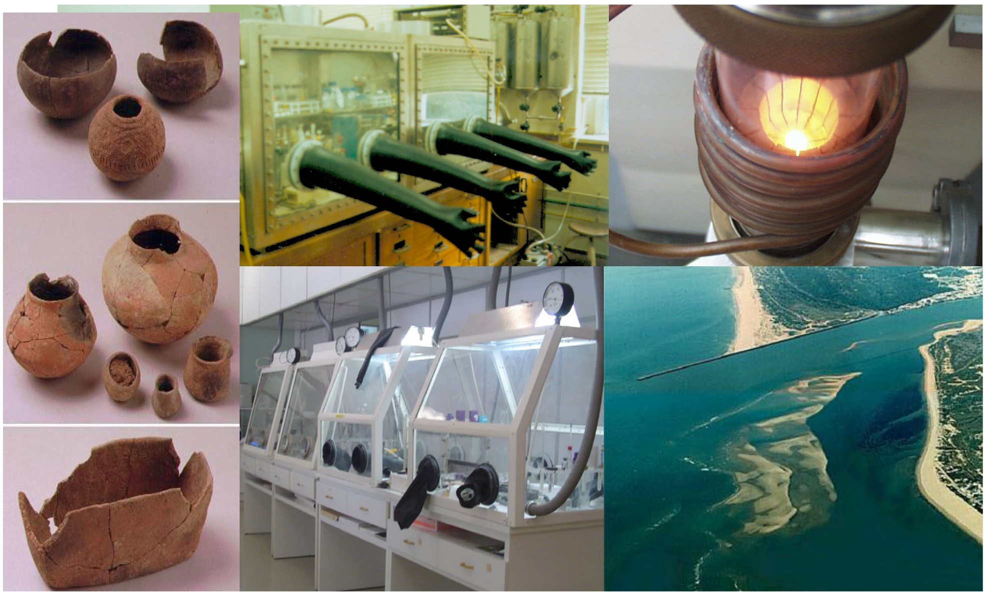
Chemistry Sector



Chemistry

Maria de Fátima Araújo

Research conducted at the Department is dedicated to the development on the synthesis of inactive and radioactive compounds oriented to the progress in health and materials sciences and catalysis. A major field is the use of nuclear based and related methods to environmental and earth sciences and cultural heritage. Activities are organized in five areas:

Solid State – the group focus its research activity on new materials with unconventional electrical and magnetic properties. It combines a high expertise on preparative chemistry of molecule based conducting and magnetic materials and of intermetallic compounds with a wide range of specialized solid state techniques. The group has started officially its participation in the EC Network of Excelence MAGMANet.

Inorganic and Organometallic Chemistry – group is concerned in the synthesis, characterization and chemical reactivity of 4f and 5f compounds. Gas-phase ion chemistry studies of highly radioactive actinides by FTICR/MS have been continued. Oxidation studies of monopositive and dipositive actinide ions were pursued, with a focus on Pa and Cm. Studies on the reactivity of [U(TpMe2)2I] have been accomplished as well as those based on the U(III) and U(IV) complexes, [U({SiMe2NPh)3-tacn}] and [U({SiMe2NPh)3-tacn}X] (X = halide and diphenylamide). New enthalpies of formation for alkaline-earth metal and lanthanide substituted phenoxides were measured.

Inorganic and Radiopharmaceutical Chemistry – the research of the group is focused on the design, synthesis and characterization of specific radioactive probes with potential interest on Nuclear Medicine diagnostic or therapy, namely halogen and metal *d*- and *f*- based radiotracers. Synthesis and evaluation of radiohalogenated estradiol analogues pursued and unprecedented $^{99/99m}$Tc building blocks for labelling biomolecules and promising Ln complexes for bone pain palliation have been introduced. Among different training activities IRC team coordinated a Master Course, participated in the European Radiopharmacy Course/INSTN, has been partner in the EC/COST RTD ACTION, Virtual Radiopharmacy/V Framework Program and in the Coordination-Action on Education and Training in Radiation Protection/VI Framework Program.

Environmental Analytical Chemistry –research is focused on Instrumental Analytical Chemistry, Environmental Geochemistry, Isotope Hydrology, Oceanography, and Archaeometry. Some domains were reinforced, in particular the use of light isotopes on the assessment effects and vulnerability due to agricultural practices and industrialised areas as sources of pollution in sediment and diverse hydrological domains. Sediment transport and evolutionary patterns of recent and palaeo-environments along the Iberian shelf were evaluated.

Cultural Heritage and Sciences – Geochemistry of the earth surface, mineralogy and absolute dating are the main research domains, applied to archaeometry, environmental geology and palaeoenvironmental reconstruction. The study of movable and immovable cultural heritage has proceed, and it is also important to emphasize the analysis of former coastal and archaeological environments, by using nuclear methods and luminescence dating, contributing to a better knowledge of the Portuguese Quaternary climate change scenario and landscape evolution.

National and international projects with the scientific coordination of the Department are been carried out. Under the National Scientific Infrastructure Programme 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 and news laboratories are being installed

Education and training of Undergraduate, MSc, PhD and Post-doc students due to our specialized existing facilities has been highly enlarged as well as the participation of Researchers in advanced training activities in collaboration with many universities and in the context of international networks.

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

Chemistry Staff

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Cultural Heritage and Sciences

M. Isabel Prudêncio

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

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

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. These methods allow a detailed characterisation of archaeological and geological materials and the establishment of chronologies.

The application of ITN methodologies unique in Portugal, are fundamental for archaeology and geology, which are the main domains of the research projects of the CHS activity, through protocols, financed projects, collaboration with national and international laboratories and universities, and contracts/services with private or public institutions.

This group is specialized in trace-element analysis and geochemistry (i.e., geochemical fingerprinting) of archaeological specimens for the purpose of determining their provenance (source) by using the above mentioned analytical techniques as tools. To the best of our knowledge, we are the only 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. So, considering those main achievements, we can summarize the principal research domains of CHS group in the following:

1) Cultural Heritage
    a. Archaeological / Museum artefacts (such as ceramics, metals, stones)
    b. Monument stones
    c. Sites surroundings characterization
2) Palaeoenvironmental Reconstruction
    a. Landscape evolution
3) Earth Surface environments
    a. Clay research
    b. Natural weathering processes
    c. Anthropogenic inputs to natural background environments

One of the CHS group most important activities involves the education and training of students from national and international universities. Because our students participate in the entire analysis beginning with sample preparation, irradiation, and measurement and continuing through the statistical analysis and data interpretation, they are well prepared to conduct research in academic and industrial environments.

The improvement of the scientific research based on nuclear techniques of analysis and its application to environmental studies by characterizing pollutants and determine their source and methods of reduction, as well as archaeological studies to fingerprint artefacts and determine the place of origin as a way to understand the activities of humans in the past, is a rolling target of the CHS group.

Research Team

Researchers

M. I. PRUDÊNCIO, Princ. , Group Leader
M. I. DIAS, Aux. (Invited)
A.M. SOARES Princ. (until Oct. 2005)

Students

M. J. TRINDADE, PhD student, FCT grant
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S. VILELA, MSc student
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Collaborators

M. A. GOUVEIA

Palaeoenvironmental Reconstruction

M. I. Prudêncio, M. I. Dias, M. A. Gouveia, J. C. Waerenborgh[1]*
A. C. Valera[2], L. Osterbeek[3], F. Rocha[4], L. Rebelo[5]

The palaeoenvironmental reconstruction research is concerned with investigating and explaining environmental change on different spatial and temporal scales ranging from the geological through to present day situations and the modelling of change into the future. The group's research is particularly relevant in our understanding of the impact of climate change, supporting archaeological investigation, and assisting 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.

Research undertaken by the group involves the analysis of former coastal environments and archaeological environments. Research techniques include palaeosol and sediment analysis, namely absolute dating and chemical and mineralogical characterization. Recent and current projects have included working with other research laboratories and universities.

The group is currently developing research in the following areas:

- Evolution of coastal environments
- Fluvial terrace geomorphology / chronology
- Sediment investigation of archaeological sites
- Application of paleoenvironmental habitat management

Research also involves managing and conserving the natural environment and embraces an array of environmental issues, in order to understand impacts and how humans have been affected by natural and human- induced environmental changes and may be affected by future change.

The study of palaeogeographic / palaeoclimatic evolutions within a certain context is of great interest, especially if some stratigraphic indetermination occurs, namely considering the principal stratigraphic discontinuities, for which the use of several types of non-biostratigraphic markers, such as mineralogicals and geochemicals, became of great interest.

To achieve the main goals of the running projects the most used tools consists on the use of sedimentology / geochemistry to solve sedimentological problems, by using nuclear methods, such as chemical analysis by instrumental neutron activation analysis (INAA), and the absolute dating by luminescence; these methods are complemented mainly with XRD, SEM, Mössbauer:

- to examine the relationships between clay minerals associations, iron oxides, chemical elements distribution, lithology and facies types;

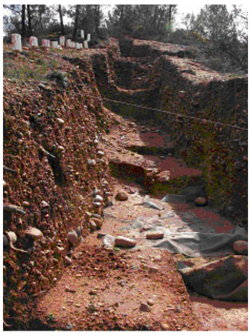
- to assess both the capabilities and the limitations of clay sedimentology and chemostratigraphy in the study of sedimentary sequences;

- to contribute to the refinement of the paleogeomorphology of the Portuguese territory with well established chronologies, by luminescence methods;

- to identify useful mineralogical and geochemical fingerprints which able a reconstruction of the past in a certain geomorphological context.

These research fields aims 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.

These themes combine to explore the very origins of our present environment.



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[1] QFES ITN group
[2] GAFAL archaeologist (C.M. F. Algodres), Portugal
Era Arqueologia S.A. Portugal
[3] Instituto Politécnico de Tomar
[4] Departamento de Geociências da Universidade de Aveiro
[5] IGM - INETI
* Collaborator

Movable Cultural Assets – An example of results obtained in one "archaeometry of ceramics" project Pre-historic pottery technology and provenance in the upper Mondego valley (central/northern Portugal)

M. I. Dias, M. I. Prudêncio, M. A. Gouveia, R. Marques, D. Franco, A. Jorge[1], A. C. Valera[2], P. Day[1]*

This archaeometric project aims to study 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 and on raw materials resources of populations through the third millennium BC in the upper Mondego basin at a local/regional scale. Three main methodological approaches were done to ceramics and potential raw materials (clays): neutron activation analysis (INAA), thin-section petrography and X-ray diffraction, evolving pottery assemblages from 10 settlements: 3 from the Early Neolithic, 3 from the Late Neolithic, and 4 from the Chalcolithic to Early Bronze Age. One of the foremost achievements concerns the technological variability of pottery assemblages recovered from those various domestic contexts, which well definition will be very helpful in the archaeological running project. On the basis of preliminary results, some observations regarding ceramic style and exchange can be introduced. In each site a clear main group of samples was discriminated in both chemical and petrographic terms. The clay pastes do not vary according to morphological types and/or decorative techniques, but with raw materials availability closest to the site. The results obtained so far reinforce the image of cultural homogeneity drawn from previous morphological studies, at both intra- and inter-site level, but petrographic and chemical 'outliers' agree in suggesting a possible non-local origin for a small number of pots.

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[2] Era Arqueologia S.A. Portugal. GAFAL archaeologist (C.M. F. Algodres), Portugal .
* Collaborator

Non-Metallic Portuguese Resources. Inventory, chemical and mineralogical characterization of clays

M. I. Dias, M. I. Prudêncio, M. A. Gouveia, M. J. Trindade[1], F. Rocha[2], J. Coroado[3]*

This project makes part of a PhD thesis, whose main objectives are to make an inventory of availability of potential raw materials for ceramic production in the southern and occidental Portuguese borders, followed by an evaluation of chemical and mineralogical transformations of clay materials of different nature, during ceramics production processes, and its implications on provenance and technological procedures studies of archaeological ceramics. So far, important accomplishments were already obtained, such as a geochemical and mineralogical characterization of clay deposits from different origins/geological formations, mineralogical characterization of clay deposits from different origins, a very detailed (chemical, mineralogical and technological) characterization of the corresponding clay (< 2 μm) fraction. Different chemical and mineralogical composition was noted, like important variations in Ca, Mg and REE, which able to establish geochemical fingerprints for the main geological levels, specially the clayey ones, with more importance for ceramic production. Experimental studies are in course, evolving physical-chemical transformations with different temperature and atmosphere conditions reached upon heating processes.

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Luminescence of inorganic systems. Dating and structural studies of mineral assemblies.

M. I. Prudêncio, M. I. Dias, G. Cardoso, L. Oosterbeek[1], L. Rebelo[2], A.C. Valera[3]

The application of luminescence technique for dating various kinds of samples of diverse archaeological and or geological contexts was a major objective, and important results were already obtained for the Quaternary chronological boundaries of Portuguese territory. Also age authentication of old ceramic wares was done, for which it gives the approximate date of the last firing. Nevertheless new applications of this methodology were implemented, especially concerned with a refinement of ascertain firing temperatures of ancient ceramics during technological procedure, minimizing pos-depositional contaminations which might induce bad temperatures rates with other methods, such as X-ray diffraction.

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[1] Instituto Politécnico de Tomar.
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Environmental Analytical Chemistry

Maria de Fátima Araújo

The activities within the Environmental 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}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}C and ^{3}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 reinforced our skills, by the implementation of new techniques and through new approved proposals. The installation of the ICP-MS, financed by the "*Programa Nacional de Re-Equipamento Científico*" is being initiated. Besides, the operation of the Elemental Analyser coupled to mass spectrometer unit allowed the development of new fields of study by isotopic techniques ($\delta^{15}N$ and $\delta^{18}O$ in nitrates and determination of organic $\delta^{13}C$ and $\delta^{18}O$ in sediment and water samples), leading to the expansion of different working domains in Isotope Hydrology and Isotope Geochemistry.

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 financed by several research projects, particularly the *CRIDA* project, to evaluate the consequences caused by the changes that occurred during the last centuries in the main Iberian river basins. Further studies have contributed to assess the stratigraphic succession of the sedimentary record of Minho estuary, lagoons and interdune depressions of the SW coast to recognize the environmental changes occurred during the Late Quaternary. Moreover, studies concerning the marine reservoir effect off the W margin of Iberian Peninsula, based on ^{14}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.

The expansion of the Isotope Hydrology domain was achieved by the approval and financial support of four new research projects in new fields of Isotope Hydrology, namely: Urban Areas; High Mountain Areas; Arid and Semi Arid Zones and Gas Geochemistry in CO_2-rich Thermomineral Waters. These important environmental issues are being addressed in the exploitation and future development of regional water resources and the delimitation of protection areas.

The development of research projects have given support to political decisions, taking into account the sustainable regional development and the appropriate use of the water resources and management on the basis of several European and national directives, namely vulnerable regions and EC Water Framework.

Research on pre-historical metallic artefacts has been enlarged by using other techniques (Metalography, Microfluorescence). Besides, a new project was approved by the FCT, in order to characterize the technological and social conditions of Late Bronze Age metal production, circulation and consumption in Central Portugal.

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

Research Team

Researchers

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Environmental Geochemistry – Elemental and Isotopical Research

M.F.Araújo, P. Carreira, A.M. Monge Soares, D. Burdloff, P.G. Fernandes, F. Moreno, C. Corredeira, D. Nunes, P. Valério, O. Margo, M. Correia, A. Amaro

Objectives

The improvement, promotion and coordinate research on Earth and Environmental Sciences using and implementing the following analytical techniques:

1. Multielemental characterization (Z>10) using X-Ray Fluorescence spectrometry in solid samples;
2. Light isotope (δ^2H δ^{13}C, δ^{15}N and δ^{18}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 broadly applied to the understanding and management of natural coastal environments, particularly aquifers, rivers, lagoons, estuaries 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

A multidisciplinary study on the stratigraphic succession of Holocene sedimentary records of Minho estuary allowed the recognition and distinction of relevant palaeoenvironmental units belonging to the Late Quaternary. Geochemistry studies have revealed to be an important tool in the study of transitional environments, giving particular indications in the marine/terrigeneous origin of the deposited materials and allowing to recognise and evaluate some temporal changes occurred during the last 11000 years.

The assessment of terrigeneous and marine supplies during the last centuries in muddy deposits on the middle shelf off the three largest Iberian river mouths (Douro, Tejo and Guadiana) was obtained by the study of large size sediment cores collected at similar depths at the Portuguese Continental Shelf. According to our data, 20 to 70 %, 50 to 80 % and 60 to 100 % of fine-sized organic matter is derived from terrestrial sources, respectively for Guadiana, Tagus and Douro. Douro river load has the most significant contribution to the North-western sedimentary deposits, although an absence of heavy metal enrichment, suggests that it was depleted in metals during transport. The narrow shelf adjacent to Tagus and the local circulation pattern favours the deposition of sediments directly from the river discharge and an anthropogenic continental signature is measurable as a result of urban wastes and industrial effluents due to the presence of naval construction works and several industries settled in a high-populated region. 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. Also, a gradually decreasing sedimentation rate (N towards S) is in agreement with the continental supply decrease with respect to those of marine source.

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, several pairs of samples of marine shells and charred wood or bones closely associated collected at several Iberian archaeological sites, representing different periods of time in the Holocene, were radiocarbon dated and the regional reservoir effect, ΔR, was calculated. The results enable not only a clarification of the variability of the coastal upwelling off Atlantic Iberia but also the identification of episodes of abrupt shifts in oceanic circulation, probably coupled with abrupt climatic changes.

Geochemistry of fine sediments deposited along the Portuguese continental shelf

M. Fátima Araújo, C. Corredeira, A. Gouveia[1]

The geochemical characterisation of fine sediments collected along the Portuguese Continental Shelf and adjacent to main Iberian river basins (Douro, Tagus and Guadiana), was used to assess the influence of the river sediment load into the coastal marine environment. Douro is the main source of the shelf fine sediments, although sediments do not present signals of anthropogenic contamination. Probabbly, sediments pass through many remobilisation and mixing processes during a long transport until being deposited in the shelf. Since Douro River seems to have a substantial contribution to the sedimentary deposit located in the middle of the adjacent shelf, the absence of heavy metal enrichment suggests their depletion by geochemical processes, during the long suspension time before deposition. In case of Tagus, the narrow shelf and the local circulation pattern favour the deposition of sediments directly from the river discharge and anthropogenic contamination is observed at the shelf, probably as a result of urban wastes and industrial effluents due to the presence of naval construction works and several industries settled in a high-populated region. Southwards, at Guadiana, shelf sediments present an important continental contribution. The main sources of pollution are probably the mineral wastes of mining activities resulting from the ore exploitation along the Iberian Pyrite Belt. Contaminated sediments have been transported, probably by Guadiana River and the anthropogenic signatures at the shelf sediments seem to be able to last for several centuries.

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[1] Cultural Heritage and Sciences group, ITN.

Organic carbon sources to the northern and southwestern Portuguese shelf sediments

M. Fátima Araújo, D. Burdloff, J-M. Jouanneau[1]

In this study, we provide an elemental (organic carbon and total nitrogen) and isotopic ($\delta^{13}C$) record of fine-sized (<63µm) particulate organic matter in Portuguese continental shelf sediments. Studies were carried out in large size sediment cores (~3 m) collected at similar depths. The aim of the work is the assessment of terrigenous and marine supplies in muddy deposits on the middle shelf off the three largest Iberian river mouths during the last centuries. The first-order linear correlations displayed between $\delta^{13}C$ values and OC/TN ratios for each core is usually interpreted as a mixing trend between terrestrial and marine sources of organic matter, providing depleted and enriched isotope ratios, respectively. Assuming constant $\delta^{13}C$ end-member values for marine (-20 ‰) and terrestrial (-27 ‰) fine-sized organic matter supply along each core, we can make a semi quantitative estimation of the continental contribution. According to our data, 20 to 70 %, 50 to 80 % and 60 to 100 % of fine-sized organic matter is derived from terrestrial sources, respectively in cores CRIDA 05, MD 992332 and KSGX 57. Thus, the gradually increasing trend of sedimentation rate: 0.12-0.13 $cm.yr^{-1}$, 0.20-0.24 $cm.yr^{-1}$ and 0.45 $cm.yr^{-1}$, respectively, goes with an increase of supplies coming from continent with respect to those of marine source. The variability on the sedimentary organic matter supply results from differences in the transported sediment load, hydrodynamism and morphological environment along the continental shelf.

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[1] Université Bordeaux I, Bordeaux, France.

Palaeoenvironmental geochemical patterns in the Holocenic evolution of Minho estuary

M. Fátima Araújo, A. Lobato, A. Cruces, T. Drago[1]

A multidisciplinary study on the stratigraphic succession of Holocene sedimentary records of Minho estuary permitted the recognition of relevant paleoenvironmental units. The cores reached the regional substrate rock (granite) and the sedimentological infill begins with a gravelly basal unit (Unit I), constituted essentially by quartzite and round gravels and particulate OM that correspond to a fluvial environment (11380±60BP). After 8090±60BP, there are variations in Al and Si related to alternate layers of sandy and muddy sediments. These units have higher concentrations Ca, Sr, Cl and Br suggesting a major marine influence. In unit III this marine signal decreases and in core 1 at the top of the unit (Unit IIIB) a sudden impoverishment in these “marine” elements is observed. The topmost unit (Unit IV) is constituted by a monotonous sequence of sands (high Si and low Al contents) disturbed by a singular event: a muddy organic layer with fragments of charcoal, low contents of Si, K and Rb (terrrigeneous), high contents of S, Cl and Br. Geochemistry contribution is an important tool in the study of transitional environments giving particular indications in the marine/terrigeneous origin of the deposited materials and allowing to evaluate some temporal changes occurred during the last 11000 years.

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[1] Instituto Português de Investigação das Pescas e do Mar.

Groundwater resources as indicators and archives of palaeoclimatic changes

P.M. Carreira, P.G. Fernandes, J.M. Marques[1], F. Monteiro Santos[2], M.O. Silva[3], D. Nunes

The regional geomorphology of the region seems to favour 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 $\delta^{18}O$ 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}C content (between 4.82 ± 1.00 pmc and 7.43 ± 0.34 pmc) of Caldas de Monção thermomineral waters (TDIC) together with the absence of ^{3}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 $\delta^{13}C$ determinations give values in the range of -7 to -6 $^{o}/_{oo}$, indicating a "complex" origin for the CO_2 in these waters (mixture between atmospheric CO_2, decay of organic matter and upper mantle 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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[1] Dep. de Engenharia de Minas e Georrecursos (LAMPIST), Instituto Superior Técnico.
[2] Instituto de Ciência da Terra e do Espaço, Faculdade de Ciências da Universidade de Lisboa.
[3] Centro de Geologia, Faculdade de Ciências da Universidade de Lisboa.

High mountain areas in catchment water resources

P.M. Carreira, D. Nunes, J.M. Marques[1], J. Espinha Marques[2], H. Chaminé[3], P. Fonseca[4]

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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[1] Dep. de Engenharia de Minas e Georrecursos (LAMPIST), Instituto Superior Técnico.
[2] Centro de Geologia da Universidade do Porto.
[3] Instituto Superior de Engenharia do Porto.
[4] Dep. de Geologia da Universidade de Lisboa.

National network for isotopes in precipitation

P.M. Carreira, M. Fátima Araújo, D. Nunes, P. Valério, M. Correia, L. Gourcy[1]

Interpretation of the isotopic composition in terrestrial water (groundwater 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 factors 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 (^{2}H, ^{3}H and ^{18}O) and to establish temporal and spatial variations for hydrological investigations. The large depletion in the isotopic composition in vapour and rain events are associated to the depressions over the Atlantic (Mid North Atlantic) or over the British Islands. Regional variations in the ^{3}H between littoral and interior stations are probably a result of the oceanic dilution of the ^{3}H in the atmospheric water vapour. Isotopic results are used in international hydrogeological and climatologic studies, being compiled in the IAEA Data Base and disseminated via IAEA publications (www.iaea.org/programs/ri/gnip/gnipmain.htm).

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Hydrology in urban areas

P.M. Carreira, D. Nunes, H. Chaminé[1,2], M.J. Afonso[1,2], F. Rocha[2], J.M. Marques[3]

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 ^{2}H and ^{18}O in water and ^{15}N and ^{18}O in nitrate (in liquid and solid samples), in combination with major and trace hydrogeochemical indicators. 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 related 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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Groundwater resources assessment by anthropogenic and natural contamination sources

P.M. Carreira, P.G. Fernandes, O. Margo, M.O. Silva[1], D. Nunes, L. Ribeiro[2], E. Peralta[3]

The work is focused on the study of the quality of groundwater sources for Human supply and groundwater resource protection and management, through the identification and quantification of pollution sources traced by environmental isotopes (δ^{13}C, δ^{15}N, δ^{18}O, δ^{2}H and ^{3}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 pollution can then be determined, e.g. natural, industrial, agricultural or domestic. Isotope techniques can also identify incipient pollution, providing an early warning before chemical or biological indicators. Agricultural practices and high industrial areas must be seen as new inputs of pollution in the environment (sediment and hydrological domains) through demographic density increase and growing of organic and toxic contamination. In the particular case of nitrogen isotopes, this tool can offer a direct mean of source identification The relative contribution of these two sources to groundwater or surface water can be estimated by mass balance. The analysis of δ^{18}O of nitrate in conjunction with δ^{15}N improves the ability to trace nitrate sources and cycling. This area of work 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 the establishment of vulnerable regions.

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Gas Geochemistry in CO_2-rich Thermomineral Waters

P.M. Carreira, D. Nunes, M.R. Carvalho, J.M. Marques[1], G. Capasso[2], F. Grassa[2]

In Portuguese mainland, the greatest number of hot (~76 ºC) and cold (17 ºC) CO_2-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 isotopes will give new insights on the sources of gas constituents (crustal rocks, mantle, etc.) and reservoir temperatures. Chemical and isotopic water signatures, 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

P.M. Carreira, D. Nunes, F. Monteiro Santos[1], A. Pina[2], A. Mota Gomes[2], J.M. Marques[3]

A multidisciplinary approach has been applied to evaluate the hydrogeological potential of arid zones and environmental / climatic changes at Santiago Island (Cabo Verde). The combination of these different methodologies have been applied in this island with the goal of monitoring fresh-water – salt water interface. The $\delta^{18}O$ and $\delta^{2}H$ data will be used to identify and characterize the recharge areas and also to quantify the percentage of mixture between seawater and fresh water. Besides, tritium measurements will allow obtaining the mean residence time of the water system. ^{3}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 at the islands is distributed in the following medium periods: 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[1], A. Ávila de Melo[2]

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_2). 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 Cultural Heritage 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.

The reservoir effect of coastal waters off the western margin of the Iberian Peninsula

A.M.M. Soares, J.A. Alveirinho Dias[1]

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. ^{14}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 (ΔR) calculated: 940±50 to -160±40 ^{14}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

António Pires de Matos

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 **energetics 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. We are starting to apply our knowledge to environmental studies, particularly concerning radioactive waste containing actinides. Of interest to this activity is an ongoing collaboration project with Plastval/Sociedade Ponto Verde dealing with non-radioactive waste. Collaboration is also given to the Radiation Technologies: Processes and Products group (Physics Sector) in a study of the gamma radiation effect on several waste water sources.

Ongoing research to develop new coordination environments for *f*-elements is continuing with two main purposes: to create new reactive centres with unusual reactivity patterns and to explore the ability of the new ligands in Ln/An separation.
During the last year we developed protocols for the synthesis of a monoanionic tacn based ligand [(SiMe$_2$NPh)-tacn(^{i}Pr)$_2$] and the dianionic bisalkoxide- and bisdiamide-diamine ligands. Reactivity studies of these ligands with lanthanide halides and uranium triiodide are under investigation.

Pursuing previous work on binary lanthanide (LnCu$_2$ (Ln = La, Ce, Pr, Nd, Eu, Gd, Dy, Tm, Yb) and actinide (ThCu$_2$ and AnNi$_2$; An=Th, U) intermetallic compounds as catalytic precursors, leading to heterobimetallic oxides, 3CuO.Ln$_2$CuO$_4$ or 2CuO.Ln$_2$Cu$_2$O$_5$ and 2MO.ThO$_2$ (M=Cu, Ni) or 2CuO.UO$_3$, a systematic study of their acid-base properties was undertaken. Two methods were used: 2-propanol dehydrogenation/dehydration and the temperature programmed desorption of CO$_2$. The results show a correlation between the catalysts basicity and the catalytic activity, which decreases along the lanthanide series. For the actinides uranium oxide behaves better than thorium oxide: stronger and richer basicity together with higher activity and better selectivity for C2 products (oxidative coupling of methane). These results clearly indicate that the f-block element plays a role in the heterobimetallic oxides properties.

Gas-phase ion chemistry studies of highly radioactive actinides by FTICR/MS have been continued. Oxidation studies of monopositive and dipositive actinide ions were pursued, with a focus on Pa and Cm. It was found that PaO$_2^{2+}$, formally a Pa(VI) species, catalyzes the oxidation of CO by N$_2$O.

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. Joint projects with the Faculty of Fine Arts of the University of Lisbon and the New University of Lisbon on new lanthanide based fluorescent glasses and with the Glass Museum of Marinha Grande on provenance studies of Portuguese glasses continued.

The work made was financially supported by seven projects of FCT, three FCT PhD grants and one Post-doc FCT grant. A new project approved by FCT will support the installation of an ESI mass spectrometer

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Gas-Phase Ion Chemistry of Actinides and Lanthanides

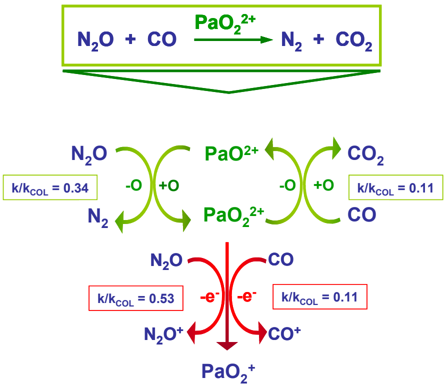
J.Marçalo, A.Pires de Matos, J.P. Leal, M. Santos[1],
J.K. Gibson[2], R.G. Haire[2]

Objectives

The gas-phase reactivity of "bare" and ligated actinide and lanthanide ions with organic and inorganic molecules is studied in order to obtain kinetic, mechanistic and energetic information that can be correlated with the electronic structure of the ions and compared with data from condensed phases. For the actinides, the aims are also to gain insight into a potential 5f electron contribution to the chemistry in the first half of the series, and to estimate thermodynamic data for species that may be of interest for condensed-phase processes. The experimental work is based on the use of Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS), a technique that is specially suited for the study of the chemistry of ion/molecule systems in the gas phase.

Results

Oxidation studies of monopositive and dipositive actinide ions were pursued [1-4,6], with a focus on Pa and Cm. Reactions of atomic and ligated, monopositive and dipositive Pa ions were studied. Notably, it was observed that PaO^{2+} was oxidized by N_2O to yield PaO_2^{2+}, formally a Pa(VI) species. The experimentally determined $IE[PaO_2^+] \approx 16.6$ eV was in agreement with theoretical calculations performed by R. Tyagi and R. M. Pitzer from Ohio State University (Columbus, Ohio, USA). It was found that PaO_2^{2+} catalyzes the oxidation of CO by N_2O (see Scheme); such O atom transport via a dipositive metal oxide ion is distinctive.



Preliminary studies of oxidation reactions of "bare" and ligated, monopositive and dipositive Cm ions were also performed. Oxidation reactions of Gd and Lu ions were examined for comparison.

Comparative studies of the reactivity of actinide and lanthanide cations with organic molecules were continued [3-6]. The reactivity of doubly-charged cations An^{2+} (An = Th, Pa, U, Np, Pu, Am, Cm) and Ln^{2+} (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) with alkanes and alkenes was examined. The reaction channels observed were highly dependent on the metal ion and typically consisted of combinations of dehydrogenation and/or alkane-losses with electron, hydride and/or methide transfers. The early actinide cations, Th^{2+}, Pa^{2+} and U^{2+}, were the most reactive; Th^{2+}, in particular, efficiently induced the dehydrogenation of methane, yielding $ThCH_2^{2+}$ as single product. La^{2+}, Gd^{2+} and Lu^{2+} were the most reactive lanthanide cations, but Lu^{2+}, due to its high electron affinity, reacted only via transfer channels.

Published or in press work

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2. J.K. Gibson, R.G. Haire, J. Marçalo, M. Santos, A. Pires de Matos, J.P. Leal, Determination of the Ionization Energy of NpO_2 and Comparative Ionization Energies of Actinide Oxides, *J. Nucl. Mater*. 2005, 344, 24-29.
3. , J.K. Gibson, J. Marçalo, New Developments in Gas-Phase Actinide Ion ChemistryCoord. Chem. Rev., *in press*.
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6. J.K. Gibson, R.G. Haire, J. Marçalo, M. Santos, A. Pires de Matos, Reactions of Actinide Ions in the Gas Phase: New Issues in Molecular Actinide Chemistry, *Pacifichem 2005*, Honolulu, December 2005.

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[1] *PhD* grantee (FCT/SFRH/BD/10465/2002).

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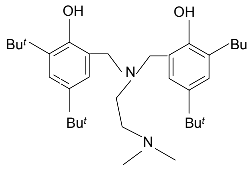
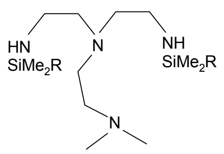
f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

M. A. Antunes, S. Barroso, J. Cui, J. M. Carretas, N. Marques

This project aims to develop new coordination environments for *f*-elements with two main purposes: to create new reactive centres with unusual reactivity patterns and to explore the ability of the new ligands in Ln/An separation. These two areas are supported by the projects POCTI/QUI/36015/2000, POCTI/QUI/46202/2002 and POCTI/QUI/46179/2002. Studies on the reactivity of $[U(Tp^{Me2})_2I]$ have been accomplished as well as those based on the U(III) and U(IV) complexes, $[U(\{SiMe_2NPh)_3\text{-tacn}\}]$ and $[U(\{SiMe_2NPh)_3\text{-tacn}\}X]$ (X = halide and diphenylamide). Now we are involved on the synthesis of mono- and difunctionalized tacn ligands. The synthesis of the monoanionic $(\{SiMe_2NPh)\text{-tacn}(^iPr)_2\}]$ ligand has been achieved, but our efforts to get the dianionic $(\{SiMe_2NPh)_2\text{-tacn(Me)}\}$, failed so far. Hence, we changed our strategy to the synthesis of the new dianionic bisalkoxide and bisamide diamines.





Reactivity studies of these ligands with lanthanide halides and uranium tri-iodide are under active investigation.

Molecular Energetics of Organic, Inorganic and Organometallic Compounds

J. P. Leal, M. T. Fernandez[1], C. Hipólito, P. Madeira[2], L. Richard[3], R. Simões[3]

The main objective of this research line is to collect data and rationalize it in a systematic way that enables a deeper knowledge of energetics on molecules (both inorganic and organic compounds). Special importance will be 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 (alkoxides, phenoxides, thiolates and cyclopentadienyls) and hydrocarbons were studied.

During 2005 new enthalpies of formation for alkaline-earth metal and lanthanide substituted phenoxides were measured. The gas-phase acidity of substituted phenols (a key value for the knowledge of O-H bond strength) was determined by several different methods using the FT-ICR mass spectrometer facility. Those values are keystone for the evaluation of anti-oxidant properties of substituted phenols (e.g. Vitamin-E derived compounds).

A critically accessed compilation of existing enthalpies of formation for hydrocarbons was finished and those values were used to parametrize an extended Laidler method of additive contributions. The newly parametrized method allows to estimate 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. New fluoroapatite compounds were sinthezised and their thermal and structural properties studied.

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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. S. Correia, A. Pires de Matos

Alkaline and alkaline-earth metal alkoxides are very good models for rare-earth alkoxides and easier to synthesize. Some of the rare-earth alkoxides (Sc, Y, La) 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 substituted phenoxides were synthesized. Different positions of the substituents and also different substituents were used. Their characterization, both energetic and structural, was performed. The measurement of the enthalpies of formation of the phenoxides was made by reaction-solution calorimetry. For the structural characterization powder X-ray and EXAFS were used.

Following previous work on lanthanide heterobimetallic oxides (Eu-M-O, M=Ca, Ba), the study of their acid-base properties was undertaken.

f-Block Element Intermetallic Compounds as Catalysts Precursors

J. Branco, A. Pires de Matos

New methods for the preparation of supported metal catalysts are of great interest. Intermetallic compounds of lanthanide or actinide metals combined with d metals have been found to be active in a variety of reactions; however, the starting compounds decompose under the reaction conditions. The main objective of this project is to study binary copper- or nickel/f block element as catalysts or catalytic precursors.

Pursuing previous work on binary lanthanide ($LnCu_2$; Ln = La, Ce, Pr, Nd, Eu, Gd, Dy, Tm, Yb) and actinide ($ThCu_2$ and $AnNi_2$; An = Th, U) intermetallic compounds as catalytic precursors, leading to heterobimetallic oxides, $3CuO.Ln_2CuO_4$ or $2CuO.Ln_2Cu_2O_5$ and $2MO.ThO_2$ (M = Cu, Ni) or $2CuO.UO_3$, a systematic study of their acid-base properties was undertaken. Two methods were used: 2-propanol dehydrogenation/dehydration and the temperature programmed desorption of CO_2. The results show a correlation between the catalysts basicity and the catalytic activity, which decreases along the lanthanide series. For the actinides uranium oxide behaves better than thorium oxide: stronger and richer basicity together with higher activity and better selectivity for C_2 products (oxidative coupling of methane). These results clearly indicate that the f-block element plays a role in the heterobimetallic oxides properties.

Immobilized Surface Rare Earth and Actinide Aryloxides. Activation of Small Molecules (CO_2, CH_4, C_2H_6)

T. Almeida Gasche, A. S. Correia, J. Branco

One objective of surface organometallic chemistry is to immobilise organometallic complexes on solid surfaces such as oxides and zeolites to prepare well-defined surface species acting as highly selective heterogeneous catalysts. For several years, we have been studying the synthesis and reactivity of lanthanide and actinide aryloxides. Some divalent and trivalent samarium and ytterbium 2, 6-di-*tert*-butyl-4-methylphenoxo complexes were immobilised on amorphous silica. For the divalent complexes, the results pointed that after reaction with silica only one aryloxide group remains bonded to the metal, with formation of a η^2 type complex involving two Si-OH groups and oxidation of the divalent complexes. In order to obtain additional information on these immobilised systems, the cuboctameric silsesquioxane monosilanol $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ was used as a homogeneous model system. The silanol mentioned belongs to the polyhedral oligomeric silsesquioxanes family (POSS) which are used to model the surface structure of partially dehydroxilated silica and therefore infer information about the coordination sphere of metal complexes directly supported on silica. During 2005 synthesis of divalent ytterbium and europium 2,6-di-*tert*-butyl-4-methylphenoxo complexes with $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ was performed. The organolanthanides silanol systems were characterized by NMR, IR, elementary analysis, TGA and DSC. The DSC results showed only exothermic processes. It was also concluded that the Yb-POSS bond is stronger than the Eu-POSS bond. The results obtained so far corroborate the ones obtained for the divalent lanthanide aryloxides after deposition on silica.

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 glass samples containing several rare earths, uranium and thorium oxides have been synthesized.

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 concerns the development of new glasses for art applications, the other involves provenance studies of Portuguese glass from the 15th to the 20th century. The historical glasses have started to be analysed by XRF spectrometry and by ICP/MS. A series of new luminescent glasses with rare earths have already been prepared.

Gamma Irradiated Chitosan/pHEMA Membranes for Drug Release Systems

M. H. Casimiro, J. P. Leal, M. H. Gil[1]

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 γ irradiation from a ^{60}Co source.

From previous work on chemical and physical characterisation, we have selected the most interesting synthesis conditions and done microbiological, biocompatibility and antibiotic release studies on the obtained membranes.

Results point out that membranes naturally exhibit antimicrobial properties and that over the studied range values, drug loaded membranes display an insignificant level of haemolysis and present a fast rate of amoxicillin release. In order to optimise the drug release rate we intend to do further work on membranes thickness.

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Inorganic and Radiopharmaceutical Chemistry

Isabel Rego Santos

The **main activity** of the Group **is the design, synthesis and characterization of novel specific radioactive probes with potential interest on Nuclear Medicine diagnostic and/or therapy.** These probes are useful for non-invasive **molecular imaging** of targeted macromolecules and biological processes associated to different pathologies. By using **β^- or Auger emitters,** they might be suitable for **therapy**.

The group **is multidisciplinary**, combining expertise on organic, inorganic and organometallic chemistry of *d*- and *f*-elements, on radiochemistry as well as on animal and cell studies. This combination, **unique in the country,** is possible due to our expertise and 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 facilities, laboratories and equipment for animal studies, cell culture and biological evaluation of radioactive compounds.

The expertise and infrastructures enable basic and applied-oriented research in modern Radiopharmaceutical Chemistry, an important topic in Life Sciences. This justifies our participation in National and International research projects, the support of a Pharmaceutical Company and funding from FLAD. Our know-how on chemistry, radiochemistry and radiopharmacy, and our facilities, have been also used to provide training and education to undergraduate, graduate and post-graduate students.

Research: During 2005**,** we went on with our studies on **halogen and metal *d*- and *f*-based radiotracers for biomedical applications**. In terms of targeting our interest is on cancer and CNS pathologies. **The main scientific achievements are reported in the next pages.**

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 protocol, our facilities are also used, every year, during two weeks by the 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 Therapeutical Applications* (DR nº 123, 26/05/04, II série**).** For this Master Course the group established a protocol with the University of Lisbon (Faculties of Sciences, Pharmacy and Medicine), Hospital Garcia da Orta and Instituto Português de Oncologia/Lisboa. We have also participated in a PhD Teaching Program organized by ITQB/UNL. Physicians resident in Nuclear Medicine (*Portaria 555/2003, 11 June)* have also been trained in our laboratories.

At the **International level**, we have participated in the European Radiopharmacy Course, INSTN and have been partners in the EC/COST RTD ACTION, Virtual Radiopharmacy/V Framework Program and in the Coordination Action on Education and Training in Radiation Protection/VI Framework Program.

We have also trained several young scientists, funded by FCT grants, namely **BIC, 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

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L.GANO, Aux.
F. MARQUES, Aux.
P. RAPOSINHO, Aux.

L.MARIA, Pos-Doc, FCT grant

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M. VIDEIRA, Undergraduate student
B. GONZÁLEZ, Undergraduate student
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I. VIEGAS, Undergraduate student

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

M. Videira, A. Almeida, M.C. Oliveira, L. Gano, F.M. Marques, I. Santos, T. Thiemann[1]*, M. Watanabe*[1]*, G.R. Morais*[1]*, F. Botelho*[2]*, A.C. Santos*[2]*, C. Oliveira*[3]

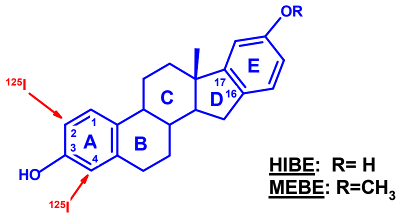
Objectives

Synthesis of novel radioiodinated (^{123}I/^{125}I) estradiol analogues potentially interesting as probes for imaging or for therapy of estrogen receptor (ER) containing tumours. In these radiotracers the presence of the Auger electron emitters ($^{123/125}$I) might allow a highly selective target radiotherapy, with virtually no damage to the surrounding cells, if the compounds have the ability to achieve DNA causing double strands.
These studies may contribute to the development of new radiopharmaceuticals with potential application in the clinical care of breast and ovarian cancer patients.

Results

In our search for novel ER directed radioligands two families of estradiol derivatives are being explored: (**A**)areno-annelated estra-1,3,5(10),16-tetraen-3-ol and (**B**)C7-substituted estra-1,3,5(10),6-tetraen-3,17β-diol.

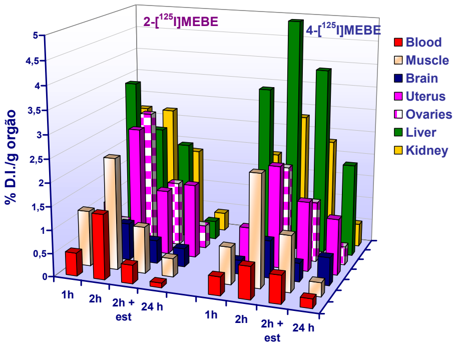
(**A**) Two novel **areno-annelated estra-1,3,5(10),16-tetraen-3-ol** with a hydroxyl **(HIBE)** or a methoxyl **(MEBE)** substituent on the E ring have been synthesised and characterized.



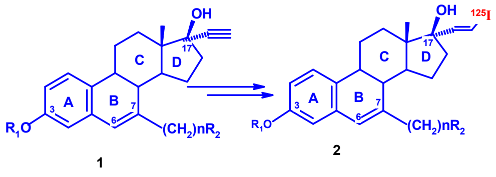
Radioiodination (^{125}I) at the *orto* position of the A ring lead, for both compounds, to the formation of two radioisomers with high specific activity after purification by High Performance Liquid Chromatography (HPLC). All the radioligands studied are stable *in vitro*, more lipophilic than estradiol and have shown low binding to plasma proteins.

The effect of the site of radioiodination (C_2 vs C_4) on the biological behaviour of the radioiodinated **MEBE** was evaluated through biodistribution studies in immature female Sprague-Dawley rats. The two isomers, **2-[^{125}I]-MEBE** and **4-[^{125}I]-MEBE**, are stable *in vivo* and are mainly excreted through the hepatobiliary pathway. Both localize in the uterus and ovaries *via* a receptor mediated process having the **2-[^{125}I]-MEBE** isomer higher specific ER binding and uterus selectivity.

Due to the favourable *in vitro*/*in vivo* stability and biodistribution profile of these radioligands the evaluation of **HIBE** radioisomers is currently under investigation.



(B) Several radioiodinated 17α-ethynyl analogues (**1**) have been synthesised and characterized to be used as precursors in the synthesis of novel radioiodinated **C7-substituted estra-1,3,5(10),6-tetraen-3,17β-diols** (**2**). The *trans* isomer of 7-(6´-cyanohexyl)-3-benziloxy-17α-iodovinylestra-1,3,5(10),6-tetraen-17β-ol and its non-carrier-added [^{125}I]iodovinyl analogue (**2a**) were synthesized, *via* destannylation of the corresponding *trans* tributylstannyl intermediate stereoselectively prepared from (**1a**). A radioiodinated compound with high specific activity was obtained after HPLC purification and has shown to be very stable *in vitro*. To get insights into the chemical structure/biological activity relationships the radiolabelling and biological evaluation of the other compounds is presently underway.



a: n=6, R_1=Bn, R_2=CN
b: n=4, R_1=H, R_2=CN
c: n=6, R_1=H, R_2=CN
d: n=10,R_1=H, R_2=CN
e: n=5, R_1=H, R_2=$CONH_2$
f: n=6, R_1=H, R_2=$CONH_2$

Published or in press work

1. G.R. Morais, M.C. Oliveira, T. Thiemann, Synthesis of C7-substituted Estra-1,3,5(10),6-tetraen-3,17β-diols *Lett. Org. Chem.* In press.
2. M. Videira, Estrogénios radioiodados para diagnóstico e terapia de tumores da mama Graduation Thesis, FCUL (2005).

---

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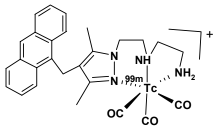
[3] Clínica Ginecológica, CIMAGO, FMUC, Coimbra

Technetium-99m Complexes with DNA Binding Ligands for Selective Tumour Radiotherapy

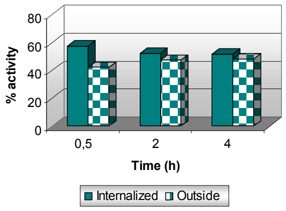
R. F. Vitor, F. Marques, A. Paulo, P. Raposinho, I. Santos, I. Correia[1]*, J. C. Pessoa*[1]*, A. S. Rodrigues*[2]*, J. Rueff*[2]

A series of ^{99m}Tc and Re complexes anchored by tridentate pyrazole-diamine chelators functionalized with anthracenyl fragments were prepared and evaluated. At macroscopic level, the interaction of the Re complexes with calf-thymus DNA has been studied by spectrophotometric, fluorescence, circular and linear dichroism (CD/LD) techniques. For the ^{99m}Tc congeners, cellular uptake, nuclear internalization and radiotoxicity studies have been performed in normal V79 and tumour B16F1 murine cells. One of the complexes (**APZ**) displays an enhanced radiotoxicity in B16F1 cells, which reflects most probably its ability to interact with DNA and its moderate to high cellular uptake and nuclear internalization. Future work involves the functionalization of this promising compound with a tumour seeking peptide, as well as the introduction of other DNA binding fragments, in order to increase the radiotoxicity of the complexes.



(APZ)

Nuclear internalization of APZ in B16F1 cells



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[1] Centro Química Estrutural, Instituto Superior Técnico, Lisboa

[2] Centro de Investigação de Genética Molecular, Universidade Nova de Lisboa, Lisboa

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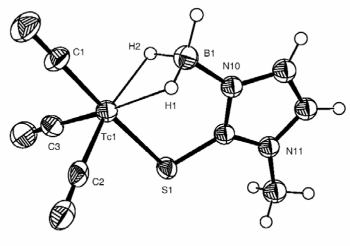
Tc(I)/Re(I) Tricarbonyl Complexes Anchored by Trihydro(monoazolyl)borates: Novel Building Blocks for Labelling Small Biomolecules with ^{99m}Tc

L. Maria, R. Garcia, A. Paulo, I. Santos, R. Alberto[1]

Following our previous work on poly(mercaptoimidazolyl)borate Tc(I)/Re(I) complexes for radiopharmaceutical applications, we have introduced a novel class of soft scorpionates of the trihydro(mercaptoazolyl)borate type and evaluated their coordination capability towards the *fac*-$[M(CO)_3]^+$ (M = Re, ^{99}Tc, ^{99m}Tc) moiety. At macroscopic level, X-ray crystallographic analysis of some of the resulting complexes confirmed the presence of the unprecedented donor atom set combining one sulphur atom and two agostic hydrides. Due to their lipophilicity and small-size, trihydro(mercaptoazolyl)borate technetium tricarbonyl complexes are being explored for designing radiopharmaceuticals for the targeting of brain receptors. These building blocks will be explored using the so-called pendant or integrated approaches, as exemplary demonstrated by the synthesis of complexes containing an appended piperazinyl fragment with affinity for serotonergic 5-HT_{1A} receptors or an integrated benzothiazolyl fragment for the recognition of β-amyloid plaques.



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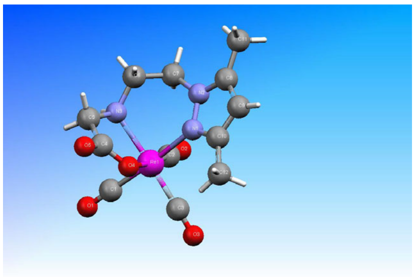
[1] Institute of Inorganic Chemistry, University of Zürich, Switzerland.

Novel Nuclear Imaging Agents for Targeting Epidermal Growth Factor Receptors (EGFR)

C. Fernandes, C. Oliveira, L. Gano, I. C. Santos[1]*, l. Santos*

The epidermal growth factor receptors (EGFR) belong to the ErbB family of receptor tyrosine kinases (TK) involved in the proliferation of normal and malignant cells. Our main goal is to find ^{125}I or ^{99m}Tc probes based on quinazoline derivative inhibitors of tirosine kinase activity, for early detection and staging of cancers overexpressing EGFR. The bioactive precursor, N-{4-[(3-chloro-4-fluorophenyl)amino]quinazoline-6-yl}-3-bromo propionamide was synthesized and labelled with ^{125}I, via halogen exchange, and also coupled to a novel monoanionic asymmetric pyrazolyl containing ligand, [2-(3,5-dimethyl-pyrazol-1-yl)-ethylamino]-acetic acid, for labelling with ^{99m}Tc. The radioactive compounds, obtained with high radiochemical purity, were characterized and their *in vitro* and *in vivo* stability evaluated. The potential of these compounds as SPECT biomarkers for molecular imaging of EGFR positive tumours is currently under investigation. Using these two compounds it will be possible to evaluate the effect of the chelator and/or metal center on the biological activity of the quinazoline pharmacophore.



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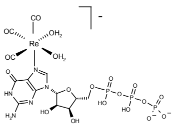
[1] QFES ITN group

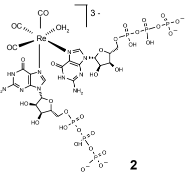
Radioactive Probes for in vivo and Non-Invasive Assessment of Gene Expression

C. Xavier, I. Santos, R. Alberto[1]

For imaging endogenous gene expression the ribonucleotide coding sequence is the target, and radiolabelled complementary oligonucleotides may be used as a probe. To achieve this goal direct or indirect labeling of DNA sequences has to be explored. To get a better insight into the so-called direct labelling of a DNA sequence, some basic research has been conducted, namely reactions of fac-$[\mathrm{Re(CO)_3(H_2O)_3}]^+$ with GMP, GDP or GTP. The organometallic moiety selectively binds to guanine (N7) base, but also to an oxygen atom of the phosphate, leading to a mixture of species of the type **1**- **3**. Species **3** predominates when the number of phosphates increases. This basic research will continue in order to find novel strategies for direct or indirect labeling of oligonucleotides.



1



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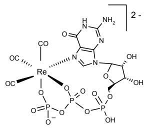

3

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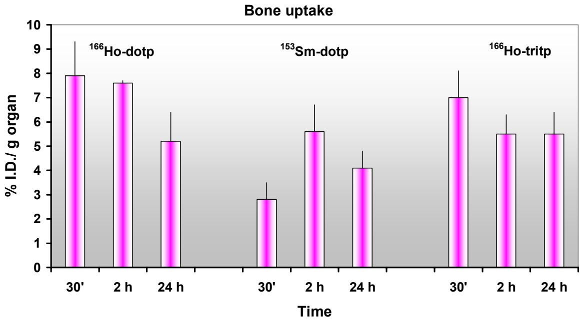
[1] Institute of Inorganic Chemistry, University of Zürich, Switzerland.

^{153} Sm and ^{166}Ho Complexes as Potential Therapeutic Bone Agents

M. P. C. Campello, F. Marques, L. Gano, S. Lacerda, I. Santos.

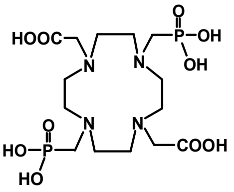


As part of our on going research work on radiolanthanides, ^{153}Sm and ^{166}Ho complexes with macrocyclic ligands containing methylphosphonate and/or methylcarboxylate pendant arms have been studied. Among the evaluated complexes, we found that ^{153}Sm and ^{166}Ho-tritp were prepared with high labeling efficiency, are very stable *in vitro* and *in vivo*, being also significantly taken by the bone. In particular, ^{166}Ho-tritp has 5-6% I.D./g bone, a high rate of total excretion and a rapid washout from main organs, which led to quite favourable bone/blood and bone/muscle ratios. The values found are comparable to those of ^{166}Ho-dotp, a compound which is presently in clinical trials. Thus, our studies support the potential interest of ^{166}Ho-tritp in bone pain palliation.

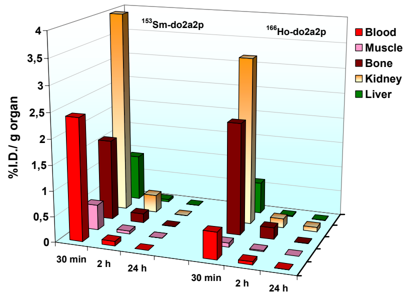
Biological Evaluation of ^{153}Sm and ^{166}Ho Complexes with a Novel Bis(methylphosphonate) Tetraazamacrocycle

M. P. C. Campello, L. Gano, F. Marques, S. Lacerda, T. Esteves ,I. Santos.

To find the effect of the cavity size and/or the nature of the pendant arms on the biological profile of the Ln complexes, a novel bis(methylphosphonate) *do2a2p* was synthesized and characterized by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy. With this novel ligand ^{153}Sm/^{166}Ho complexes have been prepared and evaluated. The complexes are obtained in high yield, are anionic, hydrophilic, present a high stability in human serum, up to 48 h, and a moderate plasmatic protein binding. A relative high *in vitro* hydroxyapatite (HA) adsorption was found for the ^{166}Ho-do2a2p complex in comparison with ^{153}Sm-do2a2p. *In vivo* studies indicated a high stability for both complexes, a fast washout from most organs and a rapid total excretion. A relative high bone uptake was also observed, but the value rapidly decreases over time. These results clearly demonstrate that 12-membered macrocyclic ligands lead to very stable complexes with a biological profile adequate to targeted radiotherapy, being possible to increase and maintain bone targeting by using other bone-seeking groups than methylphosphonates.

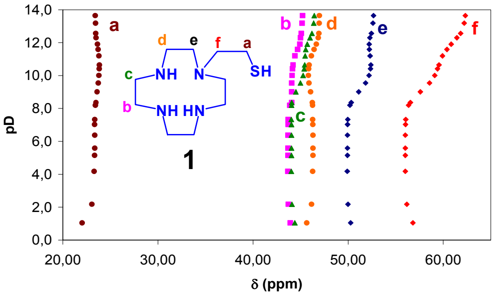


do2a2p



Copper Complexes for Diagnostic and/or Therapeutical Applications

S. Lacerda, M. P, C. Campello, I. Santos, R. Delgado[1]



Cu offers an almost unique combination of radionuclides for imaging ($^{60\text{-}62/64}Cu$) and for targeted radionuclide therapy ($^{64/67}Cu$), being ^{64}Cu the most versatile as it can be used for PET imaging and for targeted radiotherapy. Moreover, their physical properties also allow its use in centres remotes from cyclotron. We have been exploring novel chelators to form stable and inert complexes with Cu. A novel macrocycle (**1**) was synthesised, characterised (^1H, ^{13}C-NMR, MS) and its protonation and thermodynamic stability constants with Cu^{2+}, Zn^{2+} and Cd^{2+} determined by potentiometry and/or by ^{13}C-NMR spectroscopy (Figure 1). The values found indicated that K_{ML}[Cu**1**]>[Cd**1**]≈[Zn**1**]. The synthesis of other related ligands is in progress as well as their complexation with Cu, to select the most promising to pursue studies with ^{64}Cu.

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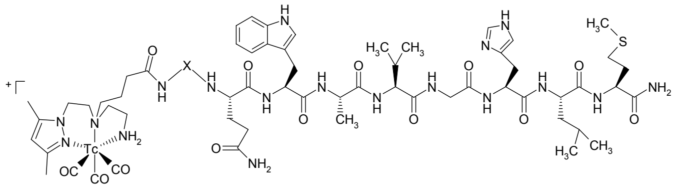
Pyrazolyl Bombesin Conjugates Labeled with the *fac*-[$^{99m}Tc(CO)_3]^+$ Moiety: Biological Behaviour

S. Alves, J. D. G. Correia, I. Santos, B. Veerendra[1], G. L. Sieckman[2], T. J. Hoffman,[2] T. Rold4, L. Retzloff,[1] J. McCrate,[1] A. Prasanphanich,[1] Charles J. Smith[1]

Following our previous results on the promising biological behaviour of the new tumor–seeking bombesin pyrazolyl conjugate labeled with the *fac*-[$^{99m}Tc(CO)_3]^+$ moiety, [^{99m}Tc-Pyrazolyl-G-G-G-Q-W-A-V-G-H-L-M-NH_2], we have introduced a new series of pyrazolyl bombesin conjugates radiolabeled via the tricarbonyl core. These new radiolabeled conjugates are based upon the general structure [^{99m}Tc-Pyrazolyl-X-BBN[7-14]NH_2] (X = β-Alanine, Serylserylserine, or Glycylglycylglycine). Results of our investigations demonstrate the ability of these new radiolabeled conjugates to specifically target the gastrin releasing peptide receptor subtype 2 which is over-expressed on human, prostate, PC-3 cancerous tissue. Therefore, these studies suggest the tridentate pyrazolyl ligand framework to be an ideal candidate for design and development of low-valent ^{99m}Tc-based diagnostic radiopharmaceuticals based upon bombesin or other targeting vectors.



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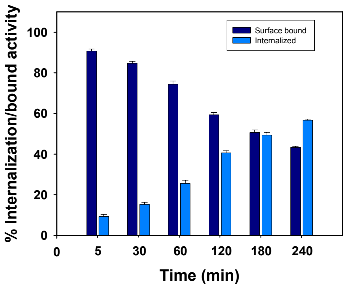
2 Research Division, Harry S. Truman Memorial Veterans' Hospital, Columbia, Missouri, United States, 65201.

Melanoma targeting with [$^{99m}Tc(CO)_3$-Pyrazolyl-MSH analogs]-conjugates

P. Raposinho, J. D. G. Correia, S. Alves, I. Santos



Radiolabeled analogs of α-MSH have been investigated for melanoma (ML) imaging due to overexpression of MC-1 receptors in both melanotic and amelanotic ML. Two analogs were conjugated to pyrazolyl (pz1), radiolabeled with the *fac*-[$^{99m}Tc(CO)_3]^+$ moiety and their potential for ML diagnosis evaluated *in vitro* (ML B16F1 cells) and *in vivo* (ML-bearing mice). The radiopeptide **1** exhibited a better biological profile than the radiopeptide **2** with a higher degree of cell internalization (about 50% at 3h) and a better cellular retention (only 38% released from the cell after 5h). Consequently, a relatively good and specific tumor uptake (4.2 ± 0.9%ID/g, at 4h, 2.7 ± 0.6%ID/g, at 24h) was observed for the *fac*-[$^{99m}Tc(CO)_3$-pz1-NAPamide]-conjugate. Other analogs, in particularly cyclic peptides, could be also promising and are under study.

pz1-MSHoct: **pz1**-βAla-Nle-Asp-**His-*D*Phe-Arg-Trp**-Lys-NH_2 (**1**)
pz1-NAPamide: Ac-Nle-Asp-**His-*D*Phe-Arg-Trp**-Gly-Lys(**pz1**)-NH_2 (**2**)

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 spectroscopy, a Mössbauer spectroscopy laboratory, magnetisation measurements by Faraday and extraction techniques and AC-susceptibility measurements, different electron transport measurements, heat capacity, in a broad range of temperature and magnetic fields. 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 a strong expertise in cryogenics. 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.

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 centered 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. During 2005 the two chain compounds, originally reported by the group almost 3 decades ago, remained at the centre of important discoveries as model quasi-1D Charge Density Wave (CDW) systems. Under moderate pressures were found quantum oscillations in magnetoresistance due to Stark inference and, for the first time in a bulk system, the quantum limit was achieved at ~20 T.

Profiting from common molecular precursors, synthetic procedures and characterisation techniques, the interests of the group in molecular materials have been extended during the last years to **molecular magnetism**. In this field the group officially started on May 2005 its participation in the EC Network of Excelence MAGMANet - Molecular Approach to Nanomagnets and Multifunctional Materials.

The research on **intermetallic compounds,** initiated in 1992 pursued. Several ternary phase diagrams of the type (f-element)-(d metal)-(p-element) were explored and the crystal structure of the new compounds was characterized. The magnetic and transport properties of ternary intermetallic compounds containing f and d elements were measured. A new emphasis on intermetallic borides and thermoelectrical materials was carried out.

A significant output of the group has been the **training and education of young scientists** which always play a major role in its projects. Besides the collaboration of group members in several educational activities such as undergraduate courses, 1 PhD thesis performed inside the group, was defended this year

Research Team

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J. C. WAERENBORGH, Aux.
A. P. GONÇALVES, Aux.
E. B. LOPES, Aux.
L. C. J. PEREIRA, Aux.
I. C. SANTOS, Aux.

D. BELO, Pos-Doc, FCT grant
P. GACZYNSKI, Pos-Doc, FCT grant
S. RABAÇA, Pos-Doc, FCT grant
S. SERIO, Pos-Doc, FCT grant[b]
O. SOLOUB, Pos-Doc, FCT grant[a]

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R. MEIRA, PhD Student, FCT grant
M. DIAS, PhD Student, FCT grant (since March)
M. FIGUEIRA, Graduate, BIC grant
J.P. NUNES, Graduate, BIC grant (since Dec.)
A. GULAMHUSSEN, Graduate, BIC grant (since Dec.)

Technical Personnel

I. SOUSA, (until October)

Collaborators

A.CASACA. Adjunct Professor, ISEL

(*) Also Members of CFMCUL

Two-Chain Compounds under High Magnetic Field

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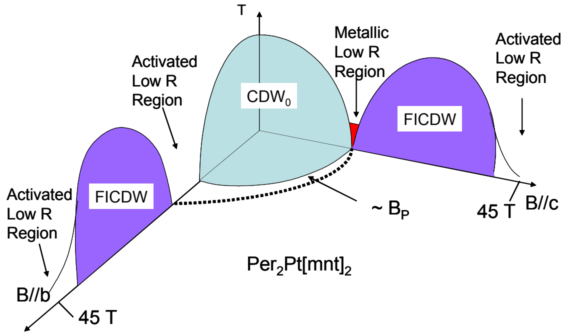
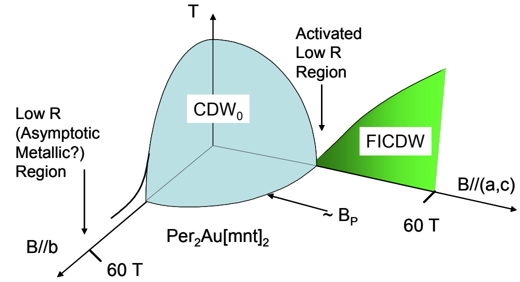
Objectives

Study the (B, T) phase diagram of (Perylene)$_2$M(mnt)$_2$ compounds with M=Au, Pt,… to investigate the coupling between the two types of chains (conducting and magnetic) present in these solids and the competition between the Peierls and spin-Peierls instabilities in each type of chain. Test the theoretical predictions for the behaviour of quasi 1D CDW systems under large magnetic fields using the Au and Pt as model compounds.

Results

Systematic electrocrystallisation essays for growth of Per$_2$Mt(mnt)$_2$ single crystals with M=Au and Pt, further than the obtention of suitable α-samples for physical measurements, demonstrated the occurrence of β-phases in the Pt compound similar to those previously described for Ni and Cu [1]. These phases may explain controversial results recently published by competing group on these compounds.





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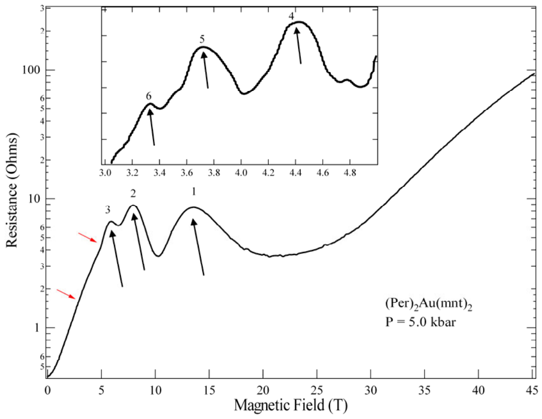
The physical studies of these samples under high magnetic fields were pursued at the National High Magnetic Field Laboratory in Tallahassee, Florida USA using in addition to resistance, Hall effect, thermopower and magnetisation, which enabled a clearer description of the rich and complex CDW phase diagram as depicted in the figure above[2,3]. In this diagram it is confirmed a subtle anisotropy with the occurrence for the Pt compound of a truly metallic ground state for B(~23T)//c separating the low field CDW state from the field induced CDW states.

The studies of these compounds under pressure show that both the critical field and the transition temperatures are quite sensitive to the pressure and at ~4-6 Kbar a metallic regime is obtained [4].



Under these pressures and at low temperatures the longitudinal magnetoresistance shows a series of oscillations, the quantum limit being reached above 20 T. The periodicity of these oscillations was found in qualitative agreement with band structure calculations, being ascribed to a Stark interference between orbits in closely spaced Fermi surfaces.

Published or in press work.

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2. J. S. Brooks, D. Graf, E. S. Choi, M. Almeida, J. C. Dias, R. T. Henriques, M. Matos, Magnetic Field Dependent Behavior of the CDW ground state in Per$_2$M[mnt]$_2$ (M = Au, Pt), *Curr. Appl. Phys.* (2005), cond-mat/0501735.
3. D. Graf, E. S. Choi, J. S. Brooks, J. C. Dias, R. T. Henriques, M. Almeida, M. Matos D. Rickel, Charge Density Wave to Mixed Density Wave Phase Transition at High Magnetic Fields in (Per)$_2$M(mnt)$_2$ (M = Au, Pt), *Synthetic Metals*, 153, .(2005) 361-364.
4. N. Mitsu, K. Yamaya, M. Almeida, R. T. Henriques, "Pressure effect on Charge Density Wave in Per$_2$M(mnt)$_2$ (M=Pt, Au)", *J. Phys. Chem. Solids*, 66, (2005)1567-1570.

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Magnetic materials Based on Decamethylmetallocenes and DCNQI Derivative Planar Acceptors

V. Gama, S. Rabaça, R. Meira, LCJ Pereira, M.T. Duarte[1], D. Simão[1]

In case of the DCNQI (NN'-dicyano-1,4-benzoquinonediimine) derivatives, the nature of the (2,5) substituents was anticipated to be determinant on the crystal structure and magnetic properties of the decamthylmetallocene based salts. This dependence is attributed to two main factors; The electron donor or withdraw nature of the substituent, as the DCNQI species can present a variety of oxidation states (neutral, monoanionic, dianionic, …), and the size of the substituents.

It was found that small atoms or groups such as Cl, Br, or Me give rise to mixed chain 1D based materials exhibiting metamagnetism, which is due to the coexistence of strong FM intrachain interactions with weaker AFM interchain interactions. Large substituents as phenyl or *t*-But were found to give rise to distinct crystal structures and to weaker magnetic interactions, this effect is attributed to the large separations between the spins due to the large substituents. A good correlation between the size of the substituents and the transition temperatures as well as the critical fields could be obtained.

With the electron donor group MeO substituent, CTS with a 1:2 stoichiometry were obtained, through the stabilization of the $(DMeO\text{-}DCNQI)_2^-$ radical. These STC exhibit a crystal structure based on segregated chains of donors and acceptors. In spite that in this case, the acceptors ¼ filled bands could be expected to lead to a significant electrical conductivity, these salts were observed to be insulators.

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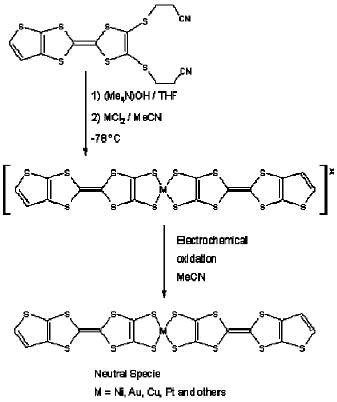
New extended dichaconide complexes for molecular materials.

D. Belo, M. Figueira, R. T. Henriques[1], V. Gama, M. Almeida, E. B. Lopes, I. C. Santos, M. T. Duarte[1], D. P. Simão[1]

This project aims at to explore new dichalcogenide complexes based on highly extended multisulfurated ligands for the preparation of conducting and magnetic molecular materials. Extended systems are expected to stabilize higher oxidation states and provide larger solid state interactions. In case of divalent ligands also containing coordinating nitrogen atoms they can be used as building blocks for heterobimetallic magnetic networks.



The Ni complexes based on novel dithiolene ligands containing both the TTF and thiophenic moieties were obtained and characterized. Although the Ni(II) complexes were obtained in anaerobic conditions they were spontaneously oxidized to the neutral state upon air exposure. So far these neutral complexes were not found metallic.

The first example of a tetra-azo substituted bisdithiolene complex, $Ni(dpesdt)_2$, was obtained as a neutral species, opening the way to the preparation of heterometallic magnetic networks.

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Metal bisdichacogenates Based Magnetic Materials

D. Belo, M.J. Figueira, S. Rabaça, L.C.J Pereira, M.T. Duarte[1], D. Simão[1], 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 bisdichalcogenates as acceptors and decamethylmetallocenes ($[M(Cp^*_2)]$) or benzylpyridinum (BzPy) derivatives as donors.

A series of salts based on $[Ni(\alpha\text{-}tpdt)_2]^-$ (S = 1/2), and different $[M(Cp^*)_2]$ and BzPy cations, was obtained. The magnetic behaviours observed, including metamagnetism, canted AFM, spin-glass, and topological frustrated magnets were correlated with the crystal structures, and analysed in terms of the acceptor spin density and spin polarization explaining the coexistence of both FM or AFM interactions, which were found to compete in a series of compounds

It was also prepared the CTS $[M(Cp^*_2)][Cu^{II}(dcdmp)_2]$, which exhibits a crystal structure consisting in an arrangement of parallel chains, where acceptors alternate with pairs of donors side-by-side, DDADDA. The magnetic behaviour is dominated by weak AFM AD intrachain interactions, this is expected to lead to ferrimagnetism, however down to 1.7 K, no magnetic ordering was observed.

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Magnetic and strongly correlated electron interactions in intermetallics based on *f* and *d* elements

J.C. Waerenborgh, L.C.J. Pereira, A.P. Gonçalves, P .Gaczyński, S. Sério, M. Almeida, M. Godinho[1]

The objective of this project is the detailed understanding of the role of U and of the rare-earths on the magnetic or strongly correlated electron behaviour of intermetallics based on *f* and *d* elements..

The magnetic properties of AFe_xAl_{12-x} compounds crystallizing in the $ThMn_{12}$ -type structure and where the rare-earth is nonmagnetic such as Y or is a 5f-element such as U have been thoroughly studied in the frame of this project. In the YFe_xAl_{12-x} ($4.4 \leq x \leq 5$) compounds the research is now mainly focused on the nanodomains with ferromagnetic interactions detected above the corresponding magnetic ordering temperatures. The $DyFe_xAl_{12-x}$ series of compounds, where 4f-electrons are involved in the magnetic interactions, were prepared. A comparative investigation of the $UFe_4Al_{8-x}Ga_x$ (x=1.0 and 1.5) and UFe_xAl_{12-x} (4:5 < x <5) compounds has shown that Fe site distribution, rather than total Fe concentration, is the determinant factor on the magnetic properties of these compounds.

Within the Dy-Fe-Sn phase diagram, the magnetic characterization of both solid solution series that were identified in is still in progress. The dependence of the Fe sublattice anisotropy on the Dy concentration in the $Dy_xFe_6Sn_6$ ($0.3 < x < 1$) compounds was established. The ^{119}Sn Mössbauer study of the antiferromagnetic-like ordering of the Dy sublattice in the $DyFe_xSn_2$ ($x \leq 0.3$) series of compounds was started.

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Materials for solid oxide fuel cells and dense ceramic membranes

J C Waerenborgh, V. V. Kharton[1,2]*, F M Figueiredo*[1]*, P.Gaczyński, J R Frade*[1]

Iron-containing oxide phases with ABO_3 perovskite structure, with electronic and ionic conductivities and high oxygen permeability, attract significant attention for applications such as electrodes of solid oxide fuel cells and dense ceramic membranes for partial oxidation of light hydrocarbons.

In 2005 our study focused on the improvement of the properties of the $SrFeO_{3-d}$ based perovskites and on a better understanding of the effect of partial substitution of Fe and Sr by Al and La, respectively. Al, a more redox- and chemical stable cation, less expensive than Cr, Ti or Ga, does not significantly affect the oxygen permeability and improves the mechanical and chemical stability under a wide range of oxygen chemical potentials. Models for proper analysis of Mössbauer spectra with several overlapping contributions were established. These models allowed the detection of charge delocalization on Fe^{4+} cations which frequently leads at low temperatures to charge disproportionation and ordering associated with magnetic ordering. Data showed that in all the compositions studied perovskites with Fe^{4+} contents lower than 0.3 per formula unit no charge delocalization is observed. In $(La,Sr)(Fe,Al)O_{3-\delta}$ progressive localization of electron holes and a mixed charge-compensation mechanism, which results in higher average oxidation state of iron when Al^{3+} concentration increases.

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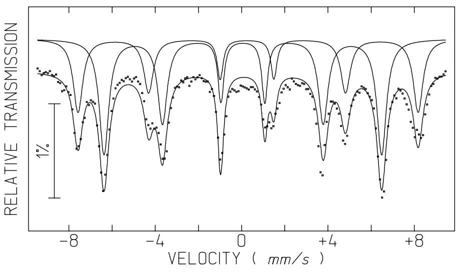
Mössbauer spectroscopy in Materials Science

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



Mössbauer spectrum of a mixed conductor oxide

A Mössbauer spectroscopy laboratory has been developed in ITN for 25 years in order to support local research projects. Presently γ-ray transmission and backscattering as well as conversion electron Mössbauer spectra may be obtained. 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. In 2005 support was given to the Mössbauer group of the Chemistry Dept. of the Faculty of Sciences of the Univ. of Lisbon. Studies of new molecule-based multifunctional materials, intermetallics and carbonate stones used as building materials have been performed in collaboration, respectively with the Univ. of Valencia, Spain, Univ. of Rennes, France and Instituto Superior Técnico, Technical Univ. of Lisbon.

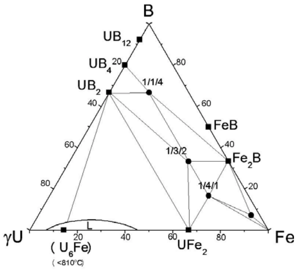
Study of Ternary Phase Diagrams based on *f* and *d* elements

A.P. Gonçalves, O. Sologub, M. Dias, L.C.J. Pereira, S. Sério, J.C. Waerenborgh, P.A. Carvalho[1], O. Tougait[2], H. Noël[2]

This project aims at 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 provides fundamental information for the preparation of single-phase samples and growth of single crystals. These studies are supported by the projects POCTI/QUI/46066/2002, and 4.1.1/GRICES/CNRS-2005-2006.

In 2005 were explored ternary systems of the type U-Fe-X, (*f*-element)-(*d* metal)-B and (*f*-element)-(*d* metal)-Sb. Preliminary results on the isothermal section at 950ºC of the U-Fe-B system indicate the existence of at least three \ternary compounds, $UFeB_4$, UFe_3B_2 and UFe_4B, the last one unreported before. Prior studies on the isothermal section of the U-Fe-Si ternary system at 900ºC show a very rich system, with nine ternary intermetallics, U_2FeSi_3, UFe_2Si_2, $U_3Fe_2Si_7$, U_2Fe_3Si, $UFe_{10}Si_2$, $U_2Fe_{13}Si_4$, UFeSi, $U_{1.2}Fe_4Si_{9.7}$ and $U_2Fe_3Si_{5.}$

The first results on the U-Fe-Ga, Y-Pd-B and R-Au-Sb (R=rare earth) phase diagrams indicate the formation of the UFe_6Ga_6, $Y_2Pd_{14}B_3$ and $R(Au_{1-x}Sb_x)_2$ compounds. These intermetallics were prepared as single-phase polycrystalline samples and as single crystals (in the case of UFe_6Ga_6) and their crystal structures and physical properties were characterised.



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High magnetic field facility

A. Casaca[1], E.B. Lopes, A. Rosa[2], J. Lucas[2], R. Borges[2]

This facility permits the study of electrical transport properties of different materials in magnetic fields up to 18 T, for temperatures between 0.3 K and 300 K. Two main areas of research were pursued: chiral molecular conductors and magnetic semiconductors.

Chiral molecular conductors are currently a topic of great interest since it is expected that they may present electrical magnetochiral anisotropy (EMCHA). The first chiral molecular metals was very recently described by a research group in Angers, France, using the Tetrathiafulvalene-Oxazoline donor, both the R and S enantiomers as well as the racemic compounds being obtained. We developed a new sensitive AC technique to search for EMCHA in these molecular metals using our 18T magnet. Using this technique it was demonstrated that both the R and S enantiomers have an EMCHA effect bellow the detection limit of our set-up (10^{-4}).

Magnetic semiconductors constitute a recent exciting field of research due to the vast possibilities of application in spintronics. We studied the magnetic field response of the DC electrical resistivity in mainly two types of samples: manganites with perovskite structure (such as $La_{1-x}Ce_xMnO_3$) and metallic ion irradiated semiconducting films (such as TiO_2 films irradiated with Ni^+ and Co^+ or ZnO irradiated with Co^+).

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