sm}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')_2]^-$ , showing that one amino-bis(phenolate) is not enough to satisfy the bonding requirements of samarium.



Molecular structure of  $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}(\text{}^t\text{Bu}_2\text{O}_2\text{NN}')]^+$

Studies on Ln/An separation continued in order to understand if one particular ligand is a promising ligand to effect the separation. The bond distances of a U(III) complex, used as a model for An, and La or Nd complexes (with similar ionic radii to that of U(III)) have to be compared in iso-structural complexes. Until now it was not possible to grow crystals adequate to X-ray crystal determinations.

### Published work

1. M.A. Antunes, M. Dias, B. Monteiro, A. Domingos, I.C. Santos, N. Marques, Synthesis and Reactivity of Uranium(IV) Amide Complexes Supported by a Triamidotriazacyclononane Ligand, *Dalton Trans.* (2006) 3368-3374.
2. S. Barroso, J. Cui, A.R. Dias, M.T. Duarte, H. Ferreira, R.T. Henriques, M.C. Oliveira, J.R. Ascenso, A.M. Martins, Titanium(III) Trisamido-triazacyclononane: Reactions with C60 and Radicals, *Inorg. Chem.* 45 (2006) 3532-3537.

<sup>1</sup> Centro de Química Estrutural, Instituto Superior Técnico, Lisboa.

**Gas-Phase Ion Chemistry of Actinides and Lanthanides***J. Marçalo, A. Pires de Matos, J. P. Leal, M. Santos, J. K. Gibson<sup>1</sup>, R. G. Haire<sup>1</sup>*

Fundamental aspects of the chemistry and physics of atomic and molecular actinide ions and neutrals continued to be examined by Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS). Experiments with atomic and molecular lanthanide ions were also performed for comparative purposes. Parallel theoretical studies of selected actinide molecular ions were also carried out via collaborations to substantiate the interpretation of the experimental observations.

The reactions of bare and oxo-ligated actinide cations ( $\text{Th}^+$  through  $\text{Cm}^+$ ) with small alkanes and alkenes were systematically studied. The reactivity trend identified for the highly reactive early actinide ions,  $\text{Th}^+ > \text{Pa}^+ > \text{U}^+ > \text{Np}^+$ , indicated significant 5f-electron participation in organoactinide  $\sigma$ -type bond formation for  $\text{Pa}^+$ . Among the studied  $\text{AnO}^+$  ions,  $\text{PaO}^+$  was distinctively reactive. Electronic structure calculations showed that its ground state is  $\text{Pa}(5f6d)\text{O}^+$  and all excited states up to 1.8 eV have a 5f-orbital occupancy  $\geq 0.8$ . The high reactivity and substantial 5f character of  $\text{PaO}^+$  are a sign of the participation of 5f electrons in hydrocarbon bond activation for oxo-ligated  $\text{Pa}^+$ .

New  $\text{AnPt}^+$  species ( $\text{An} = \text{Th}$  through  $\text{Cm}$ ) were synthesized and the chemistries of  $\text{UIr}^+$ ,  $\text{UPt}^+$  and  $\text{UAu}^+$  examined in the context of “autogenic isolobality” and the theoretical prediction of strong actinide-transition metal bonds. The reactivities of the  $\text{UM}(5d)^+$  ions were dominated by the U metal center, in accord with the concept of “autogenic isolobality”. One noteworthy result was the synthesis of  $\text{IrUO}^+$  which was predicted to exist as a stable species isoelectronic with  $\text{NUO}^+$  and uranyl,  $\text{UO}_2^{2+}$ .

<sup>1</sup> Oak Ridge National Laboratory (Oak Ridge, Tennessee, USA).

**Molecular Energetics of Organic, Inorganic and Organometallic Compounds***J. P. Leal, M. T. Fernandez<sup>1</sup>, C. Hipólito, P. Madeira<sup>2</sup>, L. Richard<sup>3</sup>, R. Simões<sup>3</sup>*

The main objective of this research line is to collect data and rationalize it in a systematic way that enables a deeper knowledge of the energetics of molecules (both inorganic and organic compounds). Special importance is given to f-element compounds (both on solid state and in solution). To achieve this goal, lanthanide and actinide (organometallic and intermetallic), alkaline and alkaline-earth compounds, and hydrocarbons, phenols and ionic liquids were studied.

During 2006, in addition to the determination of new enthalpies of formation for alkaline-earth and lanthanide compounds, the gas-phase acidity of substituted phenols was determined by using FTICR mass spectrometry. In a collaboration study with FCUL and ITQB, again using the FTICR/MS facility, the behavior of ionic liquids in the gas phase was studied showing that neutral ion-pairs are the only gas-phase molecules present. This opens the possibility to fractionally distill ionic liquids, thus allowing their purification.

A critically assessed compilation of existing enthalpies of formation for hydrocarbons was published and those values were used to parameterize an extended Laidler method of additive contributions. The newly parameterized method allows estimating the enthalpy of formation (gas and condensed phase) for virtually any hydrocarbon and, for the first time, a physical meaning was associated to the parameters. The extension of this model to CHON compounds is in progress. New routes for fluoroapatite synthesis were explored and their thermal and structural properties studied.

<sup>1</sup> CQB-FCUL. <sup>2</sup> MSc Student. <sup>3</sup> Undergraduate Student.

**f-Block Element Intermetallic Compounds as Catalysts***J. Branco, A. P. Gonçalves<sup>1</sup>*

Intermetallic compounds of lanthanide or actinide metals combined with d metals have been found to be active in a variety of reactions; however the number of active sites is very low (specific area  $< 1 \text{ m}^2/\text{g}$ ). The main objective of this project is (i) to study binary copper/ or nickel/f-block element as catalysts or catalytic precursors and (ii) to develop new methods for the preparation of nanostructured materials that are currently the focus of considerable interest. Pursuing previous work, we have applied the urea-nitrate combustion method to the synthesis of  $\text{BaO-La}_2\text{O}_3$  and  $\text{MO-CeO}_2$  ( $\text{M} = \text{Ba}, \text{Ca}$ ) nanoparticles, promising candidate catalytic systems for  $\text{CO}_2$  valorization as C1 feedstock, namely through the selective oxidation of methane (OCM reaction). Preliminary results indicate that (i) the number of active sites is clearly superior to that measured on samples obtained by conventional methods, (ii) the f-block element plays a role in their acid-base properties and (iii) under industrial conditions ( $\text{GHSV}=42000 \text{ mLCH}_4/\text{g.h}$ ), the selectivity to C2 ( $\text{C}_2\text{H}_4+\text{C}_2\text{H}_6$ ) on  $\text{BaO-La}_2\text{O}_3$  is very high ( $> 95 \%$ ).

<sup>1</sup> ITN/Chemistry Sector-Solid State Group.

**Synthesis, Characterization and Reactivity Studies of Rare Earth Alkoxides and Aryloxides***J. M. Carretas, C. Hipólito, J. Branco, T. Almeida Gasche, J. P. Leal, A. Pires de Matos*

Alkaline and alkaline-earth metal alkoxides are good models for rare-earth alkoxides and easier to synthesize. Some of the rare-earth alkoxides (Sc, Y, Ln) are easily comparable with their neighbors in the periodic table (Ca and K, Sr and Rb, Ba and Cs, respectively).

In order to explore new patterns and to achieve a deeper insight in these comparisons, alkaline, alkaline-earth and rare-earth phenoxides were synthesized. The used phenoxides possess different substituents and different substitution positions. The intention of this strategy is to understand the substituents contribution for the energetics/structure of the compounds. The measurement of the enthalpies of formation of the phenoxides was made by reaction-solution calorimetry and the structural characterization by powder X-ray and EXAFS.

**Glass Science with Applications in Radioactive Waste Vitrification, Archaeometry and Art Studies***A. Pires de Matos, J. Marçalo, M. Santos, F. Lopes*

We are developing in ITN know how in glass science to contribute to the research on radioactive waste vitrification processes. The study of old glasses and their weathering is also important as the corrosion mechanisms which lead to their alteration concerns the waste disposal. For structural information the main technique we are using is laser ablation Fourier transform ion cyclotron resonance mass spectrometry (LA-FTICR/MS), trying to correlate the gas phase clusters formed with the basic structure of the glass. Sodocalciumsilicate glasses, mixtures of these glasses with sodium tetraborate glasses and tetraborate glasses have been used as hosts for uranium, thorium, cerium, terbium, holmium, and thulium oxides. Some preliminary conclusions were drawn for uranium and terbium: The intensity ratio  $MO^+/M^+$  varies with the bond dissociation energy of the neutral oxide or the ion, the ratio  $MO^+/M^+$  increases with the % of metal oxide added to the base glass and the borosilicate glasses in general shows a more strong M-O bond than the borates or sodocalcium silicate glass.

As we are developing expertise on glass science, particularly in the synthesis and characterization of glasses, we started collaboration with university research groups supported by two FCT projects: one involves provenance studies of Portuguese glass from the 15th to the 20th century and the other concerns the development of new glasses for art applications. The historical glasses have started to be analysed by XRF spectrometry and by ICP/MS and the results obtained in an archaeological excavation in Coia were already reported in an international glass conference. Using some elements a series of new luminescent glasses with rare earths have been prepared, mainly using lanthanide oxides. Quenching of luminescence by d transition elements is being studied.

**Gamma Irradiated Chitosan/pHEMA Membranes for Drug Release Systems***M. H. Casimiro, J. P. Leal, M. H. Gil<sup>†</sup>*

With the purpose of obtaining a biocompatible and sterilized matrix for controlled drug release to be used in direct contact with skin, membranes with different contents in chitosan and hydroxyethyl methacrylate (HEMA) have been prepared by  $\gamma$  irradiation from a  $^{60}\text{Co}$  source.

Despite the fact that membranes naturally exhibit antimicrobial properties, the amoxicillin drug loaded membranes show an insignificant level of haemolysis and present a fast rate of amoxicillin release.

Studies on the influence of membrane thickness show that an optimal thickness for each membrane composition can be obtained. In these conditions, a maximum loading and release of amoxicillin was achieved.

<sup>†</sup>Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra.

# Inorganic and Radiopharmaceutical Chemistry

Isabel Rego Santos

The Group conducts basic and applied-oriented research in modern Radiopharmaceutical Chemistry, an important topic in Life Sciences. Our main goal is to find innovative radioactive tools for **molecular imaging and/or targeted radiotherapy with interest for Nuclear Medicine**. These are emerging fields that aim to integrate patient-specific and disease-specific molecular information with traditional anatomical imaging readouts and to provide *tailor made* therapy. To achieve such goal the Group has developed and implemented expertise on organic, inorganic and organometallic chemistry of *d*- and *f*-elements, radiochemistry, radiopharmacy, cell and animal studies and biochemistry. This combination, **unique in the country**, is also possible due to the facilities implemented and maintained by the Group, such as laboratories and equipment for the synthesis and characterization of inactive and radioactive compounds, animal facility, laboratories and equipment for animal studies, cell culture and biological evaluation of radioactive compounds. Our expertise and infrastructures justify the participation in national and international research projects, the support of an international pharmaceutical company and funding from CIMAGO/FLAD.

**Research:** During 2006, we went on with studies on **halogen and metal *d*- and *f*-based radioactive tools for biomedical applications**. For imaging we have explored mainly the  $\gamma$  emitters  $^{99m}\text{Tc}$  and  $^{67}\text{Ga}$ , while for therapy  $\beta$  and Auger emitters have been studied, namely  $^{153}\text{Sm}$ ,  $^{166}\text{Ho}$ ,  $^{125}\text{I}$  and  $^{99m}\text{Tc}$ . In terms of targeting our interest is on cancer, CNS pathologies and myocardial imaging. **The main scientific**

**achievements are reported in the next pages.** The quality of our basic and applied-oriented research allowed the publication in journals of high impact, as well as the filling of patent applications.

**Education and Training:** At the **graduation level**, the group teaches, in a regular way, Radiopharmacy at the ESTSeL and at the Faculty of Pharmacy/University of Lisbon. Under a collaboration protocol, our facilities are also used every year, during two weeks, by students of the Nuclear Medicine Course, ESTeSL.

**At the post-graduate level** the Group has organized, teaches and coordinates the Master Course *Biomedical Inorganic Chemistry: Diagnostic and Therapeutic Applications* (Third Edition) (DR n° 123, 26/05/04, II série). For this Master Course the group established a collaboration protocol with the University of Lisbon (Faculties of Sciences, Pharmacy and Medicine), Hospital Garcia de Orta and Instituto Português de Oncologia/Lisboa. We have also participated in PhD Teaching Programs organized by other Universities.

**At the International level**, the Group participated in the European Radiopharmacy Course, INSTN and has been partner in the EC/COST RTD ACTIONS, and Virtual Radiopharmacy/V Framework Program.

We have also trained several young scientists, funded by FCT grants, namely **BIC, MSc, PhD and Post-Doctoral** researchers. Our expertise has also been provided to some Nuclear Medicine Centers, to the Portuguese Medicines Evaluation Agency and IAEA.

## Research Team

### Researchers

I. SANTOS, Princ. Researcher, Agregação, Group Leader  
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M. P. C. CAMPELLO, Aux. Researcher  
J. G. CORREIA, Princ. Researcher  
M. C. OLIVEIRA, Aux. Researcher  
C. FERNANDES, Aux. Researcher  
L. GANO, Aux. Researcher  
F. MARQUES, Aux. Researcher  
P. RAPOSINHO, Aux. Researcher

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S. LACERDA, PhD student, FCT grant  
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# Tc(I)/Re(I) Tricarbonyl Complexes Combining a Bis-agostic ( $\kappa^3$ -H, H, S) Binding Motif with Pendant and Integrated Bioactive Molecules

L. Maria, A. Paulo, R. Alberto,<sup>1</sup> I. Santos,

## Objectives

This project aims to introduce small-sized and versatile Tc(I)/Re(I) organometallic building blocks displaying unprecedented coordination environments and suitable for the labelling of bioactive molecules.

## Results

Incorporation of a *d*-transition metal into a biomolecule for molecular imaging is quite challenging, since its metabolic fate and biophysical properties must not be affected. For radiopharmaceuticals in particular, in which *e.g.*  $^{99m}\text{Tc}$  is combined with a receptor targeting molecule the topology, size and molecular weight of the ligands are of utmost importance. Based on dihydrobis(mercaptoazolyl)borates, we were able to demonstrate that one agostic hydride binds very efficiently to the *fac*- $[\text{M}(\text{CO})_3]^+$  ( $\text{M} = \text{Re}, ^{99}\text{Tc}, ^{99m}\text{Tc}$ ) moiety in aqueous media [1]. Coupling of bioactive fragments to this type of ligands led to biocomplexes exhibiting excellent affinity and selectivity for Central Nervous System (CNS) receptors of the 5-HT<sub>1A</sub> serotonergic type [2]. Still, the two mercaptoimidazolyl groups are relatively bulky and we have introduced a novel class of ligands, trihydro(azolyl)borates (azolyl = mercaptoazolyl and benzothiazolyl) which are the smallest soft scorpionates described so far. We have shown, for the first time, that is possible to stabilize Re and Tc tricarbonyl complexes with the trihydro(azolyl)borates which coordinate through two B-H...M agostic interactions and one sulphur atom of the azolyl ring (Fig. 1) [3,4].

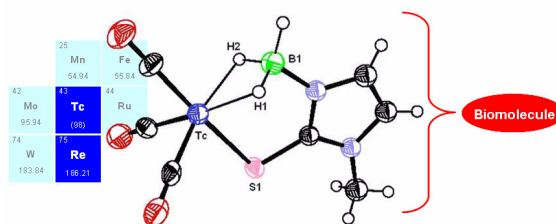


Figure 1

The resulting building blocks were already used to incorporate small biomolecules, using the so-called pendant or integrated approaches (Fig. 1). Most interestingly we have also shown that is possible to prepare these complexes at no carrier level ( $^{99m}\text{Tc}$ ), being the final complexes stable in water and also in the presence of high concentration of chloride. Despite this stability, the B-H...M bonds of some of the

compounds could be selectively cleaved by unidentate  $\pi$ -acceptors yielding "2+1" mixed-ligand complexes in a quantitative way (Fig. 2) which means that these systems can also be useful for labelling biomolecules using the so-called "2+1" approach [5].

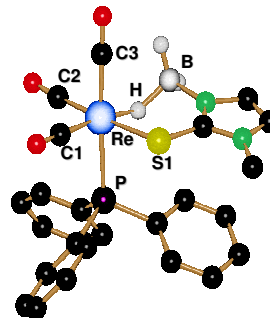


Figure 2

## Published work:

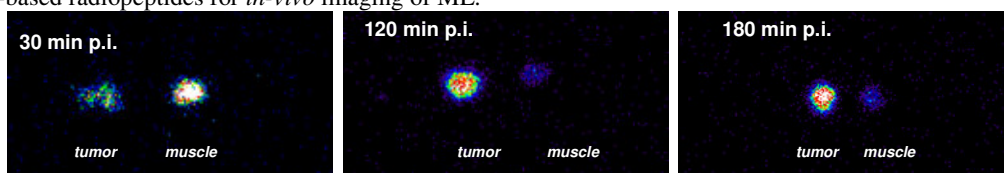
3. L. Maria, C. Moura, A. Paulo, I. C. Santos, I. Santos, Synthesis and Structural Studies of Rhenium(I) Tricarbonyl Complexes with Thione Containing Chelators, *J. Organomet. Chem.* 2006, 691, 4773-4778.
4. R. Garcia, L. Gano, L. Maria, A. Paulo, I. Santos e H. Spies, Synthesis and Biological Evaluation of Tricarbonyl Re(I) and Tc(I) Complexes Anchored by Poly(azolyl)borates: Application on the Design of Radiopharmaceuticals for the Targeting of 5-HT<sub>1A</sub> Receptors, *J. Biol. Inorg. Chem.* 2006, 11, 769-782.
5. L. Maria, A. Paulo, I. C. Santos, I. Santos, P. Kurz, B. Spingler, R. Alberto, Very Small and Soft Scorpionates: Water Stable Technetium Tricarbonyl Complexes Combining a Bis-agostic ( $\kappa^3$ -H, H, S) Binding Motif with Pendant and Integrated Bioactive Molecules *J. Am. Chem. Soc.* 2006, 128, 14590-14598.
6. L. Maria, A. Paulo, I. Santos, Tripodal Ligands with the Coordination Motifs  $\kappa^2$ -BH<sub>2</sub> or  $\kappa^3$ -BH<sub>3</sub> Relevant for Biomedical Applications of Organometallic Complexes (2006) *European Patent Application* 06075127.8.
7. L. Maria, A. Paulo, I. Santos, R. Alberto, Rhenium(I) and  $^{99m}\text{Tc}$ (I) Building Blocks Bearing the ( $\kappa^3$ -S,H,H') Coordinating Motif for the labelling of Small Biomolecules, in *Technetium, Rhenium and Other Metals in Chemistry and Nuclear Medicine* 7. SGEditoriali, Padova, 2006, pag. 127-129.

<sup>1</sup> Institute of Inorganic Chemistry, University of Zürich, Switzerland.

### Imaging of Murine Melanoma Using [ $^{99m}\text{Tc}(\text{CO})_3\text{-pz-NAPamide}$ ]-Conjugate as a Radioactive Probe

P. Raposinho, J. D. G. Correia, I. Santos, M. F. Botelho,<sup>1</sup> C. Santos<sup>1</sup>

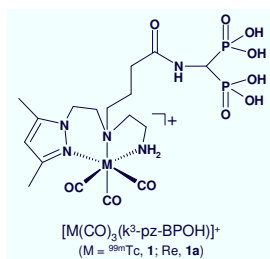
The use of radiolabeled analogs ( $\gamma$ -emitting radionuclides) of the  $\alpha$ -melanin-stimulating hormone has emerged as a promising approach for *in-vivo* targeting of the melanocortin-1 receptor (MC1R), which is overexpressed in melanoma (ML). The analog NAPamide, conjugated to the pyrazolyl-containing backbone (pz) through the Lys residue (Ac-Nle-Asp-His-DPhe-Arg-Trp-Gly-Lys(pz)-NH<sub>2</sub>), was radiolabeled with *fac*-[ $^{99m}\text{Tc}(\text{CO})_3$ ]<sup>+</sup>, and its potential for murine ML imaging was evaluated in ML B16F1-bearing mice. The radiopeptide exhibited a good tumor uptake ( $4.2 \pm 0.9\%$  ID/g, 4h), which is MC1R-mediated as revealed by *in vivo* receptor-blockade with the potent agonist NDP- $\alpha$ -MSH (*ca.* 60% tumor uptake reduction). The highly favorable tumor/muscle ratio (*e.g.* 24 at 4h p.i.) observed, and the long residence in the tumor are also key features for the development of new  $\alpha$ -MSH-based radiopeptides for *in-vivo* imaging of ML.



<sup>1</sup> IBILI, University of Coimbra, Portugal.

### A Bisphosphonate-Containing $^{99m}\text{Tc}(\text{I})$ Tricarbonyl Complex Potentially Useful as Bone-Seeking Agent

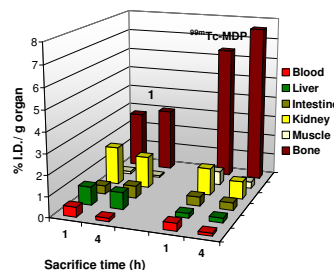
E. Palma, B. Oliveira, J. D. G. Correia, L. Gano, I. Santos



Aiming to develop new bone-seeking radiotracers with improved biological properties, we have prepared new conjugates comprising a pyrazolyl-containing backbone (pz) for metal coordination, and a pendant bisphosphonic acid group.

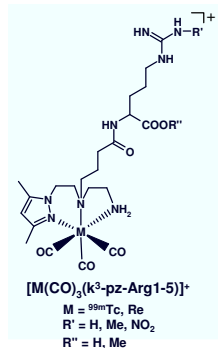
Reaction of this conjugate with *fac*-[ $^{99m}\text{Tc}(\text{CO})_3$ ]<sup>+</sup> yielded (> 95%) the single radioactive species [ $^{99m}\text{Tc}(\text{CO})_3(\text{k}^3\text{-pz-BPOH})$ ]<sup>+</sup> (**1**), which revealed high stability both *in vitro* and *in vivo*. The corresponding Re surrogate (**1a**) was prepared and used for structural characterization of the

radioconjugate by RP-HPLC. Biodistribution studies in mice indicated a fast rate of blood clearance and high rate of total radioactivity excretion, occurring primarily through the renal-urinary pathway. Despite presenting moderate bone uptake ( $3.04 \pm 0.47\%$  ID/g organ, 4 h p.i.), significantly lower than that observed for the commercial product  $^{99m}\text{Tc}$ -MDP, the high stability of **1** and its adequate *in vivo* pharmacokinetics is encouraging for further studies.



### Labeling of *L*-Arginine Derivatives with the Moiety *fac*-[ $^{99m}\text{Tc}(\text{CO})_3$ ]<sup>+</sup> using a Bifunctional Pyrazolyl-Containing Chelator: Chemistry and Radiochemistry

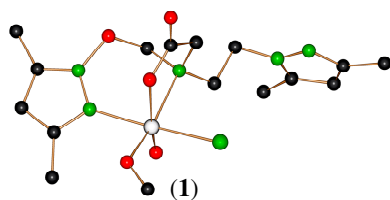
B. Oliveira, J. D. G. Correia, P. Raposinho, I. Santos



The targeting and visualization *in vivo* of Nitric Oxide Synthase (NOS) expression using a radiolabeled substrate/inhibitor of this enzyme (*e.g.* *L*-Arginine derivatives) is a challenging approach that could provide insight into a wide variety of pathophysiological processes. Taking into account our efforts in the development of new radioactive probes for *in vivo* tumor targeting we have prepared and characterized the new conjugates **pz-Arg1-5**, which contain a bifunctional pyrazolyl-containing ligand (pz) for metal stabilization and a pendant *L*-Arginine derivative (*L*-Arg). We have synthesized and characterized the stable (*in vitro*) radioactive complexes [ $^{99m}\text{Tc}(\text{CO})_3(\text{k}^3\text{-pz-Arg1-5})$ ]<sup>+</sup> (**1-5**). The corresponding Re surrogates were also prepared and fully characterized for structural identification/characterization of the organometallic radioactive complexes. Enzymatic studies and biological evaluation of the  $^{99m}\text{Tc}$ -complexes are underway.

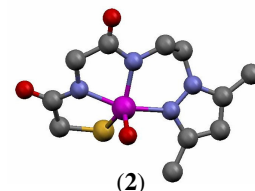
## Novel Metal Fragments Anchored by Pyrazolyl-Based Chelators for Labelling Biomolecules with Clinical Relevance

C. Moura, T. Esteves, P. Campello, A. Paulo, I. Santos



monoxocomplexes, anchored by  $\kappa^3\text{-N}_2\text{O}$  (1) or  $\kappa^4\text{-N}_3\text{S}$  (2) chelators, were fully characterized, either in the solid state or in solution, and their suitability to enter into the chemistry of related M(III) complexes is under investigation. The synthesis of M(V)/M(III) complexes at the no-carrier added level ( $^{99\text{m}}\text{Tc}$ ) is also being studied to assess their interest in the design of target-specific radiopharmaceuticals.

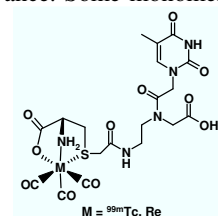
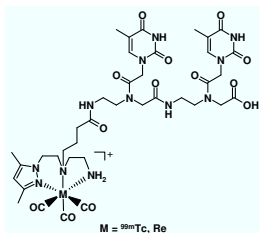
This project searches for novel labelling methodologies based on M(V)/M(III) (M = Re, Tc) metallic fragments anchored by tailor-made chelators of the pyrazolyl type. To achieve this goal, two novel classes of ligands, combining pyrazolyl groups with amino, thiol or carboxylic coordinating functions, were prepared and their coordination capability towards the  $[\text{M}(\text{O})]^{3+}$  (M = Re,  $^{99\text{m}}\text{Tc}$ ) moiety evaluated. The resulting



## Synthesis, Characterization and Stability Studies of Re(I) and $^{99\text{m}}\text{Tc}$ (I) Tricarbonyl Complexes Bearing a PNA Units

C. Xavier, R. Alberto<sup>1</sup>, I. Santos

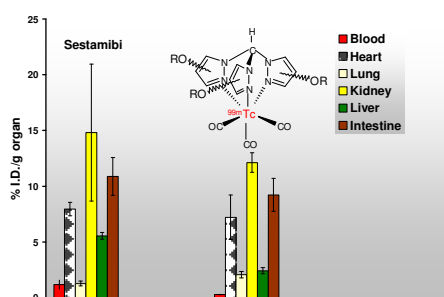
The main goal of this project is to find novel  $^{99\text{m}}\text{Tc}$  probes for non-invasive imaging of endogeneous gene expression, using the antisense approach. Such approach involves the direct or indirect labeling of DNA/PNA sequences with clinical relevance. Some monomeric and dimeric PNA's, having thymine as nucleobase, have been synthesized, characterized and coupled to two chelators with recognized affinity for the  $\text{fac-}[\text{M}(\text{CO})_3]^+$  (M=Re,  $^{99\text{m}}\text{Tc}$ ) moiety. The high specific activity of the  $^{99\text{m}}\text{Tc}$  complexes, as well as their *in vitro* and *in vivo* stability has shown the utility of these tridentate bifunctional chelators for labeling PNA sequences with clinical relevance. These studies are currently underway.



<sup>1</sup> Zurich University, Switzerland

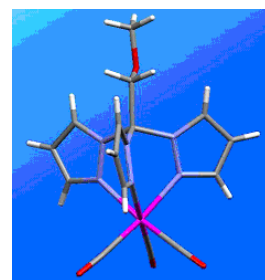
## New Myocardial Imaging Agents Based on $^{99\text{m}}\text{Tc}$ (I) Tricarbonyl Complexes

L. Maria, M. Videira, S. Cunha, L. Gano, A. Paulo, I. Santos



radiopharmaceutical in clinical use for myocardial perfusion studies. The best performing complex is being currently evaluated in other animal models, namely by dynamic studies. Chemical modifications of the tripodal ligands are also underway in order to get a better understanding on structure/activity relationship (SAR) and to further improve the biological performance of the complexes

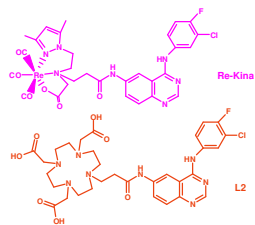
Searching for novel  $^{99\text{m}}\text{Tc}$  compounds suitable for myocardial perfusion imaging we have studied organometallic complexes anchored by tripodal chelators of the tris(pyrazolyl)methane type. When combined with the  $\text{fac-}[\text{M}(\text{CO})_3]^+$  (M = Re,  $^{99\text{m}}\text{Tc}$ ) core, some of these chelators yielded cationic and lipophilic complexes as required for myocardial perfusion imaging. Most relevantly, one of these complexes showed a biodistribution profile in mice similar to Sestamibi®, a



### Novel Biomarkers for Molecular Imaging of Epidermal Growth Factor Receptors Positive Tumours.

C. Fernandes, A. Paulo, M. C. Oliveira, R. Garcia, L. Gano, M.P. Campello, A. Bourkoul<sup>1</sup>, I. Pirmettis<sup>1</sup>, I. Santos

Epidermal growth factor receptors (EGFR) are often over expressed in cancer cells. In our search for the development of novel SPECT/PET radioligands for early detection and staging of EGFR positive tumours new radioactive quinazoline probes labelled with  $^{125}\text{I}$ ,  $^{99\text{m}}\text{Tc}$ ,  $^{111}\text{In}$  and  $^{67/68}\text{Ga}$  are being explored. *In vitro* studies indicate that iodinated quinazoline ( $^{127}\text{I}$ -Kina) inhibits A431 cell



growth possessing higher potency than the parent compound (**1**) to inhibit EGFR autophosphorylation. The coordination of **1** to a metal fragment still leads to compounds (**Re-Kina**) which inhibit significantly EGFR autophosphorylation. This, associated to the *in vitro/in vivo* stability suggests the potential of this class of compounds as biomarkers for molecular imaging of EGFR. To extend these studies to other metals ( $^{67/68}\text{Ga}$ ,  $^{111}\text{In}$ ) the novel conjugate **L2** was synthesized and the preparation of gallium and indium complexes are currently under evaluation.

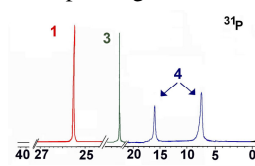
<sup>1</sup> Institute of Radioisotopes -Radiodiagnostic Products, NCSR "Demokritos", Athens, Greece



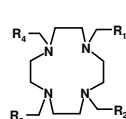
### Pharmacokinetics Tuning of Radiolanthanide Complexes by Modification of Functional Groups Anchored on Tetraazamacrocycles

M.P. Campello, F. Marques, L. Gano, S. Lacerda, M. Balbina, M. Försterová<sup>1</sup>, P. Hermann<sup>1</sup>, I. Lukes<sup>1</sup>, I. Santos

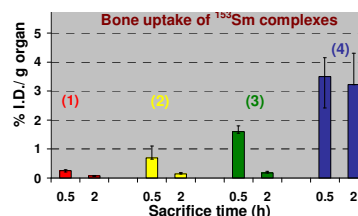
New cyclen derivatives with different pendant arms have been synthesized and characterized to evaluate the effect of the pendant arms on the pharmacokinetics of the corresponding  $^{153}\text{Sm}/^{166}\text{Ho}$  complexes. All complexes have



shown fast complexation rate, good *in vitro/in vivo* stability, rapid clearance from most organs and rapid total excretion. The main differences are related with the highest accumulation and the longest residence in bone of complexes with ligand **4**, which highlights the importance of the number and type of phosphonic appended arms. Radiochemical and biological behaviour of complexes has proven their ability for targeted radionuclide therapy.



- |                                                                                                   |          |
|---------------------------------------------------------------------------------------------------|----------|
| $\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4 = \text{P}(\text{O})(\text{OH})(\text{OEt})$      | <b>1</b> |
| $\text{R}_1, \text{R}_2, \text{R}_3 = \text{COOH}$ $\text{R}_4 = \text{P}(\text{O})(\text{OH})_2$ | <b>2</b> |
| $\text{R}_1, \text{R}_3 = \text{COOH}$ $\text{R}_2, \text{R}_4 = \text{P}(\text{O})(\text{OH})_2$ | <b>3</b> |
| $\text{R}_1 = \text{COOH}$ $\text{R}_2, \text{R}_3, \text{R}_4 = \text{P}(\text{O})(\text{OH})_2$ | <b>4</b> |

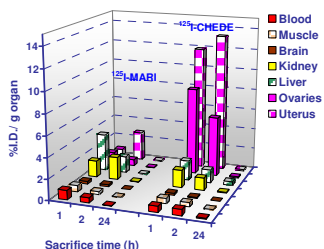


<sup>1</sup> Dpt of Inorganic Chemistry, Univerzita Karlova, Prague, Czech Republic.

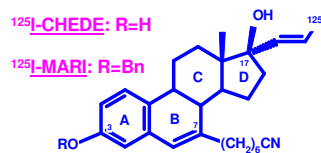
### Novel Estrogen Receptor Ligands as Potential Probes for Targeted Tumour Imaging and Therapy

C Neto, M C.Oliveira, L.Gano, F.M. Marques, G. Morais<sup>1</sup>, T. Thiemann<sup>1</sup>, A C Santos<sup>2</sup>, F. Botelho<sup>2</sup>, C Oliveira<sup>2</sup>

Following our previous work on new ligands for targeted therapy and/or imaging of breast cancer a set of radioiodinated C7-substituted  $17\alpha$ -iodovinylestra-1,3,5(10),6-tetraene-3,17 $\beta$ -diols are being evaluated to study the effect of a C7-alkyl chain on the biological behaviour of the parent compound. Thus,  $^{125}\text{I}$ -CHEDE was obtained in high radiochemical purity and specific activity. Biodistribution



studies in immature female rats have shown high target tissue uptake and selectivity suggesting the potential application of this novel class of compounds for imaging and therapy of ER rich tumours. Specific binding studies are currently underway. The influence of C3-benzyl group ( $^{125}\text{I}$ -MARI) on the biological behaviour of the compound was also evaluated by comparing the biological profiles. The sharp decrease of target tissue uptake supports the importance of a free phenol



group for estrogen receptor binding.

<sup>1</sup> Interdisciplinary Graduate School of Engineering Science, Kyushu University, Japan, <sup>2</sup> CIMAGO, FMUC, Coimbra

# Solid State

*Manuel Leite de Almeida*

The Solid State Group in the Chemistry Department has developed during the past years a broad range of expertise in complementary areas of solid state science and focused, under a global approach, on selected new materials with unconventional electrical and magnetic properties. The nature of the group is multidisciplinary combining expertise ranging from the synthetic chemistry of either molecular materials with transition metal complexes or intermetallic compounds, to many different specialised solid state characterisation techniques. Among the more relevant facilities developed, operated, and maintained by in the group are a high temperature laboratory with crystal growth techniques (Czochralski, Bridgman and float zone), X-ray diffraction (single crystals and powder), EPR and Mössbauer spectroscopy, measurements of magnetisation by Faraday and extraction techniques and AC-susceptibility, different electronic transport measurements and heat capacity, in a broad range of temperature and magnetic field. The use of all these specialised characterisation techniques, often requiring low temperatures down to 0.3 K and high magnetic fields up to 18 T, lead to the development of facilities and expertise in cryogenics unique in Portugal. The group was responsible for the installation at ITN in 1991 of a helium liquefier, which since then remains the only one operational in Portugal, serving also to many users outside ITN.

This year the cryogenic facilities of the group were moved to new labs in a recently refurbished building allowing significantly better operational conditions and a future development of activities.

The rare combination of the **preparative chemistry** expertise with the specialised **solid state physics** techniques enables the group to deal with different problems of modern materials science. Thanks to the valuable techniques developed, the group often act as a key partner of many national and international

research projects. His activities have been centred in strategic selected type of materials, namely:

- Molecule based conducting and magnetic materials.
- Intermetallic compounds with *f*-elements.

The specific ongoing research projects are described in more detail in the following sections.

The group has an established tradition of research on **molecular conductors** since its origin at Sacavém. The two chain compounds, originally reported almost 3 decades ago, remained at the centre of important discoveries as model quasi-1D Charge Density Wave systems. New, still rare, examples of metals based on single component neutral species have been obtained.

Profiting from common molecular precursors, synthetic procedures and characterisation techniques, the interests of the group have been extended during the last years to **molecular magnetism**. In the framework of the Network of Excellence **MAGMANet** the study of switchable magnetic materials with possible conducting properties was initiated.

The research on **intermetallic compounds**, initiated in 1992, pursued with emphasis on the study of phase diagrams of the type (*f*-element)-(*d* metal)-(*p*-element) were new compounds with strongly correlated electronic behaviour and complex magnetic structures have been characterized. New intermetallic borides and thermoelectric materials were also studied. The know how of the group in this field was applied in an industrial contract for fabrication of research reactors fuel elements.

A significant output of the group has been the **training and education of young scientists** which always plays a major role in its projects. The collaboration in several educational activities at the Universities including undergraduate courses was pursued.

## Research Team

### Researchers

M. ALMEIDA, Princ. Researcher, Group Leader  
R. T. HENRIQUES, Assoc. Professor, IST  
V. GAMA, Princ. Researcher  
J. C. WAERENBORGH, Princ. Researcher  
A. P. GONÇALVES, Princ. Researcher  
E. B. LOPES, Aux. Researcher  
L. C. J. PEREIRA, Aux. Researcher  
I. C. SANTOS, Aux. Researcher  
  
D. BELO, Pos Doctoral, FCT grant  
S. DIAS, Pos Doctoral, FCT grant (since November)  
P. GACZYNSKI, Pos Doctoral, FCT grant  
S. RABAÇA, Pos Doctoral, FCT grant  
S. SÉRIO, Pos Doctoral, FCT grant  
O. SOLOGUB, Pos Doctoral, FCT grant

### Students

M. DIAS, PhD Student, FCT grant  
M. FIGUEIRA, PhD student, FCT grant  
J.P. NUNES, BIC grant  
A. GULAMHUSSEN, BIC grant  
C. DUARTE, PEPAP grant  
M. MOURA, PEPAP grant  
T. MENDES, AID grant  
B. RIBEIRO, Undergraduate student, Magmanet grant  
A. NEVES, Undergraduate student

### Technical Personnel

P. LIMA, PEPAP grant.

### Collaborators

A. CASACA. Adjunct Professor, ISEL



# Magnetic and strongly correlated electron behaviour in intermetallics

J.C. Waerenborgh, A.P. Gonçalves, L.C.J. Pereira, E.B. Lopes,  
S. Sérgio, P.M. Gaczyński, M. Almeida

## Objectives

Detailed understanding of the magnetic and strongly correlated electron behaviour of intermetallics, in particular the role of the actinide or rare-earth of those based on *f* and *d* elements.

## Results

The study of  $\text{AFe}_x\text{T}_{12-x}$  ( $\text{A} = \text{Ln}, \text{An}$ ;  $\text{T} = d$  or *p* element) intermetallics, mainly crystallizing in the  $\text{ThMn}_{12}$ -type structure, has been the subject of a long-term project in the Solid State group. Their simple crystal structures, allied with the possibility of a considerable range of compositions, allow a deep study of the *f* and the neighbour elements influence on their physical properties.

Controversial and complex magnetic properties, including long-range magnetic order and spin glass behaviour, had been reported for  $\text{AFe}_x\text{Al}_{12-x}$  compounds. In a first stage of this project we have shown that their magnetic properties are strongly dependent on very small chemical and/or atomic site distribution changes and were able to establish the accurate chemical and structural configurations corresponding to different ground-state magnetic properties. Presently an investigation on the dynamic magnetic properties in the 4-300 K temperature range is performed. Linear and non-linear (2nd and 3rd harmonics) ac-susceptibility together with relaxation times deduced from Mössbauer spectroscopy evidenced uncorrelated nanosized ferromagnetic clusters in the  $\text{YFe}_x\text{Al}_{12-x}$  ( $4 \leq x \leq 6$ ) at temperatures above the onset of long-range magnetic interactions. Coexistence of ferromagnetism and cluster glass (rather than spin glass) behaviour was also established for the compounds with higher Fe content.

In the case of  $\text{UFe}_3\text{Al}_9$  an anomaly, suggestive of ferromagnetic-type transition, is observed at  $T = 25$  K

anomaly. This apparent contradiction can be explained by the Fe 75% occupation of the 8*f* crystallographic site, with the consequent formation of Fe-rich uncorrelated clusters where ferromagnetic-like order may exist. As the ordered U magnetic moments critically depend on crystalline order, randomness in Fe exchange interactions can lead to a complete elimination of long-range magnetic order.

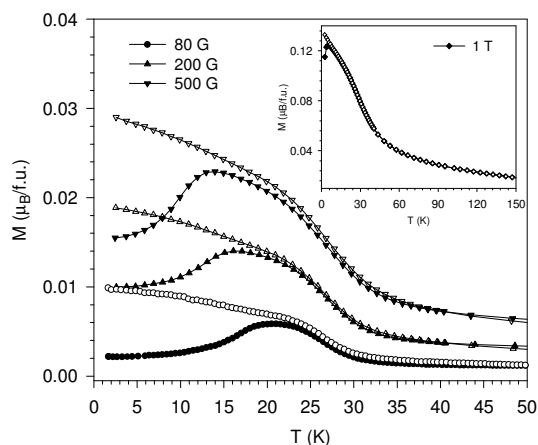
The model previously developed for the analysis of Mössbauer spectra established the effect of hydrogenation and Fe coordination on the electronic and magnetic properties of the Fe atoms in  $\text{RFe}_{11}\text{Ti}$  and  $\text{RFe}_{11}\text{TiH}_x$  ( $\text{R} = \text{Y}, \text{Gd}, \text{Er}$ ,  $x=0, 1$ ) [2].

The influence of the actinide element was analysed from the  $\text{NpFe}_4\text{Al}_8$  study [3]. This compound shows a ferromagnetic-type transition at 135 K followed by a small anomaly at 118 K, which were assigned to Fe and Np magnetic orderings, respectively. This behaviour contrasts with that observed in  $\text{UFe}_4\text{Al}_8$ , where only one transition is observed at 150 K, and can be explained by the contraction of the 5*f* orbitals along the actinide series which led to smaller (5*f*)-(Fe 3*d*) hybridisation and the consequent decoupling of the Fe and Np orderings.

Several other compositions have been studied during 2006. In particular hydrides of  $\text{U}_2\text{T}_2\text{X}$  [3], that are very sensitive to H absorption, were explored. The introduction of H, preserving the crystal structure but expanding the unit cell, enables to study the impact of the 5*f*-ligand hybridization in a systematic way.

## Published work (selected)

1. A.P. Gonçalves, L.C.J. Pereira, J.C. Waerenborgh, D.P. Rojas, M. Almeida, L. Havela, H. Noël, Crystal structure and magnetic properties of  $\text{UFe}_3\text{Al}_9$ , *Physica B* 373 (2006) 8-15.
2. P. Gaczyński, H. Drulis, J.C. Waerenborgh, Mössbauer effect studies of  $\text{RFe}_{11}\text{Ti}$  and  $\text{RFe}_{11}\text{TiH}$  ( $\text{R} = \text{Y}, \text{Gd}, \text{Er}$ ), *J. Magn. Magn. Mater.* 302 (2006) 503-510.
3. A.P. Gonçalves, M. Almeida, F. Wastin, E. Colineau, P. Boulet, P. Javorský, J. Rebizant, Electrical resistivity and specific heat studies of  $\text{NpFe}_4\text{Al}_8$ , *J. Alloys Compd.* 416 (2006) 164-168.
4. K. Miliyanchuk, L. Havela, A.V. Kolomiets, S. Daniš, L.C.J. Pereira, A.P. Gonçalves, Magnetism in hydrogen-doped  $\text{U}_2\text{T}_2\text{X}$  compounds, *Physica B* 378-380 (2006) 983-984.
5. S. Sérgio, J.C. Waerenborgh, A.P. Gonçalves, M. Almeida, M. Godinho, Effect of Fe site distribution on  $\text{UFe}_4\text{Al}_{8-x}\text{Ga}_x$  ( $x = 1.0$  and  $1.5$ ) and  $\text{UFe}_x\text{Al}_{12-x}$  ( $4.5 \leq x \leq 5$ ) magnetic properties, *J. Magn. Magn. Mat.* 302 (2006) 282-289.
6. A.P. Gonçalves, J.C. Waerenborgh, S. Sérgio, J.A. Paixão, M. Godinho, M. Almeida, Structural and magnetic properties of  $\text{UFe}_6\text{Ga}_6$ , *Intermetallics* 14 (2006) 530-536.

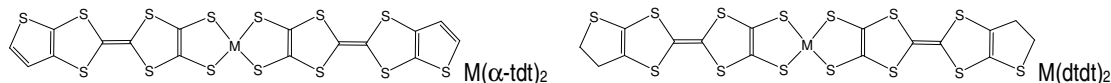


[1]. Specific heat and  $^{57}\text{Fe}$  Mössbauer data indicate that neither long-range magnetic ordering nor standard spin-glass behaviour is associated with the magnetic

**New extended transition metal-bisdichalcogenide complexes for molecular materials.**

*D. Belo, M. Figueira, J. P. Nunes, B. Ribeiro, E. B. Lopes, I. C. Santos, M. Almeida, R. T. Henriques<sup>1</sup>, M. T. Duarte<sup>1</sup>, D. P. Simão<sup>1</sup>*

This project aims to explore new bisdichalcogenide complexes based on highly extended multisulfurated ligands for the preparation of conducting/magnetic molecular materials. Extended systems are expected to stabilize higher oxidation states and provide larger solid state interactions.



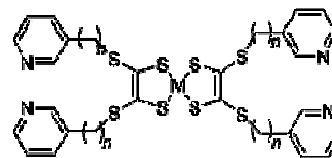
The Ni and Au complexes based on the novel dithiolene ligands containing fused TTF and thiophenic moieties ( $\alpha$ -tdt, dtdt) were obtained and characterized. These complexes are obtained initially in Ni<sup>II</sup>, Au<sup>III</sup> anionic states, in several polymorphic phases, as judged by four Au complexes crystal structures solved of and one of Ni. All these structures all very rich in S...S contacts making extended 2D networks. The anionic complexes are readily oxidized to the neutral state both by iodine oxidation and upon air exposure. The neutral complexes, so far only obtained as a microcrystalline powder were found to exhibit as polycrystalline samples a high electrical conductivity that can reach 200 S/cm with a true metallic character in the case of Ni(dtdt)<sub>2</sub> compound. Thus these compounds are new and still rare examples of a recent class of metallic materials based on neutral single molecular component. Preliminary magnetic susceptibility data show a Pauli-type behaviour. The characterization of these neutral complexes as well as the exploration of related ligands and metals is under way.

<sup>1</sup> Dept. Engenharia Química, IST, Univ. Técnica de Lisboa, Portugal.

**Complexes based on divalent thio-azo ligands for heterobimetallic networks**

*S. Rabaça, S. Dias, C. Duarte, I. C. Santos, M. Almeida*

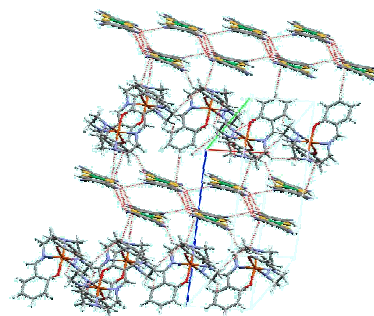
Divalent ligands containing both sulphur and nitrogen coordinating atoms have remained essentially unexplored in spite of an enormous potential to be used as key building blocks for preparing heterobimetallic magnetic networks and novel supramolecular coordination architectures. Following the synthesis of the first example of a tetra-azo substituted bisdithiolene complex, Ni(dpesdt)<sub>2</sub>, (dpesdt=bis(2-pyridylethylsulfanyl)-1,3-dithiol), the structure analysis of this neutral Ni<sup>IV</sup> complex revealed two polymorphs. Related thio-azo ligands with variable chain lengths were synthesized and the corresponding complexes were explored. The synthetic route of the divalent ligand 1,10-phenantroline-5,6-dithiol was also developed through the preparation of the corresponding dibenzyl precursor. The first nitrogen coordinated Fe complexes with these ligands, have been obtained and are currently under characterization.

**Towards Switchable Magnetic Conductors; Salts of [M(dcbdt)<sub>2</sub>] with Fe spin crossover cations**

*A. Galamhussen, L. C. J Pereira, I. C. Santos, V. Gama, M. Almeida*

The preparation of switchable magnetic conductors remains an important challenge in molecular materials science. Bisdithiolene transition metal complexes such as the series M[(dcbdt)<sub>2</sub>] prepared in our group are known as providing high conductivities in partially oxidized anionic states and therefore are good candidates to be combined with cationic spin crossover cations in order to obtain switchable molecular conductors.

The salts of [M[(dcbdt)<sub>2</sub>]]<sup>-</sup> (M = Ni, Au) anions and spin crossover cationic complexes such as [Fe(sal<sub>2</sub>trien)]<sup>+</sup>, related complexes such as [Fe(bpy)<sub>3</sub>]<sup>2+</sup> and [Fe(phen)<sub>3</sub>]<sup>2+</sup> were obtained and characterized by single crystal x-ray diffraction and magnetic measurements. In spite of segregated anions and cations in the crystal structure, with an extended anionic network of close contacts, the stoichiometry of the salts obtained does not allow high conductivity. These salts show the loss of a spin crossover behaviour but, depending on the paramagnetic (M=Ni) or diamagnetic (M=Au) nature of the anion, different magnetic behaviour are observed. These salts open however the possibility of obtaining spin crossover conducting materials upon the partial oxidation of the anions, to be undertaken subsequently.



### Metal bisdichalcogenates Based Magnetic Materials

*D. Belo, M.J. Figueira, S. Rabaça, L.C.J. Pereira, I. C. Santos, M.T. Duarte<sup>1</sup>, V. Gama, M. Almeida*

In order to achieve a better understanding of the structure-magnetic properties relationship we have studied a large series of charge transfer salts based on metal bisdichalcogenate acceptors (A) with a variety of donors (D) such as decamethylmetallocenes ( $[M(Cp^*_2)]^+$ ) or benzylpyridinium (BzPy) derivatives. The magnetic behaviour of these materials is correlated with the crystal structure and the magnetic intermolecular coupling is analysed in the framework of McConnell I mechanism.

The  $[M(Cp^*_2)]^+$  salts show a crystal structure based on arrangements of parallel mixed chains, where the repeat unit, {DA}; {(DD)/AA)} or {DDA}, in the chains is strongly dependent on the size of the acceptor. A large variety of magnetic behaviours were observed in these salts (metamagnets, ferrimagnets, frustrated magnets). Recently negative coercivity was observed in case of  $[M(Cp^*_2)][Ni(\alpha\text{-tpdt})_2]$  ( $M = Fe$  and  $Mn$ ) that is quite unusual among bulk materials, in fact this phenomena was previously reported only in two other materials.

In the crystal structure of the salts based on the BzPy derivatives, the acceptors show a tendency to form zig-zag chains, with an almost perpendicular arrangement between adjacent acceptors. Furthermore frequently side by side chains give rise to 2D acceptors sheets. A large number of these compounds show canted AFM and/or spin-glass behaviours. The canted AFM behaviour is attributed to the intrachain arrangement of the acceptors and the glassy behaviour of the magnetisation is essentially associated with *cis-trans* disorder that is present in some of the acceptors.

<sup>1</sup> Dept. Engenharia Química, IST, Univ. Técnica de Lisboa, Portugal.

### Two-Chain Compounds under High Magnetic Field

*M. Almeida, M. Figueira, R. T. Henriques, M. Matos<sup>1</sup>, J. S. Brooks<sup>2</sup>, D. Graf<sup>2</sup>,*

(Perylene)<sub>2</sub>M(mnt)<sub>2</sub> compounds with  $M = Au, Pt, \dots$  initially reported by our group more than 20 year ago still offer a unique chance to investigate the coupling between two types of chains (conducting and magnetic) in the same solid and to test the theoretical predictions for the behaviour of quasi 1D CDW systems under large magnetic fields.

Systematic electrocrystallisation essays for growth of  $Per_2Mt(mnt)_2$  single crystals of high quality were extended to other metals such as  $M = Cu, Ni, Co$  and  $Fe$  enabling, in collaboration with the NHMFL, to extend to them the physical measurements previously restricted to  $Au$  and  $Pt$  compounds. The  $Co$  compound shows a different behaviour of the CDW transition that is enhanced under pressure. The study of the magnetoresistance of  $In$  the  $Au$  and  $Pt$  compounds under pressure revealed that the CDW state is suppressed and it is recovered a metallic state with quantum oscillations of magnetoresistance, reaching the quantum limit at circa 18T which are ascribed to a Stark interference rather than to Schubnikov-de Haas.

<sup>1</sup>- Instituto Superior de Engenharia de Lisboa., <sup>2</sup>- NHMFL/Physics, Florida State University, Tallahassee, FL32310, USA.

### Study of Ternary Phase Diagrams based on *f* and *d* elements

*A.P. Gonçalves, O. Sologub, M. Dias, L.C.J. Pereira, S. Sérgio, J.C. Waerenborgh, P.A. Carvalho<sup>1</sup>, O. Tougaard<sup>2</sup>, H. Noël<sup>2</sup>*

The main objective of this research line is to explore (*f*-element)-(*d*-metal)-X ternary systems in order to determine the phase relations, and identify, synthesise and characterise new intermetallic compounds based on *f* and *d* elements. The study of ternary phase diagrams also gives fundamental information for the preparation of single-phase samples and growth of single crystals. During 2006 was continue the study ternary systems of the type U-Fe-X and (*f*-element)-(*d* metal)-B.

The isothermal section at 950°C of the U-Fe-B phase diagram was determined and two new compounds,  $U_2Fe_{21}B_6$  and  $UF_4B$ , were identified. Prior studies of the R-M-B ( $R = Y, Gd, Tb, Er$ ;  $M = Pt, Ni$ ) ternary systems allowed the identification of four new ternary compounds,  $YPt_2B$  and  $RNi_4B$  ( $R = Gd, Tb, Er$ ). These intermetallics were prepared as single-phase samples and their crystal structures and physical properties were characterised.

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### Materials for solid oxide fuel cells and dense ceramic membranes

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Development of novel materials based on iron-containing oxide phases with perovskite or perovskite-derived structures, with mixed oxygen-ionic and electronic conductivity and high oxygen permeability, attract significant attention for energy-related electrochemical technologies, such as electrodes of solid oxide fuel cells (SOFCs) and ceramic membranes for conversion of natural gas and biogas.

In 2006 our investigation on the improvement of the properties of the  $\text{SrFeO}_{3-d}$  based perovskites by partial substitution of Sr by rare-earths was mainly focused on the study of perovskite-type  $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-d}$ , by coulometric titration, thermogravimetry and Mössbauer spectroscopy. We have found that oxygen deficiency in these Pr-containing materials is significantly higher than in  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-d}$ . At 973-1223 K the presence of Pr does not alter any of the conduction mechanisms but decreases the charge-carrier mobility due to the smaller radius of the  $\text{Pr}^{3+}$  cations stabilized in the perovskite lattice. Ce and Nb doping of the  $\text{SrFeO}_{3-d}$  based perovskites was also studied. The investigation of brownmillerite-type  $\text{Ca}_2\text{Fe}_2\text{O}_5$ , undoped or with Fe and Al partially substituted by Mg and Zn was initiated.

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### Mössbauer spectroscopy in Materials Science

J. C. Waerenborgh, P. Gaczyński, S. Sério

A Mössbauer spectroscopy laboratory has been developed in ITN for 25 years in order to support internal and external research projects. In 2006 this lab was relocated in a larger space in a recently modernised building, thus acquiring better operational conditions and expansion possibilities. Presently, in the ITN Mössbauer laboratory  $\gamma$ -ray transmission and backscattering as well as conversion electron Mössbauer spectra may be obtained using 3 different spectrometers and cryostats. Transmission spectra may be taken with the sample in the 300-2.2 K temperature range and in external magnetic fields up to 5 T. The expertise developed in ITN has been, in the last years, able to assist other national or foreign research institutions in the frame of joint research projects as well as supporting those who develop their own Mössbauer facilities. During 2006 in addition to the above described projects these facilities have made possible other studies namely carbonate stones used as building materials, new molecule-based multifunctional materials and intermetallics (using both  $^{57}\text{Co}$  and  $^{119\text{m}}\text{Sn}$  sources) in collaboration, with Technical Univ. of Lisbon, Univ. of Valencia, Spain, Univ. of Rennes, France and Charles University, Prague, respectively.

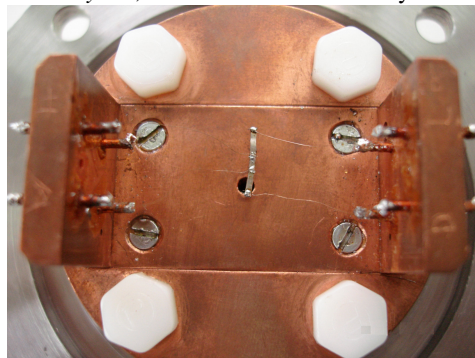
### Study of new materials for thermoelectrical applications

A.P. Gonçalves, E.B. Lopes, M. Moura, B. Ribeiro, E. Alleno<sup>1</sup>, C. Godart<sup>1</sup>

The discovery and optimization of new environment-friendly energy sources has become one of the main objectives of modern societies. Thermoelectric materials make possible to directly convert electrical energy into thermal energy (Peltier effect) and, reversibly, thermal energy into electrical energy (Seebeck effect).

The main objective of this project is to study new materials for thermoelectrical applications. Actual thermoelectric devices are based on compounds discovered in the 50s (mainly  $\text{Bi}_2\text{Te}_3$  based). The recent development of new concepts, like the *Phonon Glass* and *Electron Crystal*, has lead to the discovery of new compounds with better thermoelectrical properties, like skutterudites, clathrates, half-Heusler, oxides, etc.

During 2006 the thermoelectrical properties of several intermetallic compounds were studied. In particular compounds with the general formula  $\text{CeM}_x\text{Sb}_2$  ( $\text{M} = \text{Cu}, \text{Pd}, \text{Au}$ ) and  $\text{Ce}_6\text{MnSb}_{15}$ , were explored. This last compound was observed to behave as a metal, with a small and negative value of the Seebeck coefficient albeit the high Sb content. The  $\text{CeM}_x\text{Sb}_2$  compounds show a behaviour typical of a Kondo system, with a maximum of the Seebeck coefficient at low temperatures. However, the relatively small value of this maximum ( $\sim 30 \mu\text{V/K}$ ) prevents the use of this series of materials for cooling applications.



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**High magnetic field facility**

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This unique infrastructure in Physical above the study of electrical transport properties under magnetic fields up to 18 T and for temperatures in the range from 0.3 to 300 K, using both AC and DC techniques. The magnetic field is generated by a superconducting coil inside an OXFORD nitrogen free cryosystem. In 2006, the facility was transferred to a new and more spacious laboratory, with improved functionality and the data control and acquisition were fully automated using a LabVIEW software developed by us.

This facility allowed pursuing two main areas of research: magnetic semiconductors and boride superconductors. Magnetic semiconductors constitute an exciting field of research due to the vast possibilities of application in spintronics. We continued our studies on metallic ion irradiated semiconducting films (such as TiO<sub>2</sub> or ZnO films irradiated with Co<sup>+</sup> ions), by measuring the magnetic field response of the DC electrical resistivity.

The recently discovered Y<sub>3</sub>Os<sub>8</sub>B<sub>6</sub> ternary boride superconductor was characterised by AC resistivity measurements as a function of temperature, both in zero applied field and under different applied magnetic fields. The results clearly put into evidence a type II behaviour of the compound, with a broadening of the resistive transition under magnetic field as a result of vortex motion phenomena.

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