

Chemical and Radiopharmaceutical Sciences Unit



Chemical and Radiopharmaceutical Sciences

Maria de Fátima Araújo and Joaquim Marçalo

The **Chemical and Radiopharmaceutical Sciences Unit** (CRSU, formerly Chemistry Sector) reinforced its competence skills and pursued its activities in the synthesis and characterization of inactive and radioactive compounds with relevance in Health, Materials and Nuclear Sciences and Catalysis, and in the implementation and use of nuclear-based and related analytical techniques in Environmental and Earth Sciences and Cultural Heritage. The activities are developed by five research teams:

Applied Geochemistry & Luminescence on Cultural Heritage (GeoLuC) – dedicated to the study of the Portuguese cultural heritage materials and environmental contexts, through the application of nuclear methods, geochemistry and mineralogy. The main techniques used comprise INAA, XRD and luminescence (TL and OSL) and are applied to archaeometry, environmental geology and palaeoenvironmental reconstruction studies. Investigations of the composition and internal dosimetry of natural quartz grains with relevance for luminescence dating were newly performed.

Environmental and Analytical Chemistry – committed to elemental and isotopic analysis as applied to the research fields of environmental geochemistry, isotope hydrology, oceanography and archaeometry. ED-XRF, light isotope MS, HPLC-ICP/QMS, radiocarbon dating and tritium determinations are the main techniques used in sedimentary geochemistry, geochronology, absolute dating, palaeoecology, meteorology, water resources, and archaeometallurgical studies. Research was focused on coastal palaeoenvironmental evolution, upwelling, gas-phase composition in thermomineral waters and metallurgical processes in the Bronze Age.

Inorganic and Organometallic Chemistry – devoted to the synthesis, characterization and reactivity studies of actinide and lanthanide compounds. Catalytic studies, advanced MS techniques and calorimetry are used with the aim of understanding the influence of the electronic structure of the elements in the chemical

properties of the compounds. Studies were pursued on the activation and valorisation of C1 feedstocks, namely the catalytic partial oxidation of CH₄ using lanthanide and actinide intermetallics and the electrochemical treatment of CO₂.

Radiopharmaceutical Sciences – involved in basic/applied-oriented research and technology transfer on nuclear tools for molecular imaging and/or targeted radiotherapy. The multidisciplinary research is based on innovative organic and coordination chemistry, bioconjugation, radiochemistry, animal and cell studies and cellular and molecular biology. A myocardial imaging probe prepared in the Group is now being developed in GMP conditions for human evaluation by a pharmaceutical company.

Solid State – centred in the study of 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 *f*-element intermetallic compounds with a wide range of specialized solid state physics techniques. The elucidation of the structural details of a Co chain compound with dimerised anions and the discovery of superconductivity in a Au chain compound sharing a borderline with a non-magnetic CDW phase were recent achievements.

New **facilities/equipments** installed in the CRSU during 2008 included a HPLC-ICP/QMS with collision/reaction cell, under the National Program for Scientific Hardware Renewal, and a Microwave Peptide Synthesizer, under a ITN-ITQB partnership.

Researchers at the CRSU maintained their renowned practice of high level **training** of students at the MSc, PhD and Post-doc levels, and of participation in advanced **education** activities in the universities. National and international **projects** financed by the FCT, the EC and Pharmaceutical Companies, most with the scientific coordination of the Unit, are in progress. Further funds were obtained by Protocols, Contracts and Services with different Institutions and Industries.

Staff

Researchers

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Applied Geochemistry & Luminescence on Cultural Heritage (GeoLuC)

M. Isabel Prudêncio

The Group of Applied Geochemistry & Luminescence on Cultural Heritage (GeoLuC) is especially devoted to the **study of the Portuguese cultural heritage materials and environmental contexts**, through the **application of nuclear methods**, geochemistry and mineralogy.

The GeoLuC group has an interdisciplinary approach to the study of archaeological and geological contexts, and objects from excavations and museums. The origin, technique of manufacture, and age are the main issues in studying cultural assets. The study of these complex materials, such as pottery, minerals, stones and mortars, include field geology, nuclear and physical methods, geochemistry and mineralogy.

The GeoLuC research activities during 2008 were developed as follows:

- Composition and internal dosimetry of natural quartz grains
- Thermoluminescence (TL) and Optically stimulated luminescence (OSL) applied to dating geological and archaeological contexts
- Luminescence applied to Portuguese Faience and Chinese Porcelain produced for the Portuguese market (XVI to XVIII centuries): Dating, authenticity, materials, pigments
- Casa do Governador da Torre de Belém (Tagus estuary): Halieutical resources industry in Roman times
- Portuguese clays – geochemical and mineralogical characterization with a view to technological applications
- Archaeometry of Cultural Heritage Assets
- Applied geochemistry to the establishment of natural background of superficial environments: Iberian Peninsula and Atlantic islands

- Elemental distribution, radioisotopes and radioactive equilibrium of actinides and other trace elements in superficial environments
- Nuclear methods of analysis: development and application of luminescence techniques and neutron activation analysis

The main methodological approaches of the GeoLuC group comprise instrumental neutron activation analyses (INAA), X-ray diffraction (XRD) and luminescence (thermoluminescence and optically stimulated luminescence: TL and OSL) applied to archaeometry, environmental geology and paleoenvironmental reconstruction. SEM-EDS and Mössbauer are also commonly used. The application of these methodologies unique in Portugal, is crucial for solving archaeological and geological problems. The research is developed through financed projects, protocols, collaboration with national and international laboratories and universities, and contracts/services with private and public institutions.

Under the National Scientific Infrastructure Programme, the Project REEQ/590/CTE/2005, “Palaeoenvironmental Reconstruction using Chemical Analysis and Single-Grain Luminescence Dating. A non-biostratigraphical approach” ended, and the equipments for INAA and TL-OSL are in full operation.

The GeoLuC group activities also include education and training of students from national and international universities. Our students participate in the entire research work, including: field work and sampling, sample preparation for several types of analytical techniques, irradiations and measurements, and data management and interpretation. Thus, they become able to accomplish projects in fundamental and applied research.

Research Team

Researchers

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Composition and internal dosimetry of natural quartz grains

C.I. Burbidge, M.I. Dias, M.I. Prudêncio, L.P. Rebêlo¹, G. Cardoso, P. Brito¹

Objectives

As part of continuing studies to improve our understanding of luminescence behaviour in samples for dating, differences in signal levels obtainable from natural and laboratory irradiated grains of Mozambican quartz were investigated to evaluate:

- Average impurity concentrations and the composition of localised inclusions.
- TL and OSL signals contributing to the ~380 nm emission from these grains.
- The potential of α radiation to induce additional OSL signal beyond that produced by β irradiation, in both compact crystalline quartz (the surfaces of acid-etched grains), and in milled quartz with large numbers of defects exposed on grain surfaces.

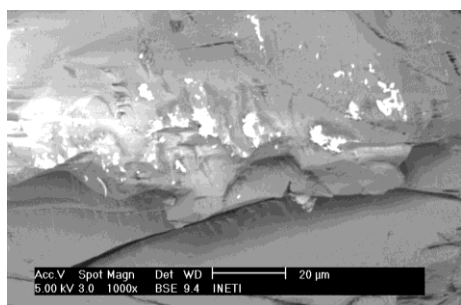


Fig. 1. BSE image of Iron Oxide inclusions in etch pits on the surface of a quartz grain.

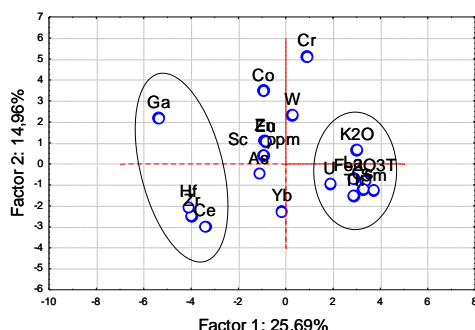


Fig. 2. PCA of INAA results indicating “Substitutional” (Zr) and “Structural” (Fe) groupings.

Results

OM, SEM, XRF and INAA, indicate the presence of various types of quartz and mineralogical inclusions. A spatial association of Th and U with Fe in structural defects was observed. Fe concentrations and inclusion sizes indicated that internal α dose rate would affect the defects that contained these impurities but would be insignificant to the bulk quartz.

A broad range of optically sensitive TL peaks were observed. The TL results suggested a preheating regime (260°C/30s) to minimise the effect of the observed inclusions and defects on absorbed dose determinations by OSL. Growth in OSL with dose from whole grains preheated in this way approached saturation by 332 Gy of β irradiation ($^{90}\text{Sr}/^{90}\text{Y}$) and by

4 kGy of α irradiation ($E \approx 3.5$ MeV, approximate natural soil spectrum average, using converted dose rate from ^{241}Am). This indicated α -efficiency (k_{eff}) at saturation of around 0.08. However, the OSL decay curves contained a small “medium” component. Structural defects introduced by milling the grains, produced a larger “medium” component with a similar decay rate under optical stimulation, which exhibited high saturation doses (>32 kGy α , >8.4 kGy β) and α -efficiency ($k_{\text{eff}} = 0.34$). Dose normalised signals from the milled material greatly exceeded those obtained from the whole grains as they approached saturation.

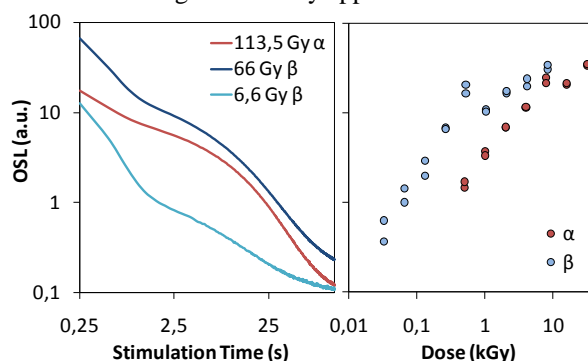


Fig. 3. Milled quartz: OSL decays and growth in signal with dose following α and β irradiation.

Conclusions

It is inferred that the presence of structural defects within a quartz crystal, similar to those produced by milling, can produce OSL components that grow to signal levels and doses exceeding those from the crystalline quartz. Samples exhibiting high saturation doses may therefore contain higher numbers of structural defects and vice versa, but the contribution to total OSL signal is expected to be small in general. When the whole crystal is irradiated, growth of these minor components at high doses may be masked by effects on signals from the bulk material, such as radiation quenching. In the present study though, such defects were found to host α -emitting impurities. High localised dose rates in nature could enhance signals from these locations without affecting the bulk crystal, making natural signal levels difficult to reproduce in the laboratory. However, association of internal α activity with Fe indicates potential for removal of the most α affected grains by magnetic separation.

Published work

Burbidge, C.I., Dias, M.I., Prudêncio, M.I., Rebêlo, L.P., Cardoso, G.O., Brito, P. Internal α activity: localisation, compositional associations and effects on OSL signals in quartz approaching β saturation, *Radiation Measurements* (in press)

¹ DGM, INETI

Thermoluminescence (TL) and Optically stimulated luminescence (OSL) applied to dating geological and archaeological contexts, archaeological artefacts and art objects

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TL and OSL absolute dating methods were applied to diverse geological and archaeological contexts from Iberian Peninsula, as well as artefacts (ceramics and lithics) on behalf of some running projects (Grices, FCT), contracts and services with national and international institutions. These studies specially aim to contribute for a better definition of the chrono-stratigraphic sequence of human occupation and/or of geological environments. Absolute dating of archaeological artefacts and authenticity tests applied to art objects was also performed. An inter-calibration program is running with Luminescence Laboratory of Instituto de Xeologia da Univ. La Coruña. Methodology involved includes physical and chemical characterization techniques (SEM, INAA, XRF and XRD), and luminescence dating techniques.



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Luminescence applied to Portuguese Faience and Chinese Porcelain produced for the Portuguese market (XVI to XVIII centuries): Dating, authenticity, materials, pigments

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Portuguese faience and Chinese porcelain produced for the Portuguese market (XVI to XVIII centuries) are being studied on behalf of an FCT project, including: (i) chemical (INAA) and mineralogical (XRD) characterization of the ceramic body; (ii) characterization (XRF and synchrotron radiation techniques) of surface coatings (glazes and pigments); (iii) TL and OSL of the ceramic body. Different composition of the ceramic raw materials may be inferred from mineralogical data. Substantial sensitisation effects were noted in the luminescence measurements. These may limit

application of conventional additive and regenerative luminescence techniques, but aid the use of predose sensitisation measurements. Absorbed doses of 1-5 Gy indicate high radioactivity and/or signals from fine grains, which absorb α radiation as well as β and γ . Ongoing analysis of sample composition and geochemistry will elucidate these issues. Further investigation of luminescence emissions in relation to the mineralogical assemblage will be undertaken.

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Casa do Governador da Torre de Belém (Tagus estuary): Halieutical resources industry in Roman times

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The study of archaeological artefacts of the production unity of fish resources transformation identified in Casa do Governador da Torre de Belém, located in the Tagus estuary, has as main purpose the chronological and functional space characterization, in order to integrate this specific site in the sphere of the production of fish-processing products in the Tagus Estuary and in a larger spectrum in the Sado Estuary, Algarve and Andaluzia. This study is an FCT running project. A typological classification of the ceramics was done by the archaeological team, and some were chosen for the archaeometric approach, namely the geochemical characterisation of amphorae paste (INAA) and mineral phases (XRD) identification. Sampling collection of sediments and paleosoils (human occupation) for luminescence dating was also performed, as well as in situ measurements of environmental radioactivity (gamma measurements).



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Portuguese clays – geochemical and mineralogical characterization with a view to technological applications

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Clay raw materials from the Meso-Cenozoic basins (Algarve and Lusitania) of Portugal are being characterized in the granulometric, geochemical and mineralogical point of view. The main goals are: (i) detailed characterization of basin sediments, particularly of clayey levels, which enable valuable palaeoenvironmental interpretations and reconstruction of the evolutionary history of the depositional environments; (ii) in addition, compositional transformations of clays with firing are study to better assess estimates of maximum firing temperatures of local ancient ceramics and to establish geochemical and mineralogical reference groups and fingerprinting clay raw materials for comparison with contemporaneous and ancient ceramics in archaeometric studies.



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Archaeometry of Cultural Heritage Assets

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Nuclear methods of analyses were applied to several archaeometric studies, namely pottery of a wide range of chronologies. Most of these studies were done in the framework of master and doctoral thesis, as well as post-doctoral programmes. Study of objects from excavations and museums, including their origin, technique of manufacture, age and conservation was done. These studies unlock information from ancient materials, such as provenance of raw materials, mainly pottery, technique of manufacture, firing technology, ancient recipes and alteration pathways, in an Iberian perspective.



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Applied geochemistry to the establishment of natural background of superficial environments: Iberian Peninsula and Atlantic islands

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Geochemistry, crystal chemistry and mineralogy are applied to the study of superficial environments (present day and paleoenvironments). The establishment of natural background and evaluation of potential anthropogenic influence, particularly in the trace elements contents, is a major goal. The geochemistry of the earth surface, principally the distribution and behavior of rare earth elements (REE) and other trace elements in secondary natural systems, and the alterations due to pollution actions in sediments and soils, have been applied in Azores Island and Cape Verde archipelago, as well as in different geomorphological/geological units of the Iberian Peninsula.



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Elemental distribution, radioisotopes and radioactive equilibrium of actinides and other trace elements in superficial environments

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Natural radioactive elements, mainly from the actinide series, are being studied in superficial environments such as soils resulting from weathering of different types of rocks, predominantly granites, and in sedimentary formations. The study of radioisotopes and radioactive equilibrium in addition to elemental concentrations distribution, enable a more accurate investigation of the mobility of elements in different geological contexts. The comparison of actinides behaviour with other trace elements, lanthanides in particular, and with mineralogy, helps on tracing sedimentary processes like weathering, sedimentary calibration and source area homogeneity. Special attention is paid to the most abundant natural radionuclides (^{232}Th , ^{238}U , ^{235}U , ^{40}K). Another important application of this study is in the determination of annual palaeodoses received by geological materials to be dated by luminescence.



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Nuclear methods of analysis: development and application of luminescence techniques and neutron activation analysis

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Instrumental neutron activation analysis is a well-established method within this group since the seventies. Based on the use of the RPI (nuclear research reactor unique in the Iberian Peninsula), this analytical method together with luminescence techniques (complemented with other methods) supports most of the research activities of the GeoLuC group. Public and private institutions often requested the group for services of both laboratories. The quality of the analytical procedures of INAA is periodically controlled through the analyses of international standards and inter-calibrations with other laboratories, in order to maintain and increment the good performance of the laboratories. The Luminescence Dating Laboratory participates in international comparisons, particularly with the IUX, Coruña, Spain. The luminescence and neutron activation laboratories were reinforced with new equipment on behalf of the national Re-equipment Program by FCT (CONC-REEQ/590/2001) and are fully running.

Environmental and Analytical Chemistry

Maria de Fátima Araújo

The activities of the Environmental and Analytical Chemistry Group (EAC) combine fundamental and methodological research related to **Elemental and Isotopic Analysis** as well as their applications in the fields of **Environmental Geochemistry, Isotope Hydrology, Oceanography** and **Archaeometry**.

Research is developed by a multidisciplinary team constituted by Analytical and Inorganic Chemists, Geologists, Biologists and Conservation scientists. Different facilities have been implemented and maintained by the team: **Energy-Dispersive X-Ray Fluorescence, Light Isotope Mass Spectrometers, Radiocarbon Dating, Tritium Unit** and a recently installed **clean Laboratory** with a **High Performance Liquid Chromatograph/Inductively Coupled Plasma Mass Spectrometer**.

During the current year the project CISTER, financed by the “*Programa Nacional de Re-Equipamento Científico*”, was executed by the installation and testing of the HPLC/ICPMS equipments, in the clean laboratory dedicated to isotopic and trace element research. Studies on the interferences of the polyatomic species and calibration procedures for trace analysis are being developed. Part of the stable isotopic ratio mass spectrometer to be associated with the laboratory dedicated to the sample preparation for AMS (Accelerator Mass Spectrometry) measurements was purchased.

Environmental Geochemistry and **Oceanographic** research was carried out under a multidisciplinary approach, including sedimentology, geochronology, absolute dating, meteorology and paleoecology. Research was focused in Sedimentary Geochemistry: to evaluate environmental changes occurred during the Holocene on the Portuguese coastal area, in particular at Minho and Sado estuaries and at the SW coastal area. Oceanographic studies concerning the marine reservoir effect, based on **Radiocarbon Dating** of

pairs of samples (terrestrial and marine) were enlarged to new regions off the W margin of Iberian Peninsula – Aveiro / mouth of Minho river and Faro / Mouth of Guadiana river.

Isotope Hydrology research studies have been developed aiming at to contribute to a sustainable regional development and appropriate use of the water resources. Investigations were carried out in different environments: Urban Areas; High Mountain Areas; Arid and Semi Arid Zones and Gas Geochemistry in CO₂-rich Thermomineral Waters, including the geothermal potential evaluation and the seismo-volcanic hazard assessment at Azores archipelago. These investigations are essential to the exploitation and future development of regional water resources and to the delimitation of protection areas.

The **archaeometallurgical research** were focused on the materials characterization, involving different analytical techniques (EDXRF, micro-XRF, optical metallography, XRD and SEM-EDS) of artefacts and other remains from different archaeological sites of the Portuguese territory along the SW Iberian region and the North Central Portugal, in order to investigate the evolution of artefact production and metallurgical operations of Copper-based alloys during PreHistory.

The study of the Macao Scientific and Cultural Center Museum **Chinese copper cash** was focused on the microstructural characterization of imperial brass coins by optical metallography, micro X-ray fluorescence, scanning electron microprobe and micro X-ray diffraction.

The EAC group is highly engaged in education and training of students from different Universities preparing their MSc and PhD thesis under our supervision.

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

Research Team

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Environmental Geochemistry – Elemental and Isotopic Research

M.F. Araújo, P. Carreira, A.M. Monge Soares, P.G. Fernandes, P. Alvarez-Iglésias, M. G. Santos, D. Nunes, P. Valério, J. Martins

Objectives

Activities aim at the development and promotion of coordinate research on Earth and Environmental Sciences in conjunction with the implementation of the following analytical and absolute dating techniques: EDXRF multielemental analysis; Light isotope determination; Radiocarbon dating; Tritium dating and HPLC/ICPMS.

Elemental, isotopic and dating techniques are being used in the understanding of natural environments, particularly aquifers, rivers, estuaries, lagoons, coastal waters and continental shelf. Our main goals are:

- 1) to establish the evolutionary patterns of coastal environments since the Holocene; identify sediment sources and evaluate the major driving factors controlling its distribution and composition; setting up regional backgrounds and the beginning and origin of anthropogenic inputs;
- 2) to determine the origin of different groundwater systems; identify the recharge areas; calculate mixture between different water bodies; 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

Geochemical and dating studies carried out in estuarine and lagoon sediments provide information about the marine/ terrigenous origin of the deposited materials and allow to identify changes occurred during the Holocene. During 2008, studies were mainly focused on: the Minho estuary; and on the salt marshes of the Sado, Mira and Guadiana estuaries. Study of Minho estuary sedimentary dated sequences reveal the influence of relative sea-level rise during the Holocene by the identification of marine inundation periods with alternating layers exhibiting a significant continental signature. Geochemistry of estuarine salt marsh sediments has permitted the establishment of natural baseline levels for many elements and the assessment of anthropogenic contamination. Baseline composition showed to be variable and highly influenced by the lithology of the catchment areas.

Environmental isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}_{(\text{SO}_4)}$, $\delta^{18}\text{O}_{(\text{SO}_4)}$ and ^3H) have been used in conjunction with conventional hydrogeological and geochemical approaches. The $\delta^{34}\text{S}_{(\text{SO}_4)}$ and $\delta^{18}\text{O}_{(\text{SO}_4)}$ values in soluble sulphates were used to conclude about its origin in

groundwaters and the water contamination extent, in Caldas da Rainha and Oporto urban area. Nitrogen isotopes determination was used to identify pollutant sources in Beja groundwater systems: fertilizer and manure. The vulnerability of Aveiro aquifer to nitrate contamination was evaluated and data were used to identify nitrogen sources (agriculture, cattle-breeding, urban and industrial) contribution to nitrogen cycle.



Radiocarbon dating is an important tool to set up chronological frameworks for the past environmental changes. As usual, it is of much use in our research. A new step in the study of the marine reservoir effect was implemented during 2008 in order to get reliable ΔR values for two coastal zones in the Atlantic Iberia badly sampled previously – Aveiro / mouth of the river Minho and Faro / mouth of river Guadiana. Besides, ΔR values were determined, for the first time, for the coastal waters of Canaries Islands. Similarly to what was done for the Atlantic Iberia, the variability of the marine reservoir effect from the beginning of colonization of the Islands till nowadays will be investigated

Published work

D. Burdloff, M.F. Araújo, J.-M. Jouanneau, I. Mendes, A.M. Monge Soares, J.M.A. Dias. Organic carbon sources to the Northern and Southwestern Portuguese shelf sediments. *Applied Geochemistry*, 23 (2008) 2857–2870.

P.M. Carreira, J.M. Marques, R. Graça, L. Aires-Barros, Radiocarbon Application in Dating “Complex” Hot and Cold CO₂ – Rich Mineral Water Systems: A Review of Case Studies Ascribed to the Northern Portugal. *Applied Geochemistry*, 23, 2817–2828.

C. Correadeira, M.F. Araújo, J.-M. Jouanneau, Copper, zinc and lead impact in SW Iberian shelf sediments: An assessment of recent historical changes in Guadiana river basin, *Geochemical Journal*, 42 (2008) 319 – 329.

Geochemical record of environmental changes in Minho Estuary (Portugal) since the Holocene*M.F. Araújo, P. Alvarez-Iglesias, T. Drago¹*

The overall objectives of this work are the recognition of the environmental changes which have occurred during the Holocene in the Minho estuary, by using a comprehensive study of the sedimentary record. Sedimentary record of transitional environments constitutes an archive of their temporal evolution, which can be assessed by multidisciplinary analytical approaches. The Minho River (about 300 km long) represents one of the main basins draining to the NW Iberian Peninsula. Its basin has around 17000 km², and comprises from Paleozoic to Cenozoic rocks, being mainly constituted by granites, schists and greywackes. We have assessed the palaeoenvironmental evolution of the Minho Estuary for the last millennia by a detailed geochemical and sedimentological study of two long sediment cores (~30m) retrieved at the mouth of the Minho Estuary. Two percussion cores were collected at the Coura (Minho tributary) marsh. Samples were characterized by EDXRF and complemented with previously results obtained by INAA and sedimentological analyses. Data integration have pointed out that the evolution of the Minho Estuary for the last millennia showed a succession of four units: (1) fluvial: coarse grained, high Si, LREE enriched with a significant negative Eu anomaly; (2) marine: increased fine-grained particle content, high carbonate, S, Br, Cl, Ca, Sr and HREE and almost flat REE normalized profiles; (3) estuarine: alternating coarse and fine-grained layers, intermediate LREE/HREE ratios, significant Ca and Sr contents; and (4) sand barrier: constant sand content (high Si and Rb), intermediate LREE/HREE ratios.

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Geochemical and sedimentological characterisation of salt marsh sediments from Portuguese estuaries (Sado and Mira)*S. Moreira¹, M.F. Araújo, M.C. Freitas¹, F. Fatela¹*

Salt marshes are transitional zones located along the intertidal estuarine region, characterized by low hydrodynamic conditions that favour the accumulation of metals and other contaminants in sediments. Salt marsh sediments from two Portuguese estuaries located at the SW coastal area: Sado and Mira, have been studied. At Sado estuary, a total of 66 superficial samples collected seasonally (fall and spring) in the intertidal domain (tidal flat, low and high marsh) along four transects were characterized. At Mira estuary, studies were focused on short cores collected in the left margin in Vila Nova de Mil Fontes salt marsh. Research involved geochemical and sedimentological approaches, including elemental composition, organic matter, grain size, carbonates, pH determinations and sedimentation rates (for the core sediments). The superficial sediments of the Sado's salt marshes of Faralhão, Carrasqueira and Alcácer do Sal are in general muds with high levels of organic matter; despite in Tróia being essentially sandy sediments with diverse organic matter levels. Regional Cu, Zn and Pb background was assessed, which allowed to conclude that salt marsh areas are heavy metal enriched. A Pb increase is observed from the mud flat and low marsh to the high marsh in one transect. Cu and Zn enrichments are comparable, whereas the Zn enrichment for ALC-S transect (Alcácer do Sal) is higher. Cores from Mira were sub-sampled for sedimentological and geochemical analyses. Organic matter content was determined for all the subsamples, EDXRF analyses and the determination of sedimentation rates by ²¹⁰Pb and ¹³⁷Cs are in progress.

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The marine reservoir effect – its quantification and variability*A.M. Monge Soares, J.M. Matos Martins, J.M. Alveirinho Dias¹*

Following previous research (see 2007 ITN Report), a new step in the study of the marine reservoir effect was implemented during 2008 in order to get reliable ΔR values for two coastal zones badly sampled previously – Aveiro / mouth of the river Minho and Faro / mouth of river Guadiana. The first zone is in the transition between two regions of an intense upwelling (Aveiro / Cape of S. Vicente and Western Galician Coast), while the second one is in the transition between a region with a coastal upwelling of some strength (Cape of S. Vicente/ Cape of S. Maria) with a region with a non-existent upwelling (Eastern Gulf of Cadiz). In complement to the above mentioned research, ΔR values were determined, for the first time, for the coastal waters of Canaries Islands. Here the oceanographic conditions are different from those of the Atlantic Iberia and, similarly to what was done for this region, we will investigate the variability of the marine reservoir effect from the beginning of colonization of the Islands till nowadays. For this research we are having the collaboration of Spanish archaeologists, which have been providing pairs of samples from archaeological contexts located in different islands and with different chronologies.

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Hydrology in urban areas

P.M. Carreira, D. Nunes, P. Valério, M.F. Araújo M.J. Afonso^{1,2}, H. Chaminé^{1,2}, J.M. Marques³

Environmental isotopes, such as $\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}_{(\text{SO}_4)}$, $\delta^{18}\text{O}_{(\text{SO}_4)}$ and ^3H , are tools that can be used to complement the conventional hydrogeological and geochemical approach to evaluate the impact of urban recharge in groundwater.

Isotope techniques, mainly $\delta^2\text{H}$ and $\delta^{18}\text{O}$ measurements and environmental ^3H , have been employed in Oporto urban region in combination with major hydrogeochemical indicators. The isotopic depletion found in groundwater samples collected along gutters are ascribed to meteoric waters infiltrated along the granitic weathering zone. Besides, groundwaters resulting into a direct infiltration of meteoric waters along the fractured granitic rocks present higher ^3H concentrations. Besides the $\delta^{34}\text{S}_{(\text{SO}_4)}$ and $\delta^{18}\text{O}_{(\text{SO}_4)}$ values of dissolved sulphate will be used to conclude about the origin of sulphate in local groundwaters, in order to assess the extent of water contamination.



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Groundwater resources assessment by anthropogenic and natural contamination sources

P.M. Carreira, P.A. Fernandes, D. Nunes, L. Ribeiro¹, E. Peralta², M.A. Marques da Silva³, M.T.C. Melo³



Related to anthropogenic inputs that lead to the degradation of water resources, studies were focused on origin/sources of nitrate in water resources (surface and groundwater bodies) using nitrogen isotopes. Two areas, Aveiro and Beja have been investigated. The determination of nitrogen isotopes ($^{15}\text{N}/^{14}\text{N}$ ratios) offers a direct way to identify the pollutant sources in groundwater systems. In Beja two major sources of nitrate were identified – fertilizer and manure. The relative contribution of these two sources to groundwater or surface water was estimated by mass balance. At Aveiro region the isotope techniques were used to evaluate the aquifer

vulnerability to nitrate contamination. Groundwater samples were collected from wells and springs for isotopic analysis. Nitrogen isotopes were used to identify nitrogen sources and assess agriculture, cattle-breeding, urban and industrial contribution to nitrogen cycle in Aveiro ecosystem.

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Arid /semi arid zones hydrology

P.M. Carreira, P.A. Galego Fernandes, D. Nunes, F. Monteiro Santos¹, A. Pina², A. Mota Gomes², J.M. Marques³, M. Bahir⁴

Overexploitation of coastal aquifers and pollution are among the main problems related to groundwater resources assessment and management in Santiago Island (Cabo Verde). Brackish groundwater for agriculture and human supply is being provided to numerous parts of the Island, as the only type of available water. Results indicate water-rock interaction mechanisms as the major process responsible for the groundwater quality (mainly calcium-bicarbonate type), reflecting the lithological composition. Anthropogenic contamination was identified, in several points of the island. Isotopic techniques combined with geochemistry provided comprehensive information on groundwater recharge, and identification of salinization mechanisms (e.g. seawater intrusion, salt dissolution, and marine aerosols) of the groundwater systems, at Santiago Island. At Essaouira Basin (Morocco) a multidisciplinary approach has been applied to evaluate the hydrogeological potential of arid zones and estimate groundwater supply of the region.



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High mountain areas in catchment water resources*P.M. Carreira, D. Nunes, J.M. Marques¹, J. Espinha Marques², H. Chaminé³*

Serra da Estrela Mountain “normal” groundwaters belong to the Na-Cl and HCO₃-Na *facies*, with low TDS,



considered as good signatures of local recharge and hydrolysis of Na-plagioclases, respectively. The high Na-Cl concentrations found in some of the waters of this group could be ascribed to the local use of NaCl to promote snowmelt in the roads during the winter season. Mineral waters from Caldas de Manteigas Spa are characterised by: high pH values (≈ 9), EC values around 300 $\mu\text{S}/\text{cm}$, the presence of reduced species of sulphur ($\text{HS}^- \approx 1.7 \text{ mg/L}$), silica contents of about 50 mg/L and high F⁻ concentrations (up to 7 mg/L), indicate that the reservoir rock should be mainly the granite. The most important isotopic signature is ascribed to the fact that no influences of a lighter isotope component in the

groundwater samples from winter campaigns was found and explain the mixing process between different groundwater bodies, with the tendency to the homogenisation of the isotopic composition.

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Gas geochemistry in CO₂-rich thermomineral waters a contribution to the geothermal potential evaluation and the seismic-volcanic hazard assessment*P.M. Carreira, D. Nunes, J.M. Marques¹, M.R. Carvalho², G. Capasso³, F. Grassa³, J.C. Nunes⁴, P. Madureira⁵*

The chemical and isotopic data of HCO₃-Na-CO₂-rich thermomineral waters (NE Portugal) revealed that the CO₂-rich thermomineral waters are part of an open system to the influx of CO₂ gas from a deep-seated reservoir. The chemical composition of both hot and cold mineral waters suggests that water-rock interaction reactions is mainly controlled by the amount of dissolved CO₂(g) rather than by the water temperature. The ³He/⁴He and ⁴He/²⁰Ne ratios measured in the gas phase are consistent with a two-component mixing of prevailing radiogenic and a mantle origin. This hypothesis is supported by the stable carbon isotope data that corroborates an external source of CO₂ of inorganic origin. $\delta^{13}\text{C}_{\text{CO}_2}$ values ranging between -7.2‰ and -5.1‰ are consistent with a two-component mixture between crustal and mantle-derived CO₂. In parallel two sampling campaigns were performed in Azores archipelago in order to: i) characterize the chemical and isotopic composition of groundwaters, fumaroles and gas emissions related with hydrothermal/geothermal systems and volcanologic/seismic settings.



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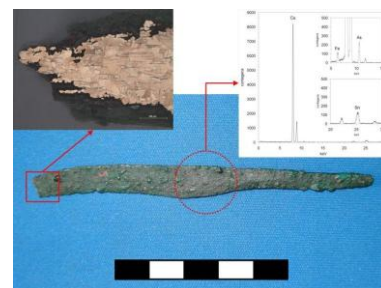
Radiocarbon dating applied to archaeological contexts – building up the South-Western Bronze Age Chronology*A.M. Monge Soares, J.M. Matos Martins*

As we said in the 2007 Report, since the beginning of the radiocarbon laboratory, twenty years ago, one of its important tasks has been to build up reliable and precise prehistoric chronologies in closed cooperation with archaeologists. Nevertheless, some cultural periods still fall short of absolute dates that allow a reliable chronology for their phases and sub phases. It is the case for the Bronze Age of the South-Western Iberian Peninsula. Recent mitigation works, as a result of Environmental Impact Assessments related to the Alqueva Dam Project, have been carried out by archaeological companies that led to the discover of several Bronze Age and Early Iron Age settlements and burials. These archaeological contexts, at first sight, seem to be largely diachronic belonging to different cultural phases from Early to Late Bronze Age, with prolongations to Early Iron Age contexts in some of them. Organic samples, i.e. charcoal and bones, have been recovered after archaeological excavations that will allow a good precision and reliability for the chronologies that are actually in process of building up. Since the beginning of this research a few tens of radiocarbon dates were already obtained, strongly changing the previous situation concerning the absolute chronology for the Proto-History of SW Iberia.

Archaeometallurgy – Provenance, technology and use of metallic artefacts

M.F. Araújo, P. Valério, E. Figueiredo, A.M.M. Soares, R.J.C. Silva¹, F.M. Braz Fernandes¹, J.C. Senna-Martinez²

The archaeometallurgical research combines material characterization, involving different analytical techniques (EDXRF, micro-EDXRF, optical metallography, XRD and SEM-EDS), with archaeological evidences, in order to investigate the evolution of artefact production and metallurgical operations of Copper-based alloys during PreHistory on the SW Iberian region and on North Central Portugal. Metallic artefacts from Late Bronze Age and Early Iron Age archaeological sites of the South-western Iberian Region, namely Castro dos Ratinhos, Santa Margarida, Salsa 3 and Casarão da Mesquita 3, were found to be made of binary copper-tin alloys (Sn~ 8-12%) with low lead content (Pb<1%). The presence of copper and tin residues aggregated to the inner surfaces of several Late Bronze Age crucibles from Entre Águas 5, Martes and Casarão da Mesquita 4, establish the practice of bronze metallurgy at those sites. Regarding the Central and Northern Portuguese regions a large set of artefacts, fragments, scraps, and other metallurgical remains (crucibles, slags and moulds) from Bronze to Iron Age recovered from different archaeological sites (Castro de Nossa Senhora da Guia de Baiões, Castro de Santa Luzia, Castro de São Romão, Cabeço do Couço and Dólmen de Fiais da Telha in Beira Alta region, and Fraga dos Corvos in Trás-os-Montes) have been analysed. Analyses show during the Late Bronze Age artefacts from the Beira Alta region had very low Pb contents (Pb<1%) wherever the bronze corresponding to an early Iron Age period from the Trás-os-Montes region had frequently ~2%Pb. The tin content for both periods and regions is regularly around 8-13%. Artefacts microstructures were variable, exhibiting characteristic evidences (e.g. annealing twins and deformation bands) of different thermo-mechanical finishing operations, involving for instance mechanical deformation and/or annealing.



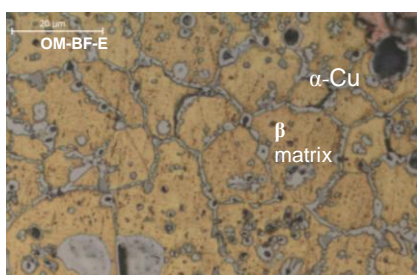
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Composition and microstructures of imperial brass Chinese coins

M.J. Furtado, M. Fátima Araújo, Rui Silva¹

On the sequence of the EDXRF analyses on the c. 400 coins last year, copper cash (round coins with a square centred hole) from the Macao Scientific and Cultural Centre's Museum (Lisbon) the study of the collection has continued by the characterization of their (bulk) composition and microstructures through micro-EDXRF, SEM-EDS and micro-XRD. About 25 selected coins (brasses) were prepared for analyses, with minimal damage to the coins surface: the coins were mounted on resin and c. 1mm² of the rim was abraded to access the metallic (patina/corrosion free) surface. The EDXRF results of the cleaned area did not show significant variation from the previously obtained, except a slight increase in the zinc content. This is in agreement with the observed microstructures that have clearly indicated a superficial dezincification. Microstructures observed are typical of as-cast structures although very fine due to their size and thickness. Lead was found to form globules in the structure and EDS analysis reveals the presence of S, that wasn't detected with EDXRF. The main phases are *alpha-beta* of Cu-Zn system (in brasses) and *alpha-delta* in Cu-Sn systems (bronzes). Other elements as Pb, Fe, Sb or As tend to group together in grain boundaries. An important find was that the presence of small amounts of Sn in brass alloys (up to 3%) inducing the appearance of a third phase, Sn or Sb rich. This phase is congruent with Cu-Zn-Sn ternary system (*gamma*₁) has been identified through micro-XRD.



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Inorganic and Organometallic Chemistry

Joaquim Marçalo

The activities of the Group comprise the synthesis, characterisation and chemical reactivity studies of inorganic, organometallic and intermetallic compounds of actinides and lanthanides with the aim of understanding the influence of the electronic structure in the chemical properties of their compounds. Chemical reactivity is assessed by stoichiometric reactions and by homogeneous and heterogeneous catalytic studies, which are also carried out in an effort to find new applications for lanthanide and actinide compounds. Gas-phase ion chemistry studies with the same elements and studies of the energetics of their compounds, using advanced mass spectrometric and calorimetric techniques, are also undertaken with the same objective.

Relevant facilities maintained by the Group are a laboratory for handling highly radioactive actinides, a laboratory for catalytic studies, a laboratory for calorimetric studies and thermal analysis, and two select mass spectrometers, a FTICR with EI and LDI sources, and a QIT with ESI and APCI sources. The QIT mass spectrometer was acquired with the support of the "National Program for Scientific Hardware Renewal" of FCT and is part of the National Mass Spectrometry Network.

Pursuing previous work on environmental issues, we continue to apply our knowledge to the activation and valorisation of methane and carbon dioxide as valuable C1 feedstocks, namely through the catalytic partial oxidation of CH₄ (POM reaction) and electrochemical treatment of CO₂. Of interest to the latter activity is the ongoing collaboration with OMNIDEA, Lda., a start-up company dedicated to R&D of aerospace technology and energy systems (ITN-OMNIDEA cooperation protocol).

We have studied the POM reaction on catalysts obtained by two routes: i) an intermetallic route, using LnCu₂ and LnNi₂ (Ln = from La to Yb) or AnNi₂ and ThCu₂ and ii) a sol-gel route (urea or citric acid methods) to obtain nanoparticles of heterobimetallic oxides. The electrochemical study of CO₂ activation

was also undertaken, this time using a pilot scale reactor. Both approaches allowed the production of syngas with high conversion of methane, high electric efficiency and the appropriate H₂/CO mol ratio of 2, especially for the nickel based catalysts that are cheaper and depicted an activity and selectivity comparable to that of one of the best catalysts reported so far in the literature (5 wt. % Rh/Al₂O₃).

New alkyl derivatives of yttrium bis(phenolate)-diamine complexes were synthesised. The tris(pyrazolyl)methane ligands started to be explored in the preparation of U(III) and U(IV) complexes. The photochemical properties of different complexes lanthanide complexes with tris(pyrazolyl)borate ligands started to be evaluated.

FTICR/MS was used to probe new ligations for the actinides, namely U-N, U-P and U-S. ESI-QIT/MS was employed in the speciation of U in basic solutions of ammonium and tetrabutylammonium uranates and in preliminary studies of the complexation of lanthanide nitrates by several N-donor ligands.

Studies with ionic liquids were pursued and the kinetics of some of their reactions were studied using FTICR/MS. Also, the thermal properties of some ionic liquids were studied using DSC techniques and the correspondent reactivity was explored using ESI-QIT/MS.

The collaboration with the Radiation Technologies: Processes and Products Group (UFA) was continued with studies of gamma radiation effects on gallic acid. Joint projects with the Research Unit "Glass and Ceramics for the Arts" (a collaboration between ITN, FBAUL and FCT/UNL) on new lanthanide based fluorescent glasses, on ruby glass and on provenance studies of Portuguese glasses continued.

An important part of the activity of the Group is the training of research students. Some of the group members are involved in undergraduate and MSc university courses. The work is financially supported by FCT and other sources, via research projects and PhD and Post-doc grants.

Research Team

Researchers

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T. ALMEIDA GASCHÉ, Aux.
J. M. CARRETAS, Aux.
C. C. L. PEREIRA, Aux., Contract (since Mar.)
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F-Block Element Intermetallic Compounds as Catalysts

J. B. Branco, A. C. Ferreira, T. A. Gasche, M. R. Correia¹, A. P. Gonçalves

Objectives

The main objective of this research is: (i) to study the f-block elements behaviour as catalysts or catalytic precursors, (ii) to develop new methods for the preparation of 4f and 5f nanostructured materials for catalytic purposes and (iii) to contribute for the resolution of key environmental issues.

Experimental work is based on heterogeneous catalytic reactions followed by gas chromatography. The f-block elements (lanthanides and actinides (Th, U)) catalysts synthesis was accomplished by either high temperature solid state reactions (intermetallic route) or liquid phase bench-top techniques (Sol-Gel route).

Results

F-block element binary intermetallic compounds have been found to be active in a variety of reactions. Recent years studies in our laboratories have shown that AnNi_2 ($\text{An}=\text{Th}, \text{U}$) and LnCu_2 ($\text{Ln}=\text{La-Tm}$), as Ln-Cu-O bimetallic oxides catalytic precursors, were active and selective in catalysis [1-3]. Such bimetallic oxide catalysts, Ln-Ni-O ($\text{Ln}=\text{Pr}, \text{Gd}, \text{Tm}$), An-Ni-O ($\text{An}=\text{Th}, \text{U}$) and Th-Cu-O were active and selective for the catalytic partial oxidation of methane (POM). The highest activity and stability (over a period of 24 h of time on stream) was obtained on the nickel-actinide or lanthanide oxide catalysts (Fig. 1). H_2 and CO selectivities were also very high ($> 95\%$). Therefore, the good catalytic behaviour of this nickel based catalysts and its high stability is a major achievement since the known and widely studied noble metal based catalysts are limited by their high cost, whereas the deactivation of others catalysts is the major drawback of this reaction that limit a widespread industrial application.

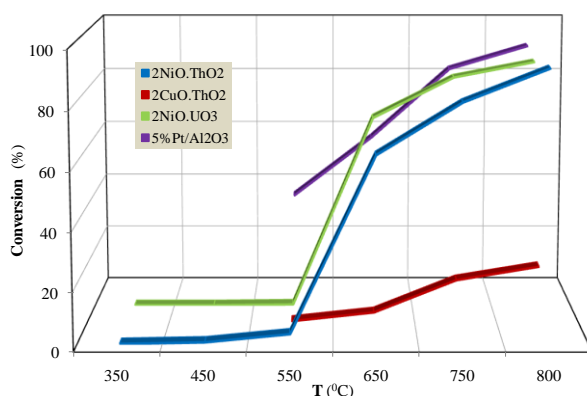


Figure 1. Activity and stability (shown for 2NiO.UO_3 at 800°C) over the An-Ni-O bimetallic oxide catalysts

On the experimental side, the Sol-Gel technique was used as an alternative preparation route to obtain cheaper and nanostructured bimetallic oxide catalysts with high specific areas, which is a disadvantage of the intermetallic route. Preliminary results confirm that the catalysts morphology is very different (Fig. 2) but, the catalytic behaviour is very similar, mainly, in the case of the lanthanide and actinide-nickel catalysts. Our results seem also to confirm that the f-block elements have a direct role in the catalytic process. RAMAN studies provided direct evidences that the d metal incorporate in the f-block element oxide lattice, instead of dispersing on the surface. XRD confirm that the MO ($\text{M}=\text{Cu}, \text{Ni}$) phase is at least partial reduced at the end of reaction, pointing for a major catalytic role of such species on the synergetic relationship between d and f metal.

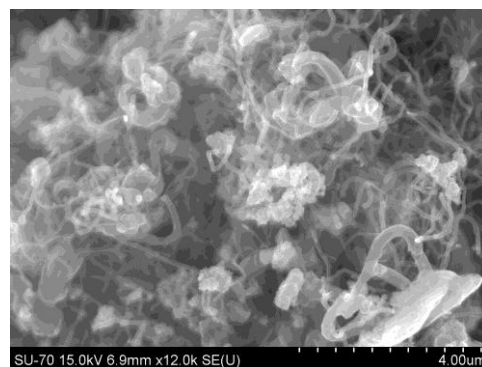


Figure 2. SEM pictures obtained after POM reaction for the Ce-Cu-O bimetallic oxide catalysts: formation of ceria oxide nanotubes and CuO platelets with an average size of $\approx 50 \text{ nm}$ instead of a solid state solution in the case the samples obtained via intermetallics.

Published work

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J.B. Branco, D. Ballivet-Tkatchenko and A. Pires de Matos, *Reduction and catalytic behaviour of heterobimetallic copper-lanthanide oxides*, J. Alloys Compd., 464 (2008) 399-406.

J.B. Branco, C.J. Dias and A.P. Gonçalves, *Thermal Studies on Oxidation-Reduction of LnCu_2 Intermetallic Compounds and their Catalytic Behavior for 2-Propanol Decomposition*, J. Alloys Compd., doi:10.1016/j.jallcom.2008.11.113. (in press)

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f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

J. Cui, J. M. Carretas, A. Carvalho, N. Marques, J. Marçalo, C. C. L. Pereira, I. C. Santos, A. M. Martins¹, C. A. T. Laia²

In order to investigate the catalytic activity of lanthanide complexes supported by the bis(phenolate)diamine ligand (${}^{\text{tBu}}\text{O}_2\text{NN}'=[\text{Me}_2\text{N}(\text{CH}_2)_2\text{N}\{\text{CH}_2-(2-\text{OC}_6\text{H}_2-\text{Bu}^{\text{t}}_2-3,5)_2\}]$) in the polymerization of cyclic esters, the search for yttrium derivatives continued during 2008. Formation of the alkyl derivatives $[\text{Y}({}^{\text{tBu}}\text{O}_2\text{NN}')(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)]$ and $[\text{Y}({}^{\text{tBu}}\text{O}_2\text{NN}')(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2)]$ was observed when $[\text{YCl}({}^{\text{tBu}}\text{O}_2\text{NN}')(\text{DME})]$ reacted with the lithium salts of the corresponding alkyls. The latter also reacted with $\text{LiCH}_2\text{SiMe}_3$ to yield the ate complex $[\text{Y}({}^{\text{tBu}}\text{O}_2\text{NN}')(\text{CH}_2\text{SiMe}_3)_2\text{LiCl}(\text{THF})]$. Recrystallization of this compound from THF gave crystals of the unusual $[\{\text{Y}({}^{\text{tBu}}\text{O}_2\text{NN}')(\text{CH}_2\text{SiMe}_3)_2\}_2(\mu\text{-O})(\mu\text{-Li})_2]$. The reactivity of the alkyl derivatives was checked in the reactions with acetonitrile. Acetonitrile inserts into the Y-C bond of $[\text{Y}({}^{\text{tBu}}\text{O}_2\text{NN}')(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)]$ to yield a product resulting from migratory insertion, $[\text{Y}({}^{\text{tBu}}\text{O}_2\text{NN}')\{(\text{HNC}(\text{Me})\text{C}(\text{H})\text{C}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{NH})\}]$. Excess of acetonitrile led to the formation of the six-membered heterocycle complex $[\text{Y}({}^{\text{tBu}}\text{O}_2\text{NN}')\{k^2\text{-(HNC}(\text{Me})\text{C}(\text{H})\text{C}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{NH})\}]$.

The anionic tris(pyrazolyl)borate (Tp) ligands have been successfully used as ancillaries for the f elements. The neutral analogues of Tp ligands, the tris(pyrazolyl)methanes (Tpm), have not received the same attention as the borates. Preliminary reactions of $\text{UI}_3(\text{THF})_{2.5}$ and UCl_4 with Tpm^* (tris(3,5-dimethylpyrazolyl)methane) in THF gave $\text{UI}_3(\text{Tpm}^*)(\text{THF})$ and $\text{UCl}_4(\text{Tpm}^*)$, respectively, and the x-ray crystal structures of these two complexes were determined.

New organic ligands (sensitizer) with potential 'antenna effect' are expected to be synthesised and anchored in several lanthanides mainly in their +3 oxidation state. Different complexes Tp_2LnCl and $\text{Tp}'_2\text{LnL}$ have been synthesised according with the literature and their photochemical properties evaluated. Preliminary results show that functionalization of the C3 of the pyrazole ring with 4-fluorophenyl in the tris(pyrazolyl)borate ligand corresponds to modifications of the emission spectra, going from a visible to ultraviolet emitter.

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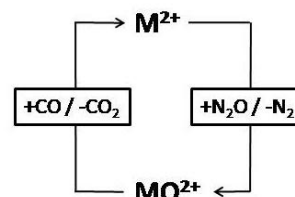
³ Dep. de Química, Faculdade de Ciências e Tecnologia, Univ.Nova de Lisboa.

Gas-Phase Ion Chemistry of Actinides and Lanthanides

J. Marçalo, C. C. L. Pereira, J. M. Carretas, A. Pires de Matos, M. Santos, A. P. Gonçalves, J. K. Gibson¹, R. G. Haire²

Fundamental aspects of the chemistry of atomic and molecular actinide and lanthanide ions and neutrals continued to be examined by advanced mass-spectrometry techniques, namely, Laser Desorption/Ionization Fourier Transform Ion Cyclotron Resonance MS (LDI-FTICR/MS) and Electrospray Ionization Quadrupole Ion Trap MS (ESI-QIT/MS). Parallel theoretical studies of selected actinide molecular ions were also carried out via collaborations to validate the interpretation of the experimental observations.

The characterization of the gas-phase thermodynamics of neutral and ionized CmO by FTICR/MS was completed; of note in these studies was also the observation that CmO^{2+} catalyzes the O-atom transport from N_2O to CO. LDI-FTICR/MS was used to probe new ligations for the actinides, namely U-N, U-P and U-S, with samples prepared by high-temperature synthesis; preliminary studies of the oxidation reactions of US^+ (and ThS^+) were also carried out. The formation of molecular uranates continued to be examined and the high-yield production of these species from anhydrous and hydrated UO_3 by LDI-FTICR/MS was achieved. In a related study, ESI-QIT/MS was used in the speciation of U in solutions of ammonium and tetrabutylammonium uranates. ESI-QIT/MS was also employed in preliminary studies of the complexation of lanthanide nitrates by several N-donor ligands; competitive CID experiments were performed with systems involving two different ligands.



¹ Lawrence Berkeley National Lab. (Berkeley, California, USA).

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Molecular Energetics of Organic, Inorganic and Organometallic Compounds

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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 of molecules (both inorganic and organic compounds). Special importance is given to f-element compounds (both on solid state and in solution). To achieve this goal, lanthanide and actinide (organometallic and intermetallic), alkaline and alkaline-earth compounds, hydrocarbons and ionic liquids were studied.

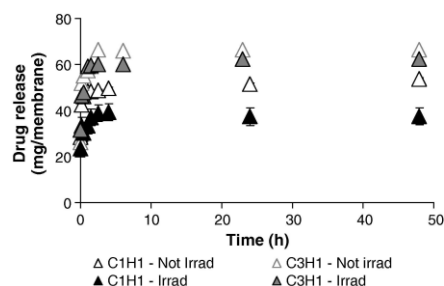
During 2008, enthalpies of formation published for CH, CHO and CHN compounds were critically revised and used to improve an extended Laidler method of additive contributions. The nature of ionic liquids in the gas phase was studied and the kinetics of some of the reactions where they are involved began to be studied using FTICR/MS. Also, the thermal properties of some ionic liquids were studied using DSC techniques and the correspondent reactivity was explored using ESI-QIT/MS. The degradation/decomposition of gallic acid and its derivatives, either gamma-irradiated or not, was also studied using ESI-QIT/MS. Using FTICR/MS, the measurement of the gas-phase acidity of methoxy di-substituted phenols was undertaken.

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Gamma Irradiated Chitosan/pHEMA Membranes for Drug Release Systems

L. M. Ferreira, M. H. Casimiro, J. P. Leal, M. H. Gil¹

To obtain biocompatible and sterilized matrices for controlled drug release to be used in direct contact with skin, films with different contents in chitosan and hydroxyethyl methacrylate (HEMA) have been prepared by γ irradiation from a ^{60}Co source. Those films naturally exhibit antimicrobial properties with good mechanical behavior. The loading with amoxicillin lead to active membranes that show an insignificant level of hemolysis and present a fast rate of amoxicillin release. Also, membranes using polyethylene as backbone polymer and HEMA as grafting molecule, produced through irradiation on a ^{60}Co source, were synthesized and the corresponding properties extensively studied.



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Glass Science with Applications in Archaeometry and Art Studies

A. Pires de Matos, J. Marçalo, F. Lopes, A. Ruivo¹, V. S. F. Muralha¹

A. Pires de Matos is coordinating the research unit VICARTE - "Glass and Ceramics for the Arts", supported by FCT, with participants from ITN, FBAUL and FCT/UNL. Expertise on glass science is being developed, particularly in the synthesis of glasses with new properties and in chemical characterisation of glasses for provenance studies.

In 2008 the archaeometric studies of portuguese glasses using several techniques continued. In the analytical characterization of Coia glasses from an archeological excavation four types of glass were identified. For comparison with glass from Marinha Grande, glass objects of the Museu Nacional de Soares dos Reis, Porto,



Museu Nacional de Machado Castro, Coimbra, and Museu do Vidro, Marinha Grande, were characterized using micro-X ray fluorescence. Comparisons with formulations in an Arcano of 1793 of Guilherme Stephens were made.

Another research area is related with the development of glasses for artistic applications. Studies on luminescent glasses with rare earths have continued, as well as the quenching of luminescence by d-transition elements. Gold and copper ruby glass were synthesized

using gamma radiation for reduction of the metal ions and to improve nucleation of the metal nano-particles.

The first experiments to characterize glass by LIBS (Laser Induced Breakdown Spectroscopy) were made using a Nd:YAG laser (ITN) and a fiber optics UV-Vis optical absorption spectrometer.

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Radiopharmaceutical Sciences

Isabel Rego Santos

Apart from the continuing improvement in equipment and technology, the success story of **Nuclear Medicine** is strongly dependent on the availability of powerful nuclear probes for molecular imaging and/or targeted therapy. The **Radiopharmaceutical Sciences Group** does **basic/applied-oriented research and technology transfer** on nuclear tools for **molecular imaging and/or targeted radiotherapy**. This is a multidisciplinary task based on innovative organic and coordination chemistry, bioconjugation, radiochemistry, animal and cell studies and cellular and molecular biology knowledge afforded by modern genomics/proteomic research. We have implemented and developed expertise on these fields and facilities to carry on such activities. Such combination, **unique in the country**, was reinforced this year with the acquisition of a Microwave-Peptide Synthesizer and justifies our participation in national and international research projects, the support of an international pharmaceutical company, and the involvement in education and training.

Our main achievements are described in this report. However, we would like to emphasize the following:

Research:

1 - The new myocardium imaging, designed and synthesized by the Group, passed pre-clinical, toxicity and dosimetry tests and is being developed in **GMP** conditions by a **Pharmaceutical Company**, for human evaluation. A significant achievement for **ITN** and **Portuguese Science and Technology**.

2 - A new methodology for preparing *in situ* metal complexes with hybrid poly(azoly)borates has been implemented, allowing a **fast in vitro screening** of the biological properties of the complexes.

3-Biological studies with new ^{99m}Tc -complexes have **confirmed in vitro** DNA damage and apoptotic cell death by **Auger electrons**.

4-Complexes of d- and f- elements with tetraazamacrocycles bearing clinically relevant pendant arms **have been synthesized, characterized in the solid state and in solution and biologically evaluated**. This was a significant improvement at the macroscopic level to correlate with the corresponding radioactive complexes.

Education and Training:

1-Graduation, the Group teaches Radiopharmacy at ESTSeL and Faculty of Pharmacy/University of Lisbon. Under a protocol, students of the Nuclear Medicine Course/ESTeSL are trained in our group (two weeks/year).

2-Post-graduation, organizes and coordinates the Master Course *Biomedical Inorganic Chemistry: Diagnostic and Therapeutical Applications*. During 2008, coordinated the Discipline Radiopharmaceutical Chemistry in the *Master Course Pharmaceutical and Therapeutical Chemistry*, Faculty of Pharmacy/UL, and the Discipline Chemical Systems and Reactivity in the 2nd Cycle in Chemistry and lectured in PhD Teaching Programs organized by Universities/Associated Laboratories.

3-International level, teaching in the European Radiopharmacy Course, INSTN.

4-Young scientists: Eighteen are trained in the group, playing a major role in our projects.

Expertise Provided: Nuclear Medicine Centers, Portuguese Medicines Evaluation Agency, IAEA and Foreigner Science Foundations.

Financial support: Mallinckrodt Medical B.V. (a Covidien Company), FCT, CIMAGO/FLAD, BILATERAL and EC/COST ACTIONS.

Publications: Peer-Review International Journals – 12; Patents – 1; Proceedings./Reports- 5; Communications – 24; Thesis: MSc – 5. **Invited Lectures and Seminars**: 8.

Research Team

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J. G. CORREIA, Princ.
M. P. C. CAMPELLO, Aux.
M. C. OLIVEIRA, Aux.
L.GANO, Aux.
F. MARQUES, Aux.
P. RAPOSINHO, Aux.
F. MENDES, Pos Doctoral, FCT grant, Aux contract since Sept.
C.FERNANDES, Ass..

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S. GAMA, Pos-Doctoral, FCT grant
P. ANTUNES, Pos-Doctoral, FCT grant
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M. MORAIS, M.Sc. student
G.CLEMENTE, M.Sc. student
M. VIDEIRA, BIC grantee, POCl

Technical Personnel

A. RODRIGUES
E. CORREIA

A New Myocardial Perfusion Imaging Agent: Evaluation in Rats and Comparison with ^{99m}Tc -Sestamibi and ^{99m}Tc -Tetrofosmin

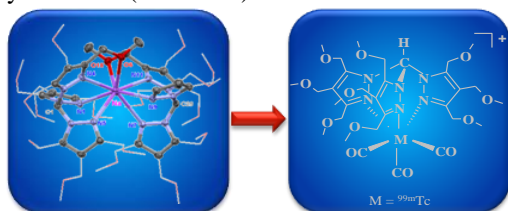
A. Paulo, V. Caveliers¹, C. Fernandes, H. Knight², M. Bauwens¹, T. Lahoutte¹, I. Santos

Objective

The main goal of this project is to find good performing nuclear myocardial probes to detect perfusion abnormalities in asymptomatic coronary artery disease (CAD) patients, avoid myocardial infarction, and apply therapeutic regimes, before irreversible myocardial damage occurs. Such probes will improve Nuclear Cardiology, an important and noninvasive tool for the clinical evaluation of patients with known or suspected CAD.

Results

The new myocardial imaging agent ^{99m}Tc -TMEOP (**1**), where TMEOP is a neutral and tridentate nitrogen donor chelator, has been quantitatively synthesized (Scheme 1).



Scheme 1: Synthesis of **1**

The chemical identity of **1** was established by comparing its HPLC chromatogram with the UV-vis trace of the Re congener (**1a**) (Figure 1).

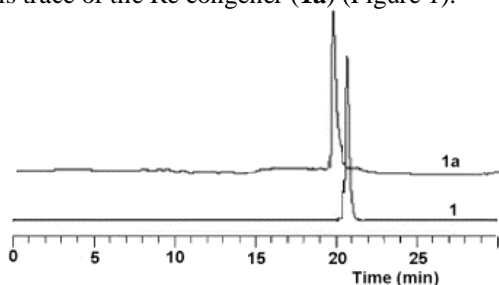


Figure 1. HPLC chromatograms: **1** (γ -detection), **1a** (UV-vis detection)

Complex **1** is stable both *in vitro* and *in vivo*. Dynamic imaging studies have shown that the cardiac uptake of **1** is comparable to ^{99m}Tc -MIBI (**2**) and ^{99m}Tc -TETRO (**3**), but presents a significantly faster clearance from the liver (Figures 2 and 3).

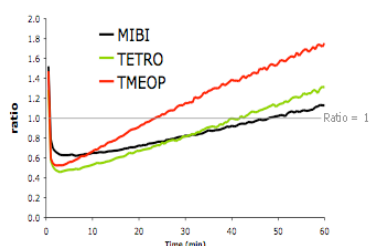


Figure 2. Heart-to-liver ratio of ^{99m}Tc -TMEOP (**1**), ^{99m}Tc -MIBI (**2**) and ^{99m}Tc -TETRO (**3**).

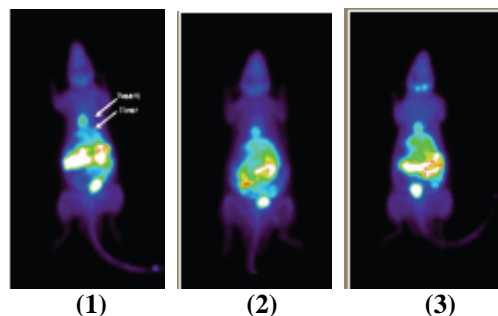


Figure 3. Rat whole body images show diminished liver activity for ^{99m}Tc -TMEOP (**1**) and a better delineation of the heart

High quality SPECT images could be obtained with the new tracer **1** (Figure 4).

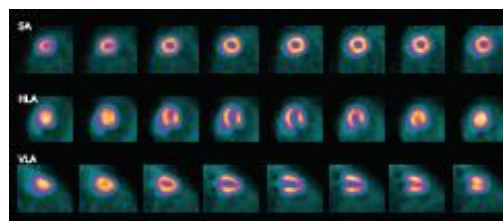


Figure 4. Short-axis (SA), horizontal long-axis (HLA) and vertical long-axis (VLA) slices of a pinhole myocardial perfusion study in Wistar rats, using ^{99m}Tc -TMEOP (**1**).

The high heart uptake and fast liver clearance of **1** should result in less artifacts and improved diagnostic accuracy for detecting CAD, making **1** a very promising compound for further evaluation in human studies.

Published work:

I. Santos, A. Paulo, Tricarbonyl Complexes with Tridentate Chelators for Myocardium Imaging, WO 2008/061792 A2.

L. Maria, C. Fernandes, R. Garcia, L. Gano, A. Paulo, I.C. Santos, I. Santos, Tris(pyrazolyl)methane ^{99m}Tc Tricarbonyl Complexes for Myocardium Imaging, *Dalton Trans.* DOI: 10.1039/b817451b. **Hot Article**, www.rsc.org/Publishing/Journals/dt/HotArticles.asp

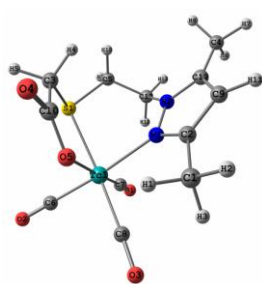
A. Paulo, V. Caveliers, C. Fernandes, H. Knight, M. Bauwens, T. Lahoutte, I. Santos, A New Myocardial Perfusion Imaging Agent: Evaluation in Rats and Comparison with ^{99m}Tc -Sestamibi and ^{99m}Tc -Tetrofosmin, 2008 World Molecular Imaging Congress, Nice (France), September 2008.

¹Dep. of Nuclear Medicine, Univ. Hospital Brussels (UZ Brussel),

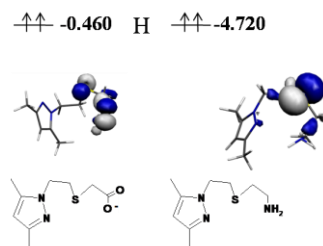
²Mallinckrodt Medical B.V., Petten, The Netherlands

Rhenium and Technetium Complexes Anchored by Tridentate Pyrazolyl-Based Chelators for the Labelling of Clinically Relevant Biomolecules

C. Moura, C. Fernandes, A. Paulo, I. Santos, M. J. Calhorda¹



Searching for building blocks suitable for the labelling of biomolecules with the *fac*-[^{99m}Tc(CO)₃]⁺ and [^{99m}Tc=O]³⁺ cores, our group has evaluated novel families of tridentate pyrazolyl-based chelators having different donor atom sets. Within the organometallic approach, *in vitro* and *in vivo* studies demonstrated that the charge of the chelator and/or donor atom set (e.g. N,N,O vs N,O,S) strongly influence the behaviour of the complexes,

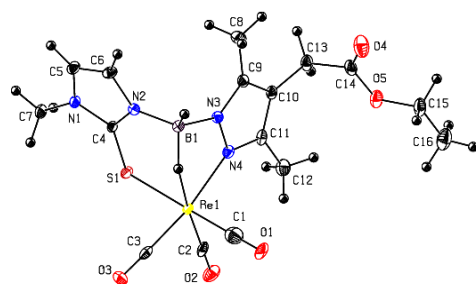


particularly in terms of their *in vitro* stability. To have a more rationale insight into such behaviour, DFT calculations were performed. These studies suggested that the differences are not controlled by thermodynamic factors; theoretical studies to evaluate kinetic aspects are underway.

¹ DQB, Faculdade de Ciências da Univ. de Lisboa, Portugal

Rhenium(I) Tricarbonyl Complexes with Hybrid Poly(azolyl)borates: A Novel Class of Compounds Potentially Useful for Radiopharmaceutical Research

M. Videira, P. Antunes, A. Paulo, I. Santos



Re(I) tricarbonyl complexes anchored by hybrid poly(azolyl)borates were formed by breaking the Re...H-B bond of the unprecedented *fac*-[Re{κ³-H(μ-H)₂B(tim^{Me})}(CO)₃] with azoles (e.g. 2-mercaptomidazoles or pyrazoles). X-ray diffraction analysis of the complexes confirmed the presence of heteroscorpionates displaying (κ³-H, S, S'), (κ³-H, S, N) or (κ³-S, N, N) binding motives. This approach represents a great advantage, since it affords more straightforwardly poly(azolyl)borate Re(I) tricarbonyl complexes, which allows a faster *in vitro* screening of their biological and/or pharmacological properties. Such improvement avoids the

independent synthesis of asymmetric scorpionates bearing bioactive vectors, a time consuming and challenging task.

Organometallic Complexes for Targeted Radiotherapy

T. Esteves, S. Gama, F. Mendes, F. Marques, A. Paulo, I. Santos, S. Casimiro,¹ L. Costa¹

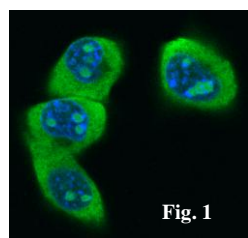


Fig. 1

Aiming to demonstrate that ^{99m}Tc compounds may hold potential for targeted radiotherapy, we evaluated *in vitro* and *in vivo* a series of Re(I) and ^{99m}Tc(I) tricarbonyl complexes with pyrazole-diamine chelators bearing

DNA-binding groups. Fluorescence microscopy studies have shown that the Re complexes can target the nucleus of murine B16F1 melanoma cells (Fig. 1). Some of the ^{99m}Tc congeners induce important damage to plasmid DNA (Fig. 2) and significant cell death through apoptotic pathways, as shown by the PARP assay (Fig. 3). So far, the results obtained indicate that the DNA damage and cell death are induced by the Auger electrons emitted by ^{99m}Tc, although being strongly influenced by the nature of the DNA-binding group.

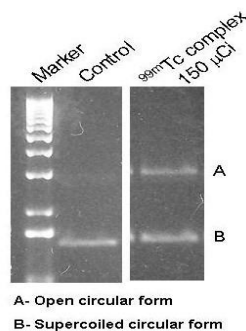


Fig. 2

A- Open circular form

B- Supercoiled circular form

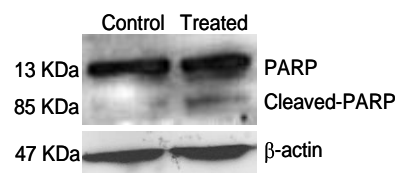


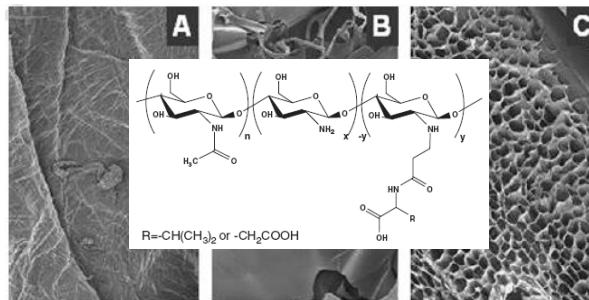
Fig. 3

¹ Inst. de Medicina Molecular, Lisboa, Portugal

Functionalized Natural Polymers (chitosan and dextran) for Delivery of Radioactivity *in vivo*

F. Marques, L. Gano, M. Morais, J. D. G. Correia, M. K. S. Batista,^{1,2} C. A. R. Gomes,² P. Gomes,¹ I. Santos,

Aiming to develop new polymeric systems for the delivery of radioactivity *in vivo* for both internal radiation therapy and radiodiagnosis, we have prepared in high yields (> 95%) ¹⁵³Sm/¹⁶⁶Ho and ^{99m}Tc complexes with amino acid-chitosan and dextran-amine-pyrazolyl-mannose polymers, respectively. These radioactive polymers presented high water solubility and stability, which are essential features for radiopharmaceutical applications. The favourable radiochemical and biological behaviour found, highlights the interest of exploring new chemical modifications of natural polymers in order to improve the biokinetics and specificity of the resulting radioactive complexes.



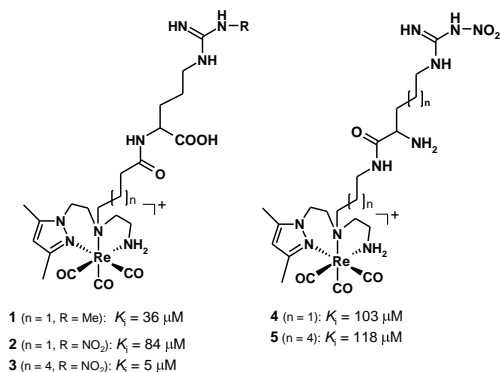
¹ CIQUP, DQ, Fac. Ciências da Universidade do Porto, Portugal

² LAQUIPAI, DQ, Fac. Ciências da Universidade do Porto, Portugal.

New Re(I)/^{99m}Tc(I) Complexes Containing Pendant L-Arg Derivatives with Enhanced Inhibitory Potency toward iNOS

B. L. Oliveira, F. Figueira, J. D. G. Correia, P. D. Raposinho, C. Cordeiro,¹ A. P. Freire,¹ I. Santos

Conjugates containing a pyrazolyl-diamine chelating unit and pendant L-arginine analogues (substrates or inhibitors of NOS) were synthesized to design radioactive compounds for probing inducible nitric oxide synthase (iNOS) levels *in vivo*. Those conjugates allowed the preparation of complexes of the type *fac*-[M(CO)₃(k³-L)]⁺ (M = Re, ^{99m}Tc). The enzymatic studies revealed that the affinity of the inhibitor-containing conjugates to iNOS seems to be less affected upon metallation than the substrate-containing conjugates. The complexes bearing N⁰-Me- (**1**) or N⁰-NO₂- (**2** - **5**) guanidine-substituted analogues of L-arginine present considerable inhibitory action, being the first examples of organometallic complexes able to inhibit the iNOS. The inhibitory potency of complex **3** is identical to that presented by the strong inhibitor N⁰-NO₂-L-arginine (*K*_i = 3 μM).



¹ DQB, Faculdade de Ciências da Univ. de Lisboa, Portugal.

^{99m}Tc(CO)₃-labeled Bisfosfonates for Bone Imaging

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

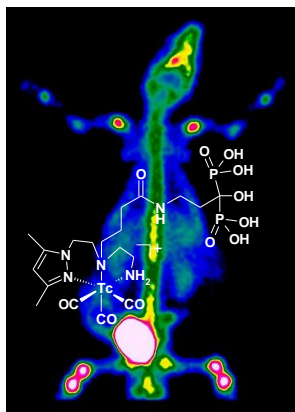


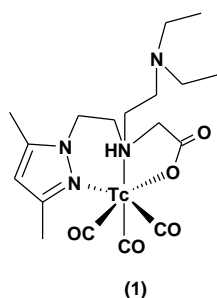
Fig. 1.

Radionuclide bone imaging is useful for evaluation of many pathologic conditions, namely bone metastasis. The radioactive complex *fac*-[^{99m}Tc(CO)₃(k³-**pz-pamidronate**)]⁺ presents improved radiochemical and biological properties as bone-seeking radiotracer. Besides a fast rate of blood clearance and high rate of total radioactivity excretion, the compound presents significant bone uptake (4.7±0.9 % ID/g organ, 4 h p.i.) and favorable bone/blood (40, 4 h p.i.) and bone/muscle (50, 4 h p.i.) ratios.

Figure 1 shows a SPECT imaging obtained when a Sprague Dawley rat model was injected with *fac*-[^{99m}Tc(CO)₃(k³-**pz-pamidronate**)]⁺. The image has confirmed the satisfactory biodistribution profile.

Melanoma Targeting with $^{99m}\text{Tc}(\text{CO})_3$ -labeled Benzamides and α -MSH analogs.

C. Moura, P. Raposo, A. Paulo, J. D. G. Correia, L. Gano, I. Santos



Cationic and neutral ^{99m}Tc (I) tricarbonyl complexes, anchored by pyrazolyl-containing chelators with (N_3) or (N_2O) donor atom sets were studied to target MC1 receptors or melanin in melanoma. The targeting of MC1R's was based on complexes bearing a lactam-based cyclic peptidic antagonist of MC1R, while the targeting of melanin was based on complexes bearing (dialkylaminoalkyl)benzamide pharmacophores or their fragments (1). Cellular uptake in B16F1 melanoma cells and tumor

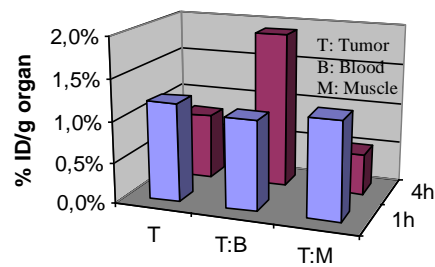


Fig. 1

uptake in melanoma-bearing mice were evaluated for all compounds. Some of the complexes have shown a moderate cellular and tumor uptake (Fig. 1). Currently, related complexes bearing the same or different pharmacophores conjugated to different positions of the bifunctional chelators are being evaluated to improve their biological performance.

Ga(III)/ In(III) Complexes for Molecular Imaging and/or Chemotherapeutic Applications

R. Garcia, F. Silva, P. Fousková¹, L. Gano, F. Marques, A. Paulo, E. Tóth¹, I. Santos

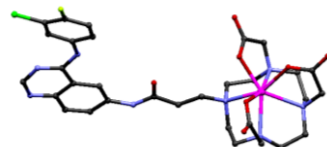
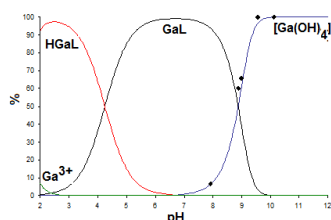
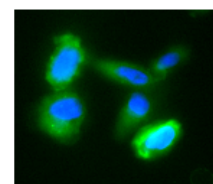


Fig. 1

Ga(III)/In(III) complexes anchored by tetraazamacrocycles bearing quinazoline moieties (Fig.1) were evaluated as radioactive probes for *in vivo* molecular imaging of EGFR's. The Ga(III) complex (Fig. 1) exhibits a remarkable high thermodynamic stability constant and the congener with ^{67}Ga was prepared in high yield/high radiochemical purity.

Other Ga(III) complexes anchored by pyrazolyl-based chelators were explored as cytotoxic metallopharmaceuticals.

Studies with human PC-3 prostate cancer cells have shown that one of the complexes presents significant cytotoxicity, inducing apoptosis (Fig. 2). The potential of these complexes for the design



(a)

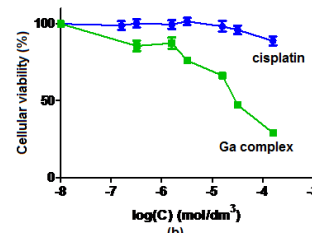


Fig.2

of imaging or antitumor drugs is currently being explored.

¹ Centre de Biophysique Moléculaire CNRS, Rue Charles Sadron, 45071 Orléans Cedex 2, France

Peptide Nucleic Acids Labelled with the $^{99m}\text{Tc}(\text{CO})_3$ Moiety for Monitoring Endogenous Gene Expression

C. Xavier, C. Giannini¹, S. Dall'Angelo¹, L.Gano, S. Maiorana¹, R. Alberto², I. Santos

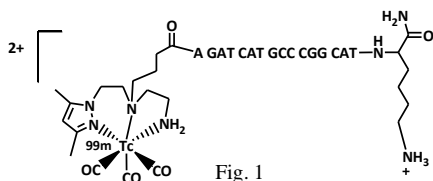


Fig. 1

The main goal of this research project is to find novel ^{99m}Tc probes for non-invasive imaging of endogenous gene expression, using the

antisense approach. Taking into account the advantages of Peptide Nucleic Acids (PNAs), we have synthesized a 16-mer PNA antisense sequence (N- A GAT CAT GCC CGG CAT-C), complementary to a region of *N-MYC* mRNA, which is overexpressed in peripheral and central nervous system tumours. This sequence was labeled with ^{99m}Tc (I) tricarbonyl, using a bifunctional approach (Fig. 1). Studies with cells expressing *N-MYC* mRNA (SH-SY5Y cell line) have shown a relatively high cellular internalization and retention of the ^{99m}Tc complex (Fig. 2). Further *in vitro* and *in vivo* studies are underway.

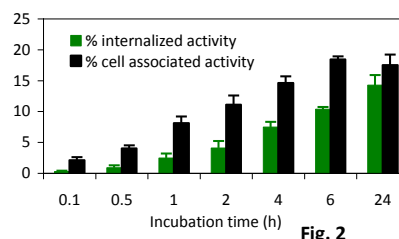


Fig. 2

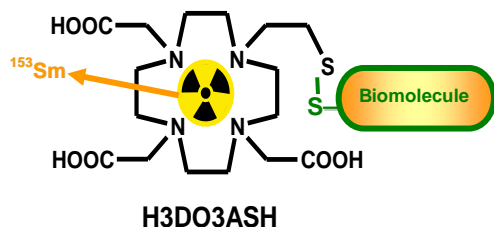
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Tetraazamacrocycle Bearing Mixed Thiolate/Carboxylate Pendant Arms for Labeling Biomolecules with Radiolanthanides

S. Lacerda, M. P. C. Campello, V. Kubiček¹, P. Fousková¹, E. Toth¹, I. Santos

Following our previous work on the synthesis of bifunctional chelators for labelling biomolecules, we have studied ^{153}Sm and ^{166}Ho radiocomplexes of do3aSH. The pharmacokinetics of these complexes prompted further studies towards the evaluation of the involvement of the thiolate group in the coordination sphere of the lanthanide ion. Protonation and stability constants of do3aSH with Ce^{3+} , Sm^{3+} and Ho^{3+} have been determined by potentiometry and UV-Vis spectroscopy. These results together with relaxivity measurements on the Gd^{3+} -DO3ASH complex, suggest that the thiolate group, even in its deprotonated form, does not coordinate to the metal. The *in vivo* stability and favourable biological profile of ^{153}Sm -DO3ASH, together with the presence of a free thiol group available, make this novel tetraazamacrocycle suitable for functionalization with clinically relevant biomolecules *via* the

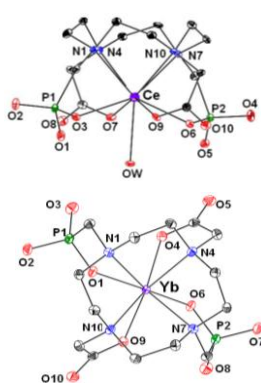


thiolate pendant arm, which is currently in progress.

¹ Centre de Biophysique Moléculaire, CNRS, Orléans Cedex 2, France

Structural Studies of Lanthanides Complexes with *trans*-H6DO2A2P.

M. Paula C. Campello, S. Lacerda, I. C. Santos, C. Geraldes¹, P. Hermann², J. Kotek², P. Luba³, I. Santos



Following our previous studies on $^{153}\text{Sm}/^{166}\text{Ho}$ -*trans*-do2a2p, we have synthesized and characterized at the macroscopic level complexes of *trans*-H₆DO2A2P with the lanthanide series. The main goal was to evaluate how the structure in the solid state and in solution changes along the series, and also to evaluate the mechanism of formation and dissociation of the complexes. We have found that the stability constants of *trans*-DO2A2P with Ln(III) ions increases along the series, while the kinetic inertness decreases. Reactions of *trans*-do2a2p with LnCl_3 yielded mono crystals suitable for X-ray crystallography. The complexes formed are of the type $[\text{Ln}(\text{trans}\text{-do2a2p})(\text{H}_2\text{O})_x]$ ($\text{Ln}=\text{Ce}, \text{Nd}, \text{Sm}, x=1$; $\text{Ln}=\text{Sm}, \text{Eu}, \text{Tb}, \text{Dy}, \text{Tm}, \text{Yb}, x=0$), in which the *trans*-H₆DO2A2P chelator behaves as octadentate. ¹H NMR paramagnetic shifts calculations agree with the X-ray data, revealing a twisted square antiprismatic structure for all the complexes (TSA, *m'* for $x=0$; CTSA, *m* for $x=1$).

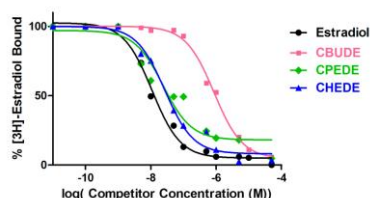
¹Dep. Bioquímica, Centro de Espectroscopia RMN e Centro de Neurociências e Biologia Celular, F. C. T., Univ. Coimbra,

²Dep. of Inorganic Chemistry, Univ. Karlova, Prague, Czech Republic.

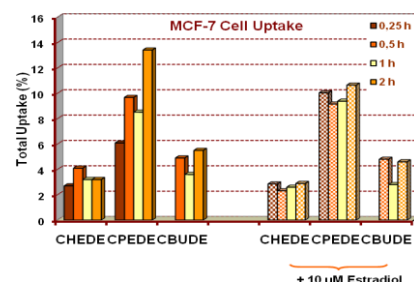
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Estradiols for Molecular Recognition of ER(+) Breast Tumour: Structure/Activity studies

C. Neto, M. C. Oliveira, L. Gano, F. Marques, I. Santos, T. Thiemann¹, A.C. Santos², F. Botelho², C.F. Oliveira²



Seeking for new probes for targeting the estrogen receptor (ER), a series of radioiodinated $\Delta^{6,7}$ -estradiol derivatives, with C7 ω -cyanoalkyl substituents of different chain length were evaluated, to relate biological behaviour/chemical structure. ER binding data indicate that, compared to estradiol, the addition of a C7 ω -cyanoalkyl chain decreases the binding affinity, but the values increase by lengthening the C7-chain. The trend found was: butyl < pentyl < hexyl (CBUDE; CPEDE, CHEDE). Cell uptake in MCF-7 cells was observed for the three radioligands. However, the cellular uptake seems to be a non ER-mediated process, as the cellular uptake does not change in the presence of estradiol.



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Solid State

Manuel Leite de Almeida

The Solid State Group 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 by and maintained in the group, are a high temperature laboratory with crystal growth techniques (Czochralski, Bridgman and float zone), X-ray diffraction (single crystals and powder), EPR and Mössbauer spectroscopy, measurements of magnetisation by SQUID, Faraday and extraction techniques and AC-susceptibility, different electronic transport measurements and heat capacity, in a broad range of temperature and magnetic field.

The use of all these specialised characterisation techniques, often requiring low temperatures down to 0.3 K and high magnetic fields up to 18 T, lead to the development of facilities and expertise in cryogenics, unique in Portugal. The group was responsible for the installation at ITN in 1991 of a helium liquefier, which since then remains the only one operational in Portugal, serving also to many users outside ITN. Funding for installing in 2009-2010 a new He liquefier, with expanded capabilities, was raised this year, thus securing the grounds for pursuing this type of cryogenic centered activities for two more decades.

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. The two chain compounds, originally reported almost 3 decades ago, remained at the centre of important discoveries as model quasi-1D CDW systems. Recent achievements include the elucidation of structural details of the Co compound with dimerised anions and discovery of superconductivity in the Au compound sharing a borderline with a non-magnetic CDW phase.

The interests of the group have been extended during the last years to **molecular magnetism**. In the framework of the Network of Excellence *MAGMANet* the study of switchable magnetic materials with possible conducting properties was developed.

The research on **intermetallic compounds**, initiated in 1992 with emphasis on the study of phase diagrams of the type (f-element)-(d metal)-(p-element) and on new compounds with strongly correlated electronic behaviour and complex magnetic structures, has been extended to borides and thermoelectric materials.

During 2008 the application of Mössbauer spectroscopy had a large impact in development of novel ferrite with mixed ionic-electronic conductivity for applications in alternative energy sources

A significant output of the group continues to be the **training and education of young scientists** which always plays a major role in its projects and the collaboration with Universities, namely in undergraduate courses, was pursued.

Research Team

Researchers

M. ALMEIDA, Coord., Group Leader
V. GAMA, Princ.
J. C. WAERENBORGH, Princ.
A. P. GONÇALVES, Princ.
E. B. LOPES, Aux.
L. C. J. PEREIRA, Aux.
I. C. SANTOS, Aux.
D. BELO, Pos Doctoral, FCT grant, Aux. contract (since March)
S. RABAÇA, Pos Doctoral, FCT grant, Aux. contract (since Feb.)
J. S. BROOKS, Visiting Scientist (Feb-July)
M. AFONSO, Pos Doctoral, ITN grant (since July)
A. BOAVIDA, Pos Doctoral, ITN grant (until June)
S. DIAS, Pos Doctoral, FCT grant
J. DIAS, Pos Doctoral, FCT grant
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M. CASTELO BRANCO, BIC grant (since September)
A. CERDEIRA, BIC grant.
M. HENRIQUES, BIC grant
A. NEVES, BIC grant
B. VIEIRA, BIC grant

Collaborators

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R. T. HENRIQUES, Assoc. Professor, IST

Mössbauer spectroscopy for the development of novel ferrite with mixed ionic-electronic conductivity for applications in alternative energy sources

J.C. Waerenborgh, E. Tsipis, V.V. Kharton¹, A. Yaremchenko¹, M. V. Patrakeev²

Objectives

Development of novel iron-containing oxides with better transport and catalytic properties, and improvement of the knowledge on the relationship between surface and bulk states of iron cations, mechanisms of redox processes, and formation of nano-scale surface centers contributing to electro-catalytic performance.

Results

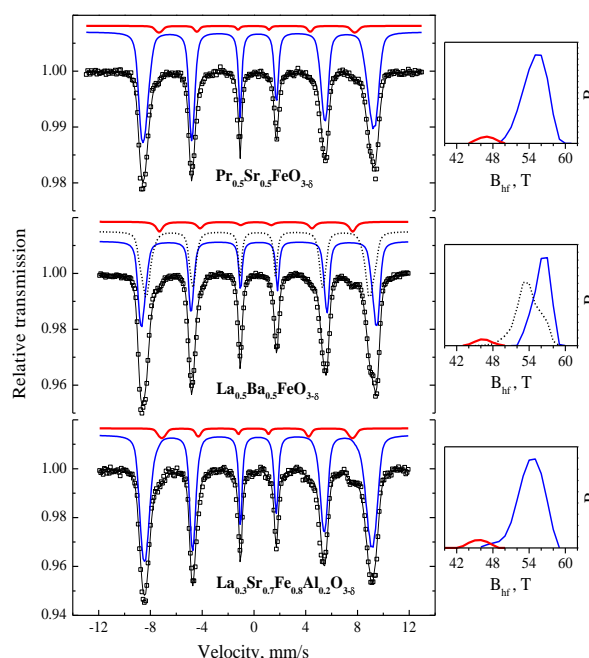
The number of iron-containing oxide phases stable under solid oxide fuel cell cathodic conditions and exhibiting significant electronic or mixed conductivity, is larger than that in the manganese systems. Our research in the last years has been primarily directed to perovskite-like $(\text{Ln}_{1-x}\text{A}_x)\text{FeO}_{3-\delta}$ (Ln = lanthanide, A = Sr) and their derivatives.

In 2008 the increasing difference of the Ln^{3+} and A^{2+} cation radii in perovskite-type $\text{Ln}_{0.5}\text{A}_{0.5}\text{FeO}_{3-\delta}$ (Ln = La, Pr, Nd, Sm; A = Sr, Ba) was found to induce higher oxygen deficiency and lower anionic and p -type electronic conductivities. The relation between the anion transport and A-site cation size mismatch is essentially similar in air and under reducing conditions when most iron cations become trivalent, thus confirming critical influence of oxygen-vacancy trapping processes induced by lattice strain. The role of surface exchange kinetics as a permeation-limiting factor tends to decrease on Ba^{2+} doping and on decreasing Ln^{3+} size. The n -type electronic conduction and low- $p(\text{O}_2)$ stability at 1223 K are substantially unaffected by the cation radius mismatch.

The layered $\text{La}_2\text{NiO}_{4+\delta}$ based compounds (K_2NiF_4 -type phase) possess relatively fast ionic transport, while their thermal and chemical expansion is much lower than that for perovskite-type materials. Further improvements may be achieved by the development of appropriate doping strategies. The substitution of iron for nickel increases the mobility of oxygen interstitials in the $\text{La}_2\text{Ni}(\text{Fe})\text{O}_{4+\delta}$ lattice at temperatures above 1150 K. It also increases the oxygen excess under oxidizing conditions, but has a minor effect on the low- $p(\text{O}_2)$ phase stability. The segregation of metallic nickel on reduction, which occurs at oxygen chemical potentials close to the low- $p(\text{O}_2)$ stability boundary of undoped lanthanum nickelate, is responsible for the high catalytic activity towards partial oxidation of methane by the lattice oxygen. Doping of the layered $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ with iron decreases oxygen non-stoichiometry, shifting the low- $p(\text{O}_2)$ stability boundary towards more reducing conditions due to the stabilization of transition metal-oxygen octahedra. The

Mössbauer spectroscopy studies confirmed that Fe cations are predominantly trivalent and are randomly distributed among the non-equivalent nickel sites.

In addition to their transport properties the recently discovered RBaCo_4O_7 (R = Ho, Y) phases show unusual oxygen-sorption ability, complex structural relationships and frustrated magnetism. In 2008 Mössbauer data obtained on samples with 1% Co substituted by ^{57}Fe detected no charge ordering and showed that Fe^{3+} magnetic moments are frozen below a critical temperature, lower than 80K and decreasing with the presence of oxygen interstitials.



Mössbauer spectra taken at 4K

Published or in press work (selected)

V. Kharton, A.V. Kovalevsky, M.V. Patrakeev, E.V. Tsipis, A.P. Viskup, V.A. Kolotygin, A.A. Yaremchenko, A.L. Shaula, E.A. Kiselev and J.C. Waerenborgh, *Chem. Mater.* 20, 6457–6467 **2008**.

V. Kharton, E.V. Tsipis, E.N. Naumovich, A. Thursfield, M.V. Patrakeev, V.A. Kolotygin, J.C. Waerenborgh, I.S. Metcalfe, *J. Solid State Chem.* 181, 1425-1433 **2008**.

V.V. Kharton, E.V. Tsipis, V.A. Kolotygin, M. Avdeev, A.P. Viskup, J.C. Waerenborgh, J.R. Frade *J. Electrochem Soc.* 155, P13-P20 **2008**.

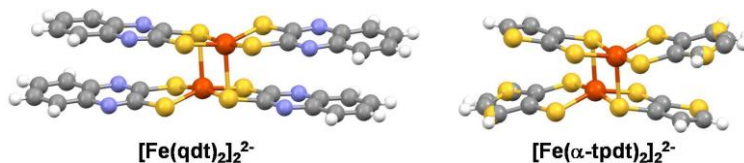
¹ – Dep. of Ceramics and Glass Engineering, CICECO, Univ. of Aveiro, 3810-193 Aveiro, Portugal

² – Inst. of Solid State Chemistry, Ural Division of RAS, 91 Pervomayskaya Str., Ekaterinburg 620219, Russia

Coordination of Fe^{III} bisdithiolene complexes; Cation and ligand roles

A.I.S. Neves, I.C. Santos, D. Belo, M. Almeida

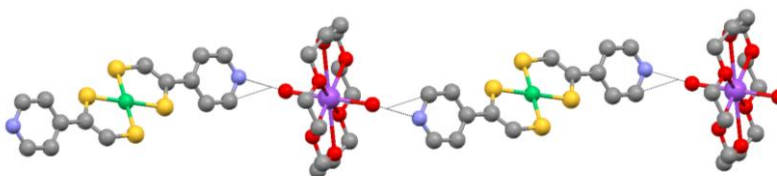
Aiming at a better understanding of the role of the cation versus the role of the ligand in the coordination geometry of Fe^{III} bisdithiolene complexes [Fe^{III}(qdt)₂]⁻ salts (qdt=quinoxalinedithiolate) with different cations or new iron bisdithiolates complexes, such as [Fe(α-tpdt)₂]₂ (α-tpdt=2,3-thiophenedithiolate) were explored. At variance with the large diversity of coordination geometries and oxidation states of bisdithiolene complexes with most metals, the Fe complexes with these ligands have been essentially restricted to Fe(III), and until quite recently all were found to adopt the same square pyramidal, 4+1, coordination geometry due to the formation of dimeric arrangements through two Fe-S bonds between distorted square based [Fe(S₂L)₂]⁻ units, [Fe(S₂L)₂]₂²⁻. The first, and so far unique, exception to this rule was the *n*-Bu₄N [Fe(qdt)₂] complex and displaying a perfectly square planar coordination geometry and a *S* = 1/2 spin state. The crystal structure of the new (BrBzPy)₂[Fe(qdt)₂]₂ complex shows a rare weak Fe^{III} bisdithiolene dimerisation with unusual molecular planarity and long apical S-Fe distances, in an anion configuration intermediate between the only monomeric Fe bisdithiolene reported so far, and the common strong dimeric geometry also observed in other [Fe(qdt)₂]₂ salts. The standard strong dimeric situation is also observed in the new [Fe(α-tpdt)₂]₂ salt with the same cation, as well as with the *n*-Bu₄N and Et₄N Cations.



New complexes based on divalent thio-azo ligands for heterobimetallic networks

S. Rabaça, S. Dias, A. Cerdeira, I. C. Santos, M. Almeida

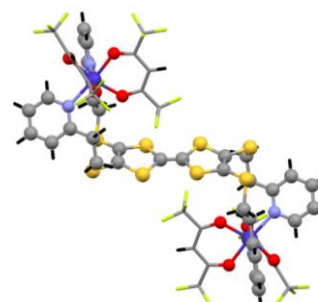
Thio-azo ligands with the capability of coordinating different metals by the S and the N poles have been synthesized and used in the preparation of new bis(dithiolene) nitrogen functionalized transition metal complexes. The ligand, if a delocalized π system, is expected to efficiently mediate magnetic interactions between metals coordinated by these different atoms at opposite ends of the ligands. Using the S coordination ability of these thio-azo ligands new members of bis(dithiolene) complexes were added to the already existing family in which TPP[M(4p-edt)₂] (M=Ni, Au, Cu) are new examples of bis-pyridine substituted bis(dithiolene) complexes. Some of the bis(dithiolene) complexes are currently being tested as key ligands for preparing heterobimetallic magnetic networks and novel supramolecular coordination architectures with the general formula: [M(L)₂][M'(dithiolene)₂], L=auxiliary ligand (cyclam, crown ether, hexafluoroacetylacetonate or acetylacetonate). From the association of the monocationic moiety [18c6Na]⁺ with a monoanionic dithiolene the first secondary polymeric coordination compound [18c6Na][Ni(4pedt)₂]·H₂O was obtained.



Pyridine functionalized TTF-substituted derivatives and their transition metal complexes

S. Dias, S. Rabaça, A.I.S. Neves, I.C. Santos, M. Almeida

Tetrathiafulvalene (TTF) derivatives have been widely studied for the synthesis of organic conductive materials and superconductors. In spite of its great interest the attachment to the core of the TTF of functional groups capable of coordination to transition metal atoms, only recently was explored. Under this project several new pyridine functionalized TTF-substituted derivatives were obtained by homocoupling of the correspondent 1,3-dithiole-2-one. These donor are ligands with the ability to coordinate with several metals, Cu(II), Ni(II), Co(II) for example, through the nitrogen atoms. This was well illustrated by a pyridine-substituted donor which was successfully used as a bridging ligand to prepare a dinuclear Co^{II}-coordination complex [TTF*Co₂-(hfac)₄] (hfac= hexafluoroacetylacetonate). This dinuclear complex presents an effective magnetic moment corresponding to nearly independent *S* = 3/2 spins with weak antiferromagnetic interactions. Currently other pyridine functionalized tetrathiafulvalenes are being explored.

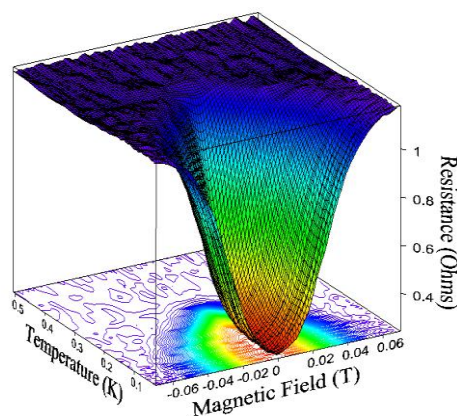


Two-Chain Compounds under High Magnetic Field

M. Almeida, J.C. Dias, R.T. Henriques, M. Matos¹, J. S. Brooks², D. Graf², and S. Uji³

(Perylene)₂M(mnt)₂ compounds with M=Au, Pt, initially reported by our group more than 20 year ago still offer a unique chance to investigate the coupling between two types of chains (conducting and magnetic) in the same solid and to test the theoretical predictions for the behavior of extreme anisotropic quasi 1D CDW systems under large magnetic fields. Along with crystallization efforts to obtain samples, the studies in 2008 were focused in Au compound where superconductivity (SC) was discovered above a pressure of 5 kBar which suppresses the CDW ground. The onset of superconductivity is ~ 300 mK and the upper critical field (perpendicular to the perylene stacking axis) is 50 mT. The CDW-SC phase diagram reveals a new situation compared with other organic compounds, where SC evolves from magnetic states.

The angular dependent magnetoresistance under pressure revealed geometrical and orbital quantum interference (QI) effects. Through magnetic field dependence and orientation, the orbital and geometrical effects were independently identified. And the results compared with well-known Bechgaard salts.



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³ - National Inst. of Materials Science, Tsukuba, Ibaraki, 305-0003 Japan.

(Per)₂[Co(mnt)₂]: Structure and anomalous pressure dependence of the electrical transport properties

E. B. Lopes, I. C. Santos, M. Almeida, E. Canadell¹, D. Graf², J. S. Brooks²

The crystal structure of (Per)₂Co(mnt)₂ was solved by single crystal X-ray diffraction clearly showing for the first time a strong chemical dimerization of the anions [Co(mnt)₂]₂²⁻. This dimerisation is responsible for a unit cell doubling along the stacking axis *b* when compared with other members of the α-(Per)₂M(mnt)₂ family of the low dimensional molecular conductors. The dimerized [Co(mnt)₂]₂²⁻ stacks and their interaction with donor chains was related to the anomalous pressure dependence of the electrical conductivity of this compound where under increasing hydrostatic pressure the conductivity decreases while the metal insulator transition temperature is enhanced. This was shown possibly to result from a pressure induced sliding of the stacked perylene molecules along alternated directions in their planes.

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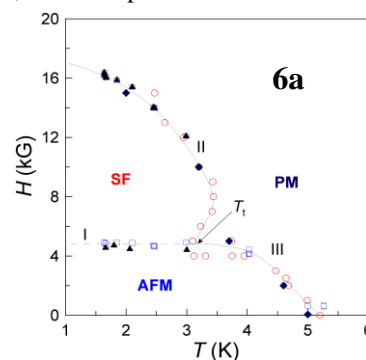
² - NHMFL/Physics, Florida State Univ., Tallahassee, FL32310, USA.

Molecular Magnets based on Decamethylmetallocenium Cations and on Metal bis-dichalcogenate Anions

S. Rabaça, D. Belo, B.J.C. Vieira, I.C. Santos, L.C. J. Pereira, M.T. Duarte¹, V. Gama, M. Almeida, J.J. Novoa², C. Rovira³, J. Veciana³,

The correlation between the crystal structure and the magnetic properties of molecular magnetic salts, as well as the effect of single ion magnetic anisotropy and the spin value of the building blocks of these salts were more clearly put into evidence by the detailed study of two families of isostructural or closely related salts. The McConnell I model was used in the analysis of intermolecular magnetic coupling in these compounds, and the predicted intermolecular couplings were found in good agreement with the experimental results.

The compounds studied include the series [M(Cp*)₂][Ni(α-tpdt)₂] (α-tpdt = 2,3-thiophenedithiolate), M = Fe (**1b**), Mn (**2b**) and Cr (**3b**) and [M(Cp*)₂][M'(tds)₂] (tds = bis[bis(trifluoromethyl)ethylene diselenolato]) M/M' = Fe/Ni (**1a**), Fe/Pt (**2a**), Mn/Ni (**3a**), Mn/Pt (**4a**), Cr/Ni (**5a**), Cr/Pt (**6a**). In the series based on the diselenolates the study of the low temperature behavior of the salts **3a**, **4a** and **6a** allowed the disclosure of the effect of the magnetic anisotropy of the cations and in the phase diagram of **6**, besides the PM and AF phases, a spin-flop (SF) phase was observed for the first time in [M(Cp*)₂] based salts.



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³ - Inst. de Ciència de Materials de Barcelona, (CSIC), Spain.

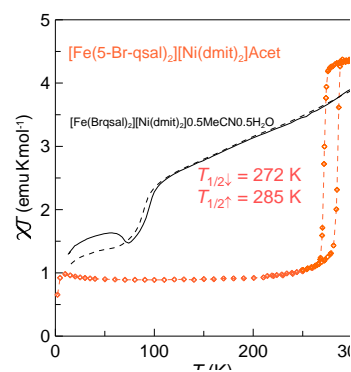
Fe(III) Spin Crossover Complexes as Building Blocks of Switchable Molecular Conductors

B.J.C Vieira, J.C Dias, A.I.S. Neves, D. Belo, J.C. Waerenborgh, L.C.J Pereira, I.C. Santos, V. Gama, M. Almeida

Aiming at to prepare switchable molecular conductors we followed a strategy that consists in the combination of mixed-valence metal-organic systems with spin-crossover (SCO) components. The work focused in the preparation of $[\text{Ni}(\text{dmit})_2]$ type salts with Fe^{III} complexes based on two types of ligands (R-qsal, sal_2 -trien) which were characterized by single crystal x-ray diffraction, magnetic measurements and Mössbauer spectroscopy.

Seven new complexes based on different R-qsal type ligands were prepared and combined with distinct anions (~ 10) giving more than 30 new salts. Although just a few of these new compounds were fully characterized they reveal quite promising properties, where most of the compounds show SCO processes and in some cases sharp transitions associated with hysteresis at high temperatures. The subsequent preparation of partially oxidized salts $[\text{Fe}(\text{L})_x][\text{Ni}(\text{dmit})_2]_n$ is still in progress. However semiconducting materials with a clear hysteresis in the conductivity at relatively high temperatures have been already obtained.

Six new $[\text{Fe}(\text{nsal}_2\text{-trien})]\text{A}$ salts were obtained with different anions. In spite of the expectations no significant cooperativity was detected in the SCO processes, which in general occurs gradually, and can be quite slow.



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

A.P. Gonçalves, L.C.J. Pereira, J.C. Waerenborgh, M. Almeida, M. Dias, M.S. Henriques, Y. Verbovytskyy, O. Sologub, P.A. Carvalho¹, O. Tougaard², H. Noël²

The main objective of this research line is to explore (*f*-element)-(*d*-metal)-X ternary systems in order to determine the phase relations, and identify, synthesise and characterise new ternary intermetallic compounds. This study is expected also to provide fundamental information for the synthesis of pure samples and growth of single crystals.

During 2008 the study of the U-Fe-B *solidus* surface was continued and a new compound, UFe_2B_6 , was identified. The study of the isothermal section at 900°C of the U-Fe-Si was performed and preliminary results for isothermal sections were also obtained on the U-Fe-Ga, U-Pd-B and R-Pt-Sb (R=La, Ce, Pr) ternary systems. These studies allowed the identification of three new compounds, $\text{RPt}_{2+x}\text{Sb}_{2-y}$ ($x=0.124$, $y=0.25$; R=La, Ce, Pr), which were prepared as single-phase samples and their crystal structures were solved and physical properties characterised.

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New materials for thermoelectrical applications

A.P. Gonçalves, E.B. Lopes, E. Alleno¹, C. Godart¹, O. Tougaard², H. Noël²

The identification, synthesis and characterization of new thermoelectrical systems with high figure of merit is fundamental for the energy optimization, by the electricity generation from waste heat or the heat extraction from micro-electronic components.

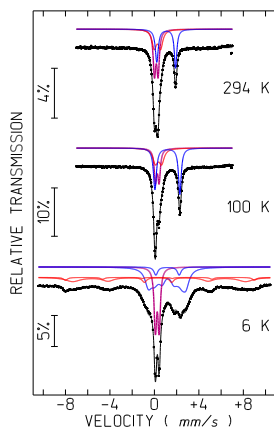
During 2008 the study of filled skutterudites, $(\text{In}_x\text{Sn}_x)\text{Co}_4\text{Sb}_{12}$, derived from CoSb_3 with double filling of the cage by (In, Sn) was continued. Their electrical transport (resistivity and thermopower) characterization show a coefficient as high as $-280 \mu\text{V/K}$ at 300K, but also a high electrical resistivity, which produces a relatively small figure of merit for these compounds. The development of new concepts, like the Phonon Glass and Electron Crystal, has lead to new approaches to thermoelectric materials, and to a better understanding of the role of the crystal structure on the electrical transport and thermal properties of compounds. With this background, several new materials were explored in order to identify new systems with high thermoelectric performances. Preliminary results indicate that two new systems, electrical conducting glasses and doped tellurium films, are good candidates as new families of thermoelectric materials.

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² Lab. Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Univ. Rennes 1, France.

Magnetic and strongly correlated electron behaviour in intermetallics

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A detailed understanding of the magnetic and strongly correlated electron behaviour of intermetallics containing *f*-elements, in particular the role of the actinide or rare-earth elements, has been the subject of a long-term project in the Solid State group. Several new compounds showing strong correlations were studied during 2008; here we report only the most significant ones.

The new compound, $\text{U}_2\text{Fe}_3\text{Ge}$, was synthesized and investigated. This compound crystallizes in the MgZn_2 -type structure, with uranium-uranium distances well below the Hill limit. Magnetization measurements indicate a ferromagnetic-type transition at 55(1) K and Mössbauer studies show that the magnetic ordering is only due to the uranium sub-lattice, pointing to $\text{U}_2\text{Fe}_3\text{Ge}$ as one of the few exceptions to the Hill's rule. UFe_5Ga_7 with a structure related to the ThMn_{12} -type, was characterised showing a ferromagnetic type ordering, with a Curie temperature of ~439 K, significantly higher than the one previously obtained for Al analogue. $\text{AnPt}_4\text{Ge}_{12}$ (An=Th, U) were reported as new members of Ge-based skutterudites.

For $\text{ThPt}_4\text{Ge}_{12}$ superconductivity develops below $T_c=4.75$ K, ascribed to intrinsic features of the Pt-Ge framework where Ge-p states dominate the electronic structure at the Fermi energy. Ruderman-Kittel-Kasuya-Yosida coupling via the Ge framework is too weak to enable magnetic ordering in the nonsuperconducting $\text{UPt}_4\text{Ge}_{12}$.

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Mössbauer spectroscopy in Materials Science

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A Mössbauer spectroscopy laboratory has been developed in ITN for 30 years in order to support local research projects. In 2008 the researcher responsible for the facility and one post-doc assured the maintenance and the running of the equipment. Several students used the facility in the frame of their specific *PhD* or *MSc* projects. Presently, in the ITN Mössbauer laboratory 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 2008 studies of Mo-Fe-O catalysts for methanol to formaldehyde oxidation, clay minerals and iron oxides in limestones, spin-crossover Fe^{III} complexes, oxalate based soluble 2D-molecular magnets and intermetallics have been performed in collaboration with the Chemical Engineering Dept. and the Petrology and Geochemical Center of the Technical Univ. Lisbon; the Univ. of Valencia, Spain; Charles University, Prague, Czech Republic; W. Trzebiatowski Inst. of Low Temperature and Structure Research, Wrocław, Poland.

Electrochemical synthesis of actinide intermetallic compounds

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The main objective of this project is the development and implementation of a new method for the electrochemical synthesis of actinide intermetallic compounds, at/or close to room temperature. The use of routes alternative to conventional high-temperature techniques is expected to expand the study to new and single-phase incongruently melting materials. Electrochemical synthesis is one of such alternatives that until now remains weakly explored with actinides.

Cyclic voltammetry and electrodeposition tests were performed with systems containing UCl_4 , NiBr_2 , CoCl_2 and SnCl_2 in DMF solutions and using vitreous carbon as working electrode. Cyclic voltammograms indicate that all the elements were reduced at a potential in the range -1.5 to -3.2 V and point to their deposition. Electrodeposited films obtained under optimized conditions were analyzed by Rutherford Backscattering Spectroscopy (RBS) and by X-Ray diffraction (XRD), confirming the electrodeposition of U, Ni and Co on the vitreous carbon surface. The electrochemical synthesis of UNi_5 , UCO_3 and USn_3 compounds is now under way.

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High magnetic field facility*A. Casaca¹, E. B. Lopes, J. S. Brooks², M. Almeida, V. Laukhin³*

This facility permits the study of electrical transport properties in magnetic fields up to 18 T, for temperatures in the range 0.3-300 K, using both AC and DC techniques. The data control and acquisition are fully automated via the LabVIEW software. During 2008, the ³He insert and probe were intensely used, both for educational and research purposes, allowing to pursue two research activities in molecular conductors, manganite multilayers, semiconducting thin films.

1. Demonstration of SC in κ -(BEDT -TTF)₂Cu(NCS)₂ ($T_c \approx 10$ K) and Shubnikov – de Haas oscillations between 10 T and 16 T for students of the “Materials, Superconductivity, and Magnetism” course.
2. La_{0.7}Ca_{0.3}MnO₃/CaO (LCMO/CaO) multilayers were characterised by magnetoresistance measurements in the range 10-300 K, and up to 16 T: systematic changes of the metal-insulator transition temperature and of the magnetoresistance were observed, which correlate with the manganite layer thicknesses, ranging from 10 nm to 100 nm. An anomalous behaviour of the resistance under applied magnetic field was observed for the multilayers with thinner LCMO layers, in correlation with an exchange bias effect for the magnetization. These results suggest the existence of a short range antiferromagnetic coupling at the layer interfaces.
3. Hall resistance measurements of CuOx semiconducting thin films to determine the charge of the main carriers in CuOx films grown by a thermal evaporation technique in glass substrates,
4. Single component molecular metals like Au(α -tpdt)₂ processed as thin films on polymeric surfaces, which were characterised by magnetotransport measurements in a wide temperature (1.4– 300 K) and magnetic field (up to 18 T).

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