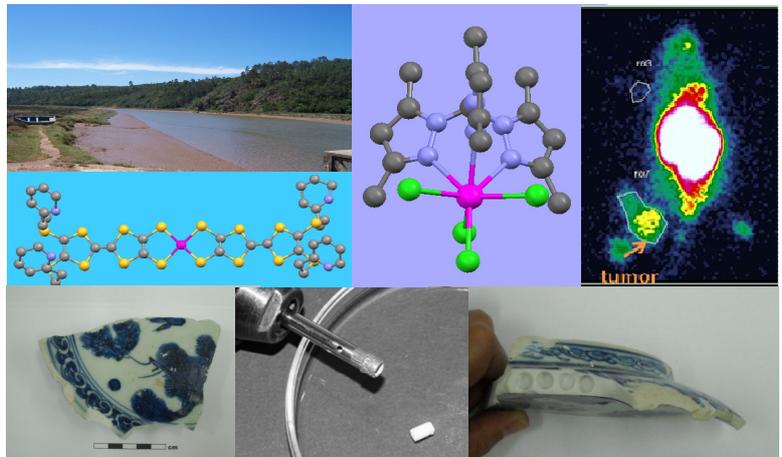


Chemical and Radiopharmaceutical Sciences Unit



Chemical and Radiopharmaceutical Sciences

Joaquim Marçalo

The **Chemical and Radiopharmaceutical Sciences Unit** (CRSU) continued to expand its research activities in the development of new inactive and radioactive compounds with importance in **Health, Materials and Nuclear Sciences and Catalysis**, and in the application of nuclear-based and related analytical techniques in **Cultural Heritage and Environmental and Earth Sciences**. The activities were carried out by five research groups:

Applied Geochemistry & Luminescence on Cultural Heritage (GeoLuC) – centred in the study of Portuguese cultural heritage materials and geo-environmental contexts using nuclear techniques and geochemistry and mineralogy methodologies. INAA, XRD and luminescence (TL and OSL) were employed in archaeometry, environmental geology and palaeoenvironmental reconstruction investigations. Dating and authenticity studies and materials characterization of Portuguese faience and Chinese porcelain from the Portuguese market (XVI to XVIII centuries) were a focus of the work.

Environmental and Analytical Chemistry – devoted to fundamental and methodological research in elemental and isotopic analysis as applied to environmental geochemistry, isotope hydrology, oceanography and archaeometry. ED-XRF, light isotope MS, HPLC-ICP/QMS, C-14 dating and H-3 determinations were used in sedimentary geochemistry, geochronology, absolute dating, palaeoecology, meteorology, water resources, and archaeometallurgical studies. Research centred on the palaeoenvironmental reconstruction of the Minho and Douro drainage basins and the assessment of ecological effects of metals on Sado tidal marshes.

Inorganic and Organometallic Chemistry – dedicated to the investigation of actinide and lanthanide compounds. Synthesis, reactivity and catalytic studies were performed and advanced MS and calorimetry techniques were used to correlate electronic structures and chemical properties of the compounds. Of note was an assessment of the gas-

phase energetics of neutral and singly and doubly charged cationic actinide monoxides and dioxides from thorium to curium, leading to a consistent set of metal-oxygen bond dissociation enthalpies, ionization energies, and enthalpies of formation.

Radiopharmaceutical Sciences – committed to basic/applied-oriented research and technology transfer on nuclear tools for SPECT and PET molecular imaging and targeted radiotherapy. The multidisciplinary work involved innovative organic and coordination chemistry, bioconjugation, radiochemistry, animal and cell studies and molecular biology. The design and synthesis of novel ^{99m}Tc(I) receptor-targeted polymeric nanoprobe, based on dextran-mannose conjugate derivatives, for sentinel lymph node detection by nuclear imaging was a highlight of the work

Solid State – involved in the study of selected new materials with unconventional electrical and magnetic properties. Expertise on the synthesis of molecule-based materials and f-element intermetallic compounds was combined with a variety of specialized solid state physics techniques. Noteworthy was the development of new multifunctional hybrid molecular materials based on cationic Fe(III) complexes with FeN₄O₂ coordination and Ni bisdithiolate anionic complexes, and displaying coexistence or synergism of spin crossover with magnetism or electrical conductivity.

In 2009, renovation of some of the CRSU **facilities**, namely the HVAC system of the main building and a few laboratories, was undertaken. The CRSU maintained its practice of high level **training** of young scientists at the MSc, PhD and Post-doc levels, and of advanced **education** activities in collaboration with the universities. National and international **projects**, mainly coordinated by the CRSU and financed by the FCT, the EC and a pharmaceutical corporation, progressed. Additional funding was obtained through protocols, contracts and services with different institutions and companies.

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 geo-environmental contexts**, through the **application of nuclear methods**.

The GeoLuC group has an interdisciplinary approach to the study of archaeological and geological contexts and materials. The study of artworks from museums is also an important activity. Origin, composition, technique of manufacture, and age, are the issues of primary importance when examining cultural assets. Analysis of these complex materials, such as pottery, minerals, stones and mortars, is based on field geology, geochemistry, mineralogy and luminescence dating. Detailed geochemical studies for the understanding of the lanthanides, actinides and other trace element behaviour in superficial environments is also a major research domain of the GeoLuC group.

The main research activities of GeoLuC group during 2009 are summarised according to the following themes:

- Dating, authenticity, materials and pigments: Portuguese Faience and Chinese Porcelain produced for the Portuguese market (XVI to XVIII centuries)
- Application of luminescence dating to understanding Iberian cultural development
- Luminescence dating of coastal geomorphological development in Portugal and Mozambique
- Casa do Governador da Torre de Belém (Tagus estuary): Halieutical resources industry in Roman times
- Distribution of trace elements and natural radionuclides of the U and Th radioactive series in superficial environments

- Applied geochemistry to the study of superficial environments in the Iberian Peninsula and Cape Verde islands - distinguishing geogenic and anthropogenic contributions

- Development of nuclear methods and applications in the archaeometry of cultural heritage assets

The main methodological approaches of the GeoLuC group comprise instrumental neutron activation analysis (INAA), X-ray diffraction (XRD) and luminescence (thermoluminescence and optically stimulated luminescence: TL and OSL) applied to archaeometry, environmental geology and paleoenvironmental reconstruction. The research is developed through financed projects, protocols, collaboration with national and international laboratories and universities, and contracts/services with private and public institutions.

Methodological testing and development of neutron activation analysis and luminescence measurements are an ongoing task, having the potential to offer a number of insights into the dating and elemental composition of different types of samples and environments.

The GeoLuC group's activities also include education and training of students from national and international universities through supervision of MSc and PhD thesis. Our students participate in the entire research programme, 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 conduct projects in fundamental and applied research.

The research team has been involved in several post-graduate and masters degree courses in universities, as well as national and international seminars and workshops.

Research Team

Researchers

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Collaborators

M. A. GOUVEIA, Princ. (Retired)

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

M.I. Dias, M.I. Prudêncio, M.O. Figueiredo¹, T. Silva¹, J.P. Veiga¹, M.A. Matos², A.M. Pais³, C. Burbidge, D. Franco, R. Marques, G. Cardoso, A. Zink⁴

Two main subjects are addressed in this FCT project: one topic aims a better knowledge of early Portuguese faience (XVII-XVIII), and the other is focused on the Chinese porcelain ordered for the Portuguese market (XVI-XVII). The general aspects to be considered in both cases are related with chronological precision, identification and differentiation of production centres and technologies, including characterisation of surface coatings (glazes and pigments). Fig.1.

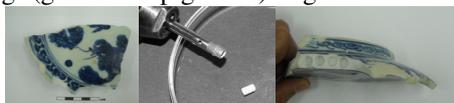


Fig.1 Sampling of ceramic pastes for analytical approaches.

Newly obtained results (INAA/XRD): (i) good chemical based identification of Portuguese faience, clearly differentiating Coimbra (Cluster 1) and Lisbon faience productions (Cluster 2 and 3), and two compositional groups for Lisbon (Fig.2)-occidental and oriental Lisbon production centers; (ii) no special correlation between stylistic/ decoration and compositional group. Faience with “rendas” (lace), usually assigned to Coimbra, but also found in Lisbon, present a geochemical pattern similar to one of Lisbon’s production. So, chemical composition confirms that this decorative style was also produced in Lisbon, imitating Coimbra; (iii) chemical homogeneity found for each compositional group may reflect the use of standardised raw materials and probably also recipes.

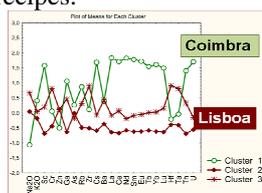


Fig.2 Geochemical groups for Lisbon and Coimbra faience.

New obtained results (TL-OSL): (i) prolonged HCl treatment of cores taken from high fired ceramics enables the extraction of powders for preparation according to mineralogy and grain-size; (ii) of all available signals, equivalent dose determination using the 110 °C TL “Simplified” PreDose response requires minimal sample material (Fig.3); (iii) due to the saturating form of the dose response from these samples, conventional linear extrapolations from laboratory dose response tend to overestimate absorbed dose and hence age, while saturating exponential fits often produce underestimates; (iv) an “Additive and Regenerative Predose” protocol has been proposed in an attempt to overcome problems relating to extrapolation (v) OSL signals appear to

have been affected by light exposure in these thin ceramics.

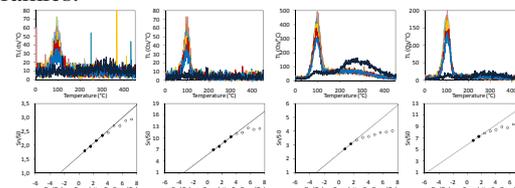


Fig.3 110°C TL PreDose on porcelain and faience

Newly obtained results of non-destructive characterisation on selected cobalt-rich blue glazes to ascertain the speciation state of the chromophore element. Co K-edge X-ray absorption spectra by irradiation of glazes at ESRF in Grenoble/France show: (i) edge energy indicates metal present in divalent state; (ii) theoretical modelling of XANES spectra from two model compounds - CoAl_2O_4 with spinel-type structure and Co_2SiO_4 with olivine-type structure was performed; (iii) these simulations and the deconvolution of the EXAFS region using IFEFFIT program corroborate a mean coordination number higher than four for the first shell of oxygen atoms around Co^{2+} ions. The presence of lead and arsenic, plus the relative contents of manganese, iron, cobalt and copper, confirms previous dating by Art Historians based on stylistic features.

Published work:

M.O.Figueiredo, T.P.Silva, J.P.Veiga, M.I.Dias (2009), “Speciation state of cobalt in blue glazes: a XAFS study on XVI century Chinese blue-and-white porcelains”, Nuclear Instruments and Methods in Physics Research B. Manuscript nr. GSRA0R1.

M.O.Figueiredo, T.P.Silva, J.P.Veiga, M.I. Prudêncio, M.I.Dias, M.A.Matos, A.M.Pais (2009), “Blue pigments in XVI-XVII cent. glazes: a comparative study between Portuguese faiences and contemporary Chinese porcelains manufactured for the Portuguese market”, Symp.3 LASMAC, XVIII Internat. Materials Research Congress, México, CD-ROM S3-29.

M.I.Dias, A.Pais, A.L.Rodrigues, R.Marques, M.I.Prudêncio (2009). Chemical characterization of Portuguese faience from 16th-18th century: a preliminary neutron activation study. Book of Abstracts, EMAC’09, UCL, British Museum, London, p. 65.

C.I.Burbidge, A.L.Rodrigues, M.I.Dias, M.I.Prudêncio, G.Cardoso, in press. ‘Optimisation of preparation and measurement protocols for luminescence dating of small samples from a suite of porcelains and faiences’, Mediterranean Archaeology and Archaeometry.

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Application of luminescence dating to understanding Iberian cultural development

M. I. Dias, M.I. Prudêncio, C. Burbidge, G. Cardoso, D. Franco, R. Marques, A.C. Valera¹, C. Fabião², C. Odriozola³, V. Hurtado³, L. San Juan Garcia⁴, L. Osterbeek^{5,6}, C. Scarre⁷, J. Munghur Medhi^{6,8}, A. Cruz⁶, P. Curá⁶, J. Garcia Gazolaz⁹, J. Sesma⁹, D. Mosquera¹⁰, J. Sanjurjo¹⁰, S. M. Espino¹¹, C. Bento¹², A. Silva¹², T. Gomes¹²

Luminescence dating of sediments, mortars, heated clay structures and ceramic artefacts, is being conducted in both research and service contexts. Samples from museums and archaeological sites across Iberia are being measured to develop and test chronological frameworks for cultural development, exchange, and population dynamics. Studies of prehistoric human occupation and activity are focussing on the Upper Ribatejo, Lower Alentejo, and Navarra regions. At such sites dating is being combined with luminescence profiling of sedimentary sequences to provide additional stratigraphic context for the dating results, to enhance understanding of archaeological site formation processes. Cultural chronologies established or tested have related to the Roman, Medieval and Post-Mediaeval periods: analysis of materials such as the roman “concrete”, lime mortar, porcelain and faiança has required substantial methodological testing and development. Some artefacts have been found to actually be modern.



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⁵ Inst. Politécnico de Tomar, Portugal.

⁶ Museu de Arte Pré-Histórica de Mação, Portugal.

⁷ Durham Univ., Dep. of Archaeology. UK.

⁸ Fundação Ernesto Lourenço Estrada, Abrantes, Portugal

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¹¹ Arqueoiberia Estudios, S.L. Madrid, Spain

¹² Coleção Berardo, Portugal

Luminescence dating of coastal geomorphological development in Portugal and Mozambique

C. Burbidge, M. I. Dias, M.I. Prudêncio, G. Cardoso, D. Franco, R. Marques, L. Rebelo¹, P. Brito¹, D. Mosquera², J. Sanjurjo².

Luminescence dating is being applied as part of ongoing research programs into the chronologies of coastal geomorphological development in Portugal, Galicia and Mozambique, in the Holocene and through the late Pleistocene. Dating of Holocene dunes has been technically straightforward. This has enabled the establishment of a chronology for the formation and mobilisation of the Troia spit, presently the subject of major tourist infrastructure development. It has also resulted in a series of dates for recent dune activation on the Mozambican coastal plain. Analysis of older sands from Mozambique and Galicia has been more technically challenging. Methodological testing and development related to these challenges has so far produced one technical publication, and has the potential to offer a number of insights into the dating of “old” samples by luminescence methods.



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

M.I. Dias, M.I. Prudêncio, R. Marques, M.A. Gouveia, D. Franco, C. Burbidge, C. Fabião¹, S. Gabriel², M. Coelho², I. Filipe²

A multidisciplinary FCT project is running in the archaeological site of the fish-salted factory of the Casa do Governador da Torre de Belém - CGTB, Lisbon, Portugal, which aims to understand one of the most important economic activities of the coastal areas of the Roman Province of Lusitania, the salted fish and salsamenta production, exported in amphorae to other areas of the Roman Empire. The CGTB will become a hotel and will preserve a part of the ruins of the roman factory and an exhibition of the research project. Compositional study of samples from amphorae finds is an ongoing task. Chemical composition was obtained by INAA by using the RPI as neutron source, and mineralogical composition was obtained by XRD. Significant chemical differences were found so far, pointing to the use of diverse raw materials. The comparative study with our database including Lusitania production centers suggests that the majority of amphorae were produced in the Tagus basin. Also luminescence dating (OSL) of in situ sediments is running for a better definition of the chronostratigraphic sequence of both human occupation levels and fluvial deposits, contributing to the establishment of a palaeoenvironmental scenario.



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Distribution of trace elements and natural radionuclides of the U and Th radioactive series in superficial environments

M.J. Trindade, M.I. Prudêncio, M.I. Dias, R. Marques, M.A. Gouveia, D. Franco, J. Sanjurjo¹, D. Mosquera¹, J. R. Vidal Romani¹

The distribution/mobility of trace elements and natural radionuclides of the uranium and thorium radioactive series are being studied in superficial environments in order to determine the causes of radioactive disequilibrium in the U- and Th-series decay. This study may have impact in various research areas, mainly in soil formation and evolution; study of the post-depositional alteration processes in sedimentary series and weathering profiles, especially the ones developed in granitic terrains; palaeoenvironmental investigations; and the study of the impact of radioactive disequilibrium on luminescence (OSL) dating of Quaternary sedimentary deposits, contributing to better constrain geological and anthropogenic events. In 2009 especial attention was paid to the study of secondary manganese oxyhydroxides formed during alteration of consolidated dunes, and their capacity in co-precipitate actinides and lanthanides.



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Applied geochemistry to the study of superficial environments in the Iberian Peninsula and Cape Verde islands - distinguishing geogenic and anthropogenic contributions

M.I. Prudêncio, M.I. Dias, R. Marques, D. Franco, M.J. Trindade, F. Rui¹, M. Abad¹, F.Rocha², E.Silva², M.M.S. Cabral Pinto^{2,3}, M.M.V.G. Silva⁴



Geochemistry and mineralogy studies were applied to superficial environments (soils and sediments) of the Iberian Peninsula and Cape Verde archipelago. Concerning Cape Verde, a detailed study of topsoils (regolith) from Santiago and Fogo islands is an ongoing project aiming a contribution for the construction of the Geochemical Atlas of these islands. The evaluation of both geogenic and anthropogenic contributions (particularly the total contents of trace elements) is a major goal. During 2009 a first sampling campaign in the Fogo island occurred. The results obtained so far for soils formed in the semi-arid climate of Cape Verde suggest the presence of chemical elements in different forms/ availability. Rare earth elements (REE) and thorium were found to be good indicators of the parent rock lithology, particularly for carbonatites. The preferential incorporation of LREE (after the breakdown of primary minerals) in Fe/Mn oxides and in clay minerals, as well as the preferential incorporation of HREE in carbonates (calcite or dolomite) was found.

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Development of nuclear methods and applications in the archaeometry of cultural heritage assets

M.I. Prudêncio, M.I. Dias, C. Burbidge, M. J. Trindade, R. Marques, M.A. Gouveia, D. Franco, G. Cardoso, A. Jorge¹, P. Day¹, F. Rocha², C. Odriozola⁴, L. Osterbeek⁵, J. Mungur-Medhi⁵, J. Sanjurjo⁶, A.C. Valera⁷, V. Hurtado⁸, L. San Juan Garcia⁸

INAA (using the RPI), together with luminescence techniques support most of the research activities of the GeoLuC group. These nuclear methods were applied to several archaeometric studies, most of them performed in the framework of master and doctoral thesis, as well as post-doctoral programmes. During 2009 the compositional database of ancient ceramics was increased. Study of objects from excavations and museums, including their origin, technique of manufacture, age and conservation was done. 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 their good performance. The Luminescence Dating Laboratory participates in international comparisons, particularly with the IUX, Coruña, Spain. These studies unlock information from ancient materials, such as provenance, mainly pottery, technique of manufacture, firing technology, ancient recipes and alteration pathways, as well as absolute chronology, in an Iberian perspective.

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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 High Performance Liquid Chromatograph/Inductively Coupled Plasma Mass Spectrometer**.

During the current year, by using the HPLC/ICPMS facility (installed in 2008) new studies in the Environmental and Biomedical (in collaboration with the Biomedical Studies Group/IBL/UFA) fields were implemented. The acquisition of the stable isotopic ratio mass spectrometer to be associated with the sample preparation for AMS (Accelerator Mass Spectrometry) measurements (in collaboration with the Ion Beam Laboratory Group/UFA) was finished.

Environmental Geochemistry and Oceanographic research was carried out under a multi-proxy approach, including sedimentology, geochronology, absolute dating and paleoecology. Research focused in Sedimentary Geochemistry aimed at the palaeoenvironmental reconstruction along the Holocene on the Portuguese coastal area, in particular at the Minho and Douro drainage basins and at the assessment of ecological effects of the metal contents on Sado tidal marshes. 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 have significantly contributed to the exploitation and development of regional water resources and to the delimitation of protection areas.

The **archaeometallurgical research** was focused on materials characterization, involving different analytical techniques (EDXRF, micro-XRF, optical metallography, XRD and SEM-EDS) of Cu and Au-based artefacts and other remains recovered in different archaeological sites from Portuguese territory. Results have shown that reduction, alloying and recycling operations were probably undertaken in several sites, and that artefact shaping was performed by diverse methods. Another study dedicated to the Chinese brass coins belonging to the collection of Macau Scientific and Cultural Centre Museum (Lisbon, Portugal) proposes to correlate the alloy elemental composition with the metallic phases. Present observations show that minor elements as Pb, Sn, Sb, Fe and As are structurally significant in these cast coins.

A study of the Macao Scientific and Cultural Center Museum **Chinese copper cash** was focused on the correlation of the alloy elemental composition with the metallic phases. Current observations showed that minor elements as Pb, Sn, Sb, Fe and As are structurally significant in these cast coins

The EAC group is highly engaged in education and training of MSc and PhD students in collaboration with different Universities.

Technical services are also available to Universities and to Public and Private Institutions.

Research Team

Researchers

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Environmental Geochemistry – Elemental and Isotopic Research

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Objectives

Activities aim at the development and promotion of coordinate research on Earth and Environmental Sciences in conjunction with the implementation of analytical and absolute dating techniques:

1. Multielemental characterization ($Z > 10$) using X-Ray Fluorescence spectrometry;
2. Light isotope determination ($\delta^2\text{H}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$);
3. Radiocarbon dating;
4. Tritium dating.
5. High Performance Liquid Chromatography coupled to an Inductively Coupled Plasma Mass Spectrometry

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 during the Holocene; identify episodes of abrupt shifts in oceanic circulation, probably coupled with abrupt climatic changes.

Results

Geochemical and dating studies carried out in estuarine and tidal marshes sediments revealed to be essential tools in the study of transitional and marine environments, providing indication about the marine/terrestrial origin of the deposited materials and allowing to recognise and evaluate changes occurred during the Holocene. During 2009, studies were mainly focused on: Minho/Coura and Douro estuaries. Results obtained in the study the radiocarbon dated sedimentary sequences reveal the influence of relative sea-level rise during the Holocene. The geochemical signatures of the drainage basins as well as the different natural (regional) background could also be identified. Metal contents on sediments showed to be a result of a wide variety of factors, including the lithology of the drainage basin and the sediment grain size distribution. In addition, preliminary studies on

the organic fraction of estuarine sediments, indicate that humic acids are usually heavy metal enriched, although they seem to preferentially accumulate specific metals, in particular Cu.

Hydrological aspects such as origin and magnitude of recharge, groundwater, dynamics, nitrate pollution, interaction between surface and groundwaters, and water quality issues have been one of the main goals, highlighted through the use of 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). During 2009 the collected gases in the CO_2 rich mineral waters N of Portugal reflect the pristine isotope composition of the C source. The measured $\delta^{13}\text{C}_{\text{CO}_2}$ values around -6‰ are consistent with a mixing between crustal marine plus metamorphic gases and mantle-derived volatiles. All the free gases measured fall very close to the field of the gas typical of a mantle origin. Release of deep-seated fluids having a mantle-derived component in a region without recent volcanic activity indicates that extensive neo-tectonic structures originating during the Alpine Orogeny are still active.



Radiocarbon dating is an important tool to set up chronological frameworks for the past environmental changes. As usual, it is of much use in several fields of our research. A new step in the study of the marine reservoir effect was implemented since 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. A significant number of ΔR values were determined for the second zone showing that this coastal region seems to have not been affected during the Holocene by an active upwelling. As the phenomenon is a wind-driven process, a nonexistent upwelling in the region probably means that westerlies were weak or not predominant during the Holocene.

Geochemical record of environmental changes in Portuguese coastal area*M.F. Araújo, C. Corredeira, M. Santos, S. Moreira¹, F. Fatela¹*

The overall objectives of this current work are the recognition of recent environmental changes which have occurred at the main Portuguese estuaries and adjacent shelf, by using a multi-proxy geochemical approach to characterize and trace the history of the sedimentary record. Studies were mainly focused on estuarine sediments from Sado tidal marshes and from Guadiana downstream basin and adjacent shelf along the Northern Gulf of Cadiz. Elemental distribution patterns on Guadiana river sediments showed heavy metal enriched sediment in specific locations, most likely related to the long exploitation of mineral resources and other recent anthropogenic activities. However, metal contamination is much more significant at the shelf due to the particular run-off behaviour of Guadiana river system induced by specific hydrographic and climate characteristics that clearly induce a major sediment exportation towards the continental shelf. On Sado tidal marshes relations between foraminiferal assemblages distribution and respective sediment contents of Cr, Cu, Zn, Pb, Ca and organic matter, coarse fraction proportion and pH, were assessed using a detrended canonical correspondence analysis ordination technique (DCCA). Considering the values measured in Sado estuary these sediment features do not seem to directly affect the distribution of marsh foraminifera. The influence of such parameters is exceeded by the marine influence and time submersion. The adaptation of foraminiferal species to these main ecological factors of tidal marshes, seems to mask the effect of other ecological and anthropogenic factors.



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The marine reservoir effect – its quantification and variability*A.M. Monge Soares, J.M. Matos Martins, J.M. Alveirinho Dias¹, A. Mederos Martín²*

Following previous research (see 2007 and 2008 ITN Reports) concerning the upwelling phenomenon off the Iberian coast of the Gulf of Cadiz it was determined that ΔR , a parameter that quantifies the marine reservoir effect, takes positive values with a weighted mean of 65 ± 20 ¹⁴C yr (south-western Portuguese coast) or negative values with a weighted mean of -135 ± 20 ¹⁴C yr (Andalusian coast). Nevertheless, between 4400 BP and 4000 BP ΔR values are strongly positive. Positive ΔR values can be correlated with an active upwelling, while negative ΔR values correspond usually to a nonexistent upwelling. Those strongly positive values suggest a very strong upwelling existed in the entire region of the Gulf of Cadiz. This does not reflect wind-driven processes, but probably an eastward extension of the Azores Front, which is characterized by locally intense upwelling, along the Azores Current that penetrated into the Gulf of Cadiz. Concerning the coastal waters of Canary Islands, another region object of our research in the same field, ΔR values that were determined are consistent with the hydrodynamic system present off Canary Islands. The eastern islands (Fuerteventura and Lanzarote) are affected by the coastal upwelling regime prevailing over the north-western African continental shelf, conversely to what happens off the other islands of the archipelago, namely off Tenerife Island, where the upwelling effect does not prevail. For Fuerteventura Island ΔR takes a positive mean value of 150 ± 40 ¹⁴C yr, while for Tenerife Island a range of negative values was obtained resulting on a mean value of -10 ± 50 ¹⁴C yr.

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Groundwater resources assessment by anthropogenic and natural contamination sources*P.M. Carreira, P.A. Fernandes, D. Nunes, L. Ribeiro¹, M.A. Marques da Silva², M.T.C. Melo²*

The application of stable nitrogen isotopes (¹⁵N/¹⁴N ratios) offers a direct way to identify the pollutant sources in groundwater systems. In 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 ($\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ from NO_3 and $\delta^2\text{H}$ and $\delta^{18}\text{O}$ from H_2O). Nitrogen isotopes were used to identify nitrogen sources and assess agriculture, cattle-breeding, urban and industrial contribution to nitrogen cycle in Aveiro ecosystem, based on the fact that the main sources of nitrate in the area have isotopic distinct $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ signatures.



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Hydrology in urban areas

P.M. Carreira, D. Nunes, M.J. Afonso^{1,2}, H. Chaminé^{1,2}, J.M. Marques³, M.M. Abreu⁴, P. Figueiredo⁵

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 one of the tools that can be used to complement the conventional hydrogeological and geochemical approach to evaluate the impact of urban recharge in groundwater. A multidisciplinary approach, using hydrogeochemical, isotopic and ecotoxicological analyses, performed to assess the nature and suitability for use of Paranhos and Salgueiros spring waters (Porto city, NW Portugal). Based on the surface activities located along the course of the springs, twenty-three water samples were collected. All the samples have been analysed for major element concentrations. The isotopic techniques employed included $\delta^2\text{H}$, $\delta^{18}\text{O}$ and ^3H . Standard acute bioassays with *Daphnia magna* were also performed. The hydrogeochemical analyses showed a nitrate and sulphate-enriched composition for these groundwaters, resulting mainly from urban drainage and sewer leakage. Concerning the ecotoxicological analyses, no significant mortality was observed in any of the tests performed. The results obtained in this study suggest that Porto urban groundwater could be suitable for irrigation uses.

Aquifers located in urban environments for the sustainable development and management of groundwater resources requires a precise assessment of its occurrence, availability and vulnerability to deterioration.

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Arid /semi arid zones hydrology

P.M. Carreira, P.A. Galego Fernandes, D. Nunes, F. Monteiro Santos¹, J.M. Marques², M. Bahir³, M. F. Ben Hamouda⁴

Overexploitation of coastal aquifers and pollution are among the main problems related to groundwater resources assessment and management. Isotopic techniques combined with geochemistry and geophysical investigations, provided comprehensive information on groundwater recharge, as well as on the identification of salinization mechanisms (e.g. seawater intrusion, salt dissolution, and marine aerosols) of the groundwater systems, at Cap Bon Area, Northern Tunisia. In addition, at Essaouira Basin (Morocco) also a multidisciplinary approach has been applied to evaluate the hydrogeological potential of arid zones.



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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

Three sampling campaigns were performed in Azores archipelago in order to: i) characterize the chemical and isotopic composition of ground waters, fumaroles and gas emissions related with hydrothermal/geothermal systems and volcanologic/seismic settings. A continuous-flow GC/IRMS technique has been developed to analyse $\delta^{15}\text{N}$ values for molecular nitrogen in gas samples. The method was tested on magmatic and hydrothermal gases as well as on soil gas samples. The analysis of nitrogen isotope composition may be prone to atmospheric contamination mainly in samples with low N_2 concentration; based on the simultaneously determined $\text{N}_2/^{36}\text{Ar}$ ratios and assuming that ^{36}Ar content in crustal and mantle-derived fluids is negligible with respect to ^{36}Ar concentration in the atmosphere, for each sample, the degree of atmospheric contamination can be accurately evaluated.

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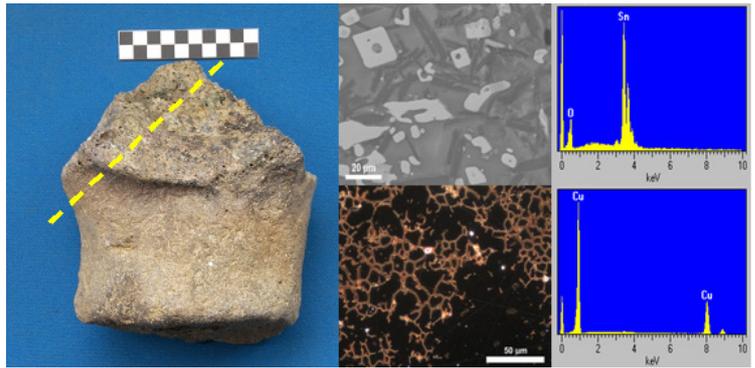
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Archaeometallurgy – Provenance, technology and use of metallic artefacts

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 as EDXRF, micro-XRF, optical metallography, XRD and SEM-EDS) with archaeological evidences, to investigate the evolution of ancient metallurgical operations and artefact production in the Portuguese territory. Metallic artefacts from Castro dos Ratinhos and Entre Águas 5 indicate that the inland region of the Southern Portuguese territory exhibits a



metallurgy of binary bronzes with “suitable” tin contents (~8-12%) at least until the end of the 8th century BC. Conversely, later bronze artefacts from Palhais (7th-6th centuries BC) present lower tin contents, which are comparable with the coeval Mediterranean tradition, perhaps pointing out to imports from this region. Furthermore, the characterization of slagged remains from Entre Águas 5 seems to indicate that a cementation process was used when the introduction of bronze in Southern Portugal occurred. The use of hammering and annealing cycles was confirmed in the production of thin gold sheets from the Chalcolithic site of Perdigões, while the solid state diffusion process had been identified for joining components at Early Iron Age gold buttons from Outeiro da Cabeça. Regarding the Central and Northern Portuguese regions a large set of artefacts, fragments, scraps, and other metallurgical remains (recovered at various archaeological sites, as Castro de Nossa Senhora da Guia de Baiões, Castro de São Romão and Medronhal) have been analysed and results have been interpreted. Analyses showed that during the Late Bronze Age artefacts had generally very low Pb contents (Pb<1%) and that the tin content is regularly around 9-15%. The microstructural studies show that different thermo-mechanical treatments were performed in the artefacts, regarding their shape. Also, some metallurgical remains from Baiões/Santa Luzia cultural group point out to various metallurgical operations, involving smelting and recycling, performed inside the settlements.

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Inorganic and Organometallic Chemistry

Joaquim Marçalo

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

Important facilities maintained by the Group are a laboratory for catalytic studies prepared for work with CO, a laboratory for handling macroscopic quantities of the more radioactive actinides, a laboratory for calorimetric studies and thermal analysis, and two select mass spectrometers, a FTICR instrument, with EI and LDI sources, and a QIT instrument, with ESI and APCI sources. The QIT mass spectrometer is part of the National Mass Spectrometry Network (RNEM).

Gas-phase chemistry studies were pursued. An overall assessment of the gas-phase energetics of neutral and singly and doubly charged cationic actinide monoxides and dioxides from thorium to curium was carried out. A consistent set of metal-oxygen bond dissociation enthalpies, ionization energies, and enthalpies of formation, including new or revised values, was proposed. Preliminary studies of the energetics of actinide sulfides were also performed.

We continued to study the activation of methane and carbon dioxide as valuable C1 feedstocks, namely through the catalytic partial oxidation of CH₄ (POM reaction) using O₂, CO₂ or N₂O as oxidants. The production of syngas with the appropriate H₂/CO mol ratio of 2 and high conversion of methane was obtained over bimetallic lanthanide and actinide/nickel based oxide catalysts. A new route for obtaining the catalysts was developed - a molten salt route using eutectic potassium-lanthanides molten chloride salts. The best results were those obtained on cerium molten

salts and the main reaction products were always hydrocarbons which is a novelty over f-block elements catalysts.

We continued the investigation of the coordination chemistry of actinides and lanthanides based on O- and/or N-donor ligands of the azamacrocyclic and polypyrazolylalkane families. A new dianionic hexadentate N₄O₂-donor ligand was used as ancillary ligand to stabilize Y and La metal complexes of the type [MLCl]. The synthesis of Nd complexes bearing 3-(2-pyridyl)pyrazolylmethane ligands was initiated. The synthesis and characterization of new ionic liquids exhibiting luminescent properties and involving Ln complexes with beta-diketonate ligands was also performed.

The study of the energetics of organic, inorganic and organometallic molecules was continued and a database of the enthalpies of formation of organic compounds was made available on-line (www.therminfo.com). The experimental study of polyalkoxides of alkaline and alkaline-earth metals was initiated.

Collaborations with the Radiation Technologies: Processes and Products Group (Physics and Accelerators Unit) in the study of the gamma radiation effect on wastes, and with OMNIDEA, Lda., a start-up company dedicated to R&D of aerospace technology and energy systems, continued.

Joint projects with the Research Unit "Glass and Ceramic for the Arts" (a collaboration between ITN, FBAUL and FCT/UNL) on provenance studies of Portuguese glasses, new lanthanide based fluorescent glasses, ruby glass and analysis of glazes in tiles were pursued.

A relevant part of the activity of the Group is the training of research students. Some of the group members are involved in undergraduate and post-graduate university courses. The financial support for the work is mainly from FCT, via research projects and PhD and Post-doc grants.

Research Team

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Gas-Phase Chemistry of Actinides and Lanthanides

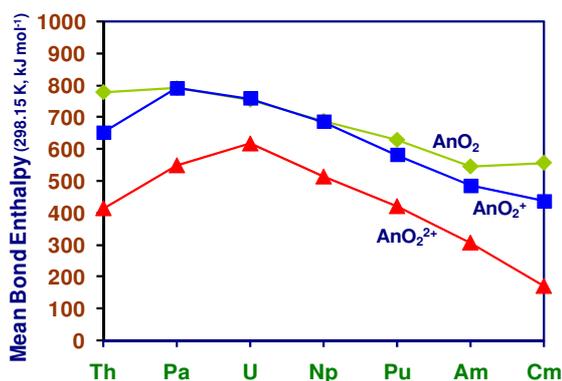
J. Marçalo, C. C. L. Pereira, J. P. Leal, J. M. Carretas, A. Pires de Matos,
A. P. Gonçalves¹, J. K. Gibson²

Objectives

The gas-phase chemistry of atomic and molecular actinide and lanthanide ions is studied in order to obtain thermodynamic, kinetic and mechanistic information that may enhance the fundamental knowledge of these elements. The experimental work is based on the use of advanced mass-spectrometry techniques, namely, LDI-FTICR/MS and ESI-QIT/MS. For the actinides, the explicit aims are to produce species with new ligations and properties, probe the role of 5f electrons in chemical bonding, and determine thermodynamic data for species of interest for condensed-phase processes. Parallel theoretical studies of selected actinide molecular ions are also carried out via collaborations to assist in the interpretation of experimental observations.

Results

The large amount of data that was gathered from our previous studies of actinide oxides from thorium to curium led to an overall assessment of the gas-phase energetics of neutral and singly and doubly charged cationic actinide monoxides and dioxides [1]. We evaluated the data from standard literature sources, tested and expanded the assessment of the known bond dissociation energies of neutral and singly-charged actinide monoxides carried out by J. K. Gibson some years ago, based on correlations with the electronic structures and energetics of the isolated metal atoms and ions, and provided correlations with condensed-phase thermochemistry. A consistent set of metal-oxygen bond dissociation enthalpies, ionization energies, and enthalpies of formation, including new or revised values, was proposed. We also proposed new estimates for the second ionization energies of the actinides from Th to Cm.



Mean bond enthalpies of neutral and cationic An dioxides

On the experimental side, we again used the FTICR/MS technique to probe this time the An-S ligation for An = Th, U and Cm [2,3]. We studied the reactions of the An⁺ metal cations with CS₂ and of the AnS⁺ species produced with selected neutral reagents. Estimates of the An metal-sulfur bond energies for the cationic and neutral monosulfides, and of the ionization energies of the neutral monosulfides could be obtained.

ESI of thorium and uranyl nitrates in water/methanol solutions generates several species in the negative ion mode which, depending on instrumental parameters or on deliberate CID, lead to different oxo- or hydroxo-containing ions [4]. The oxo ions bear special interest as the type of bonding of the oxo ligands determines the oxidation state of the metal centres.



ESI-QIT mass spectrometer
(Part of the National Mass Spectrometry Network – RNEM)

Published work

“Gas-Phase Energetics of Actinide Oxides – An Assessment of Neutral and Cationic Monoxides and Dioxides from Thorium to Curium”, J. Marçalo, J. K. Gibson, *J. Phys. Chem. A* 113 (2009) 12599–12606.

“Actinide Sulfide Ions in the Gas Phase: A Preliminary FTICR-MS Study of the Reactivity and Thermochemistry of ThS⁺ and US⁺”, J. Marçalo, C. C. L. Pereira, J. K. Gibson, *Actinides 2009*, S. Francisco, CA, USA, Jul. 2009.

“Actinide Sulfides in the Gas Phase: A Preliminary FTICR-MS Study of the Thermochemistry of Curium Sulfide”, C. C. L. Pereira, J. Marçalo, J. K. Gibson, *8th Inorganic Chemistry Conference - Sociedade Portuguesa de Química*, Curia, Oct. 2009.

“A Few Examples of the Current Research Work at the I.T.N.-Node of R.N.E.M.”, J. P. Leal, R. Melo, M. L. Botelho, J. Marçalo, I. Paiva, J. M. Carretas, C. C. L. Pereira, T. A. Gasche, *Annual Meeting of the Portuguese Mass Spectrometry Network*, Lisboa, Oct. 2009.

¹ Solid State Group, UCQR-ITN.

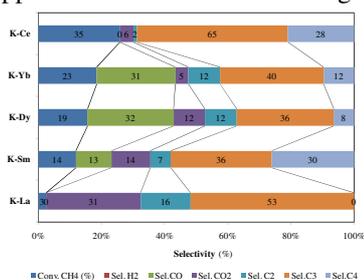
² Lawrence Berkeley National Laboratory (Berkeley, California, USA).

f-Block Elements as Catalysts

J. B. Branco, A. C. Ferreira, G. Lopes, T. A. Gasche, M. R. Correia¹, A. Rego², A. Ferraria², A. P. Gonçalves³

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.

We continued to study the activation and valorisation of methane and carbon dioxide as valuable C1 feedstocks, namely through the catalytic partial oxidation of CH₄ (POM reaction) using O₂, CO₂ or N₂O as oxidants. The catalysts were obtained by three routes: i) an intermetallic route, using LnCu₂ and LnNi₂ (Ln = from La to Yb) or AnNi₂ (An = Th, U) and ThCu₂ as bimetallic oxides precursors, ii) a sol – gel route (urea or citric acid methods) to obtain nanoparticles of bimetallic oxides and, recently, iii) a molten salt route using eutectic potassium-lanthanides molten chloride salts. Molten salts offer unique opportunities and alkali molten metal chlorides appear has a “new” and challenging group of catalysts for a number of applications. The production of syngas



with the appropriate H₂/CO mol ratio of 2 and high conversion of methane was obtained over the bimetallic nickel based oxide catalysts, cheaper materials with an activity and selectivity comparable to that of noble metal based catalysts, e.g. 5 wt. % M/Al₂O₃ (M-Rh, Pt). Taking into account the importance of NO_x as pollutants, it was established that the CH₄/N₂O molar ratio has a significant influence on the selectivity (decreases the selectivity to CO_x and increases the selectivity to hydrocarbons). The catalytic performance of the molten salts of the type KCl-LnCl (Ln = La, Ce, Pr, Sm, Gd, Dy, Yb) is clearly different and depends on the rare earth. The best results were those obtained on cerium

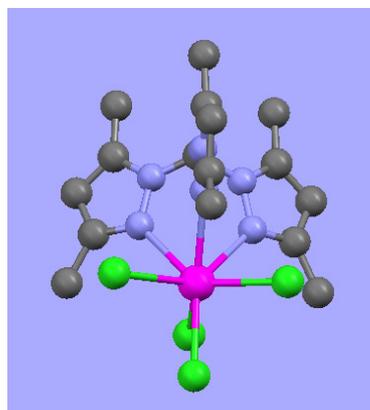
molten salts (Conv. = 35%, Sel. = 0, 5.7, 1.5, 64.6 and 28.2 % for CO, CO₂, C₂, C₃ and C₄, respectively). The main reaction products were always hydrocarbons (C₂, C₃ and C₄; Sel.C₃ > 70%) which, to our knowledge, is a novelty over f-block elements catalysts.

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f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

A. Carvalho, J. M. Carretas, J. Marçalo, L. Maria, N. Marques, B. Monteiro, C. C. L. Pereira, I. C. Santos¹, A. M. Martins², L. C. Branco³, C. A. T. Laia³

We continued the investigation of the coordination chemistry of actinides (Th and U) and lanthanides (Ln) based on O- and/or N-donor ligands, with potential interest in organic synthesis and catalysis, lanthanide/actinide separations and luminescence applications. Azamacrocyclic ligands have known a growing interest owing to their coordination properties and their range of applications, including metal mediated catalysis. A new dianionic hexadentate N₄O₂-donor ligand, 1,8-bis(methylene-di-*tert*-butylphenolate)-4,11-dimethyl-1,4,8,11-tetraazacyclotetradecane, was used as ancillary ligand to stabilize the large rare earth metal cations. Preliminary results with Y and La have shown that it is adequate to stabilize metal complexes of the type [MLCl]. The complexes have been fully characterized by ¹H NMR and ¹³C NMR, based on 2D-NMR experiments. Studies of the chemistry of Th, U and Ln with neutral ligands of the pyrazolylalkane family were pursued. Design and synthesis of new pyrazolylmethanes were performed, namely of bis- and tris-[3-(2-pyridyl)pyrazolyl]methane. The study of the synthesis of Ln complexes bearing these ligands and also the neutral “arm” 3-(2-pyridyl)pyrazole and its anionic counterpart 3-(2-pyridyl)pyrazolide was initiated using NdCl₃ and different reaction conditions. With the tris(3,5-dimethylpyrazolyl)methane (Tpm*) ligand, the x-ray crystal structure of the complex ThCl₄(Tpm*) was determined. Formation of cationic derivatives of the U complexes UCl₄(Tpm*) and UI₃(Tpm*)(THF) was investigated using AgBPh₄. Work involving the bis(3,5-dimethylpyrazolyl)methane ligand and UCl₄ and UI₃(THF)_x starting materials was also performed. The synthesis and characterization of new ionic liquids exhibiting luminescent properties in the visible region of the spectrum and involving Ln complexes was performed. Luminescent complexes of Eu with beta-diketonate ligands were synthesized in the form of tetrakis salts of the type NaEu(β-diketonate)_nCl_{4-n}. Two different β-diketones were used, β-naphtoyltrifluoroacetone (β-NTA) and dibenzoylmethane (Hdbm). The counter-ion was afterwards exchanged following the same strategy as for the ionic liquids involving organic fluorophores.



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Molecular Energetics of Organic, Inorganic and Organometallic Compounds

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The main objective of this research is to collect energetics data, rationalize it in a systematic way and explore connections between energetics and structure on molecules (both inorganic and organic compounds). Special importance was given to f-element compounds (both in 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 2009, an extended version of an empirical model for the prediction of the enthalpies of formation of hydrocarbons was published. Also, a database of the enthalpies of formation of organic compounds was made available on-line (www.therminfo.com). The nature of ionic liquids in the gas phase continued to be studied and the kinetics of some of the reactions where they are involved were investigated using FTICR/MS. The thermal properties of some ionic liquids were studied using thermal analysis techniques and the correspondent reactivity was explored using a QIT/MS apparatus. The study of polyalkoxides of alkaline and alkaline-earth metals took its first steps - synthesis and characterization of the compounds. Until now Na, K and Ca compounds with ethylene glycol were synthesized. The degradation/decomposition mechanism of gallic acid was elucidated by using pulse-radiolysis and mass spectrometry (QIT/MS). The gas-phase acidity measurements of methoxy di-substituted phenols were concluded.



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Glass Science with Applications in Archaeometry and Art Studies

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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 2009 the Arcanum of Guilherme Stephens was studied. An attempt to

clarify the chemical nomenclature and glass jargon used by Stephens was made and the probable sources of the raw materials were investigated. The production methods and equipment used in the last quarter of the 18th century at Marinha Grande were studied. A few glass samples were reproduced using several compositions referred in the Arcanum to check the validity of the proposed nomenclature and to investigate the conditions used to obtain the colours. Micro-EDXRF and UV-Vis absorption spectrometry were used to characterize and compare laboratory reproduced samples with museum collection items seemingly attributable to the Stephens production period at Marinha Grande. Another research area is related with the development of glasses for artistic applications. Studies on luminescent glasses with rare earths have continued and application in art objects was made. Gold and copper ruby glasses were synthesized using gamma radiation for reduction of the metal ions and to improve nucleation of the metal nano-particles. A collaboration with the industry in this area has started. Studies of glazes in tiles using Raman spectroscopy were performed. With the same purpose, experiments to characterize glass by LIBS (Laser Induced Breakdown Spectroscopy) using a home-built system involving a Nd:YAG laser (ITN) and an optical fiber UV-Vis absorption spectrometer were continued.

¹ VICARTE, FCT-UNL.

² Museu do Vidro, Marinha Grande.

Gamma Irradiated Chitosan/pHEMA Membranes for Drug Release Systems

L. M. Ferreira¹, M. H. Casimiro, J. P. Leal, M. H. Gil²

Membranes using polyethylene as backbone polymer and HEMA as grafting molecule, produced through irradiation on a ⁶⁰Co source, were synthesized and the corresponding properties extensively studied. New uses for these compounds were explored.

¹ UFA-ITN.

² Dep. de Engenharia Química, FCT-UC.

Radiopharmaceutical Sciences

Isabel Rego Santos

The **Radiopharmaceutical Sciences Group** developed and implemented expertise and facilities to carry on basic/applied oriented research and technology transfer *on nuclear tools for SPECT and PET molecular imaging and for targeted radiotherapy*. The group is multidisciplinary and its expertise involves organic and coordination chemistry, bioconjugation, radiochemistry, animal and cell studies, and molecular biology.

Our expertise and facilities enables to perform research in modern Radiopharmaceutical Sciences, an important topic in Life Sciences, justifying also our participation in National and International research projects and the support of an International Pharmaceutical Company. Our expertise and facilities are also extensively used to provide education and training at different levels.

The main achievements during 2009 are described in this report. However, we would like to emphasize the following:

Facilities:

Our animal housing facilities and our molecular biology laboratory have been reinforced, respectively, with the installation of equipment for nude mice and equipment for DNA analysis (PCR and Gel Documentation System). We have also fully implemented the solid phase peptide synthesis methodology using the recently acquired Microwave-Peptide-Synthesizer.

Research:

1 – Novel ^{99m}Tc (I) receptor-targeted polymeric nanoprobes, based on dextran-mannose conjugate derivatives, were synthesized. One of these nanoprobes showed favourable biological features for sentinel lymph node (SLN) detection, an important issue in the management of patients with newly diagnosed breast cancer.

2- The potencial for Multi Drug Resistance (MDR) imaging of some of our myocardial perfusion compounds was evaluated. The results obtained indicated that some of them act as Pgp substrates,

being promising for MDR imaging during anticancer chemotherapies.

3 - *In vitro* enzymatic studies with iNOS have shown that the affinity to the enzyme of the inhibitor-containing conjugates was improved upon metallation with “ $\text{Re}(\text{CO})_3$ ”. Such affinity depends on the spacer length between the inhibitor and the metal center.

Education and Training

1-Graduation:

Radiopharmacy teaching at ESTSeL and at Faculty of Pharmacy/University of Lisbon. Under a protocol, Nuclear Medicine students/ESTeSL are trained at ITN (two weeks/year).

2-Post-graduation:

a) Coordination of the Master Course Biomedical Inorganic Chemistry: Diagnostic and Therapeutical Applications (ITN/UL). Coordination and teaching of Radiochemistry and Biomedical Inorganic Chemistry in the same MSc course.

b) Coordination and teaching of Radiopharmaceutical Chemistry in the Master Course Pharmaceutical and Therapeutical Chemistry/Faculty of Pharmacy/UL.

c) Teaching of Chemical Systems and Reactivity in the Master Course in Chemistry, Faculty of Sciences/UL

d) Lectures in PhD Teaching Programs organized by Universities/Associated Laboratories, namely ITQB/UNL.

3-Young scientists:

Several young scientists are being trained in the group, playing a major role in our projects.

Expertise Provided:

Nuclear Medicine Centers, Portuguese Medicines Evaluation Agency, IAEA, Foreigner Science Foundations and International Conferences.

Publications:

Peer-Review International Journals – 17; Reports - 5; Communications – 21; Thesis: MSc – 1, PhD - 3. Invited Lectures and Seminars: 4.

Research Team

Researchers

I. SANTOS, Princ., Group Leader
A. PAULO, Princ.
J. D. G. CORREIA, Princ.
M. P. C. CAMPELLO, Aux.
M. C. OLIVEIRA, Aux.
L.GANO, Aux.
F. MARQUES, Aux.
P. RAPOSINHO, Aux.
C.FERNANDES, Aux.
F. MENDES, Aux., Contract.
G. MORAIS, Aux., Contract. (Since Sep.)
R. GARCIA, Pos-Doc, FCT grant (until Sep.)

S. GAMA, Pos-Doctoral, FCT grant
P. S. ANTUNES, Pos-Doctoral, FCT grant
M. K. S. BATISTA, Pos-Doctoral, FCT grant

Students

S. LACERDA, Ph.D. student, FCT grant (until March)
C. XAVIER, Ph.D. student, FCT grant (until March)
E. PALMA, Ph.D. student, FCT grant
C. MOURA, Ph.D. student, FCT grant
T. ESTEVES, Ph.D. student, FCT grant
C. NETO, Ph.D. student, FCT grant

B. OLIVEIRA, Ph.D. student, FCT grant
S. CUNHA, Ph.D. student, FCT grant
F. SILVA, Ph.D. student, FCT grant
M. MORAIS, Ph.D. student, FCT grant
F. LUCENA, M.Sc. student
C. FRANCISCO, BIC grantee, POCI (until Sept.)
R. FRAGOSO, Undergraduate student
M. ARAÚJO, Undergraduate student

Technical Personnel

A. RODRIGUES
E. CORREIA

$^{99m}\text{Tc(I)}$ -labeled mannosyl-dextran for sentinel lymph node detectionM. Morais, J. D. G. Correia, C. Fernandes, M. Martins¹, S. Pereira,² I. Santos**Objective**

The main goal of this project is the design and synthesis of novel $^{99m}\text{Tc(I)}$ receptor-targeted polymeric nanoprobe for sentinel lymph node (SLN) detection. These nanoprobe, which are based on dextran-mannose conjugate derivatives, aim at the improvement of accuracy in the identification and characterization of SLN by nuclear imaging, having important therapeutic and prognostic significance in patients with newly diagnosed breast cancer.

Results

The polymeric conjugate dextran-(amine)₇-(pyrazolyldiamine)₈-(mannose)₁₅ (**1**) was synthesized by functionalization of dextran with mannose units and pyrazolyl-diamine (pz) chelating units to recognize mannose receptors present in macrophages and for metal stabilization, respectively. The conjugate was characterized by $^1\text{H}/^{13}\text{C}$ -NMR spectroscopy, and its purity determined by size-exclusion HPLC. The hydrodynamic radius of the polymeric particles in solution was measured by Dynamic Light Scattering (DLS) and the Zeta Potential, at physiological pH, was determined by electrophoretic mobility using Laser Doppler Velocimetry (LDV) (Fig. 1).

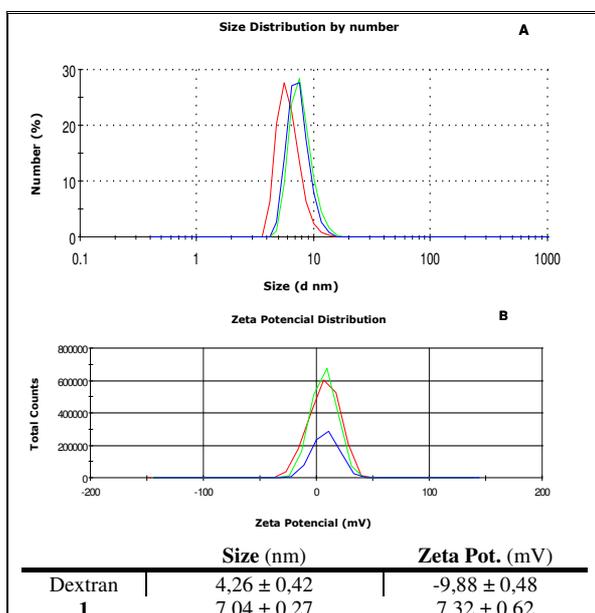


Fig.1 Hydrodynamic radius (nm) by number of particles in solution (A) and Zeta Potential (B) of dextran and **1**.

Reaction of **1** with $\text{fac-}[^{99m}\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ gave, in quantitative yield and high specific activity, the polymeric conjugate $\text{fac-}[^{99m}\text{Tc}(\text{CO})_3(\text{k}^3\text{-1})]^+$ (**2**), whose chemical identity was established by comparing its HPLC chromatogram (γ -detection) with that of the rhenium (**2a**) surrogate (UV-detection

(Fig. 2). Compound **2** is stable both *in vitro* and *in vivo*.

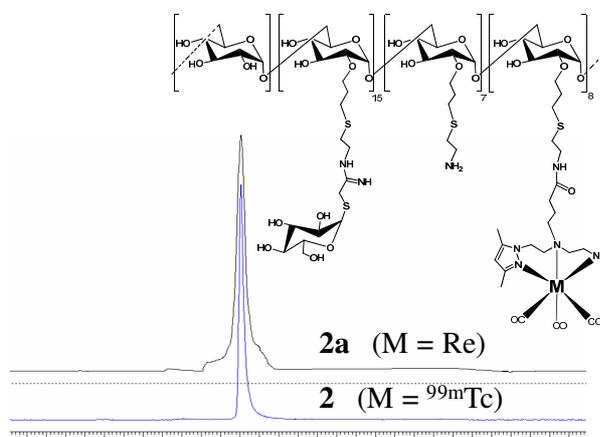


Fig.2 HPLC chromatograms of **2** and **2a**.

Static imaging studies of Wistar rats injected subcutaneously with **2** in the footpad have shown that the compound retains strongly in the first lymph node (LN), exhibiting an high 1st LN/2nd LN ratio (~10:1) at 3h post-injection (Fig. 3).

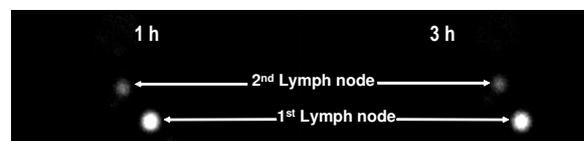


Fig.3 Gamma-camera static images of Wistar rats injected subcutaneously with **2** in the footpad at 1 h and 3 hours p.i.³

The favorable biological features presented by **2**, namely the negligible accumulation in non-target organs, make this compound very promising for further evaluation in other animal models, which is currently underway.

Published work:

M. Morais, J. D. G. Correia, I. Santos, Dextran-mannose conjugates bearing a pyrazolyl-diamine chelator for labelling with the $\text{fac-}[^{99m}\text{Tc}(\text{CO})_3]^+$ unit, IAEA Meeting, 18-22th May, Athens, Greece.

M. Morais, J. D. G. Correia, I. Santos, $^{99m}\text{Tc(I)}$ – Nanocarrier as Versatile Platform for Sentinel Lymph Node Detection., 2nd European Summer School in Nanomedicine, 12-16th June, Cascais, Portugal.

¹Dep. Chemistry, Univ. Aveiro

²CICECO., Univ. Aveiro

³ Performed by S. Subramanian, India, under the framework of a “CRP, Development of ^{99m}Tc Radiopharmaceuticals for Cancer Diagnosis and Sentinel Node Detection, IAEA.

$^{99m}\text{Tc(I)}$ Tricarbonyl complexes functionalized with melanin-binders for *in vivo* targeting of melanoma

C. Moura, L. Gano, P. Raposinho, A. Paulo, I. Santos

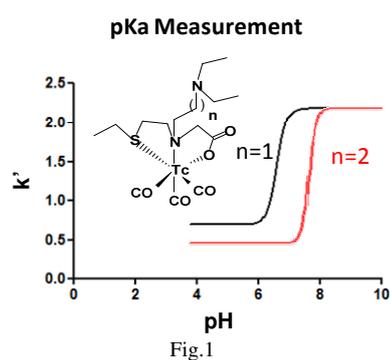


Fig.1

An enlarged family of tricarbyl $^{99m}\text{Tc(I)}$ complexes, anchored by pyrazolyl-containing chelators and bearing N-(diethylaminoalkyl) groups as melanin-avid pharmacophores, have been studied as new radioactive probes for *in vivo* detection of metastatic melanoma. All evaluated complexes showed an high *in vitro* affinity for melanin, but a rather poor tumor uptake. Looking for compounds with improved *in vivo* biological properties, related $^{99m}\text{Tc(I)}$ complexes have also been newly synthesized and evaluated (Fig. 1). These complexes showed a promising tumor uptake (1.90 - 2.17% ID/g at 1 h p.i.) in B16F1 melanoma-bearing mice (Fig. 2), which depends on the spacer length between the bioactive fragment and the metal.

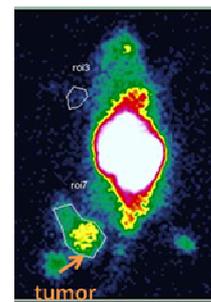


Fig.2

Evaluation of Novel Pyrazolyl-alkylamine Pt(II) Complexes as Anti-Cancer Drugs

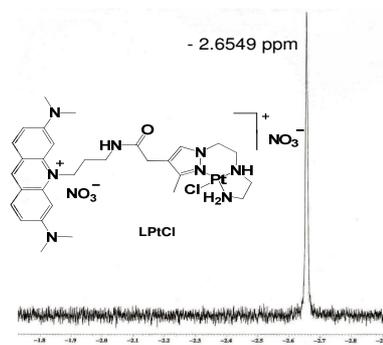
 C. S. Francisco, S. Gama, F. Marques, A. Paulo, I. Santos, M. Ravera,¹ E. Gabano,¹ D. Osella¹


Fig.1

Expecting to obtain a synergistic effect of DNA platination and intercalation on cell cytotoxicity, we have studied Pt(II) complexes anchored by pyrazolyl-diamine ligands bearing anthracene derivatives as DNA-binding groups. These complexes were characterized by common analytical techniques (e.g. ^{195}Pt NMR, Fig. 1) and their cytotoxicity evaluated against cisplatin-sensitive (A2780) and cisplatin-resistant (A2780cisR) human ovarian cancer cell lines (Fig. 2). In order to establish a structure-activity relationship, related complexes with pyrazolyl-alkylamine ligands of different electronic and/or steric properties are currently under study.

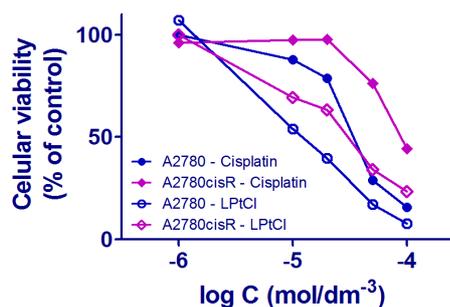


Fig.2

¹ DiSAV, Univ. del Piemonte Orientale "Amedeo Avogadro", Alessandria, Italy

Organometallic Complexes Bearing Bioactive and/or NLS Peptides for Targeted Auger Radiotherapy

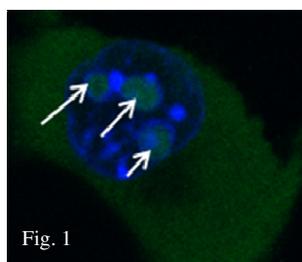
 T. Esteves, A. Paulo, I. Santos, P. Nanda,¹ C. Smith¹


Fig. 1

$^{99m}\text{Tc(I)}$ tricarbyl complexes anchored by pyrazolyl-diamine ligands bearing anthracenyl or acridine orange fragments have the ability to accumulate in the nucleus of tumor cells with a significant DNA intercalation (Fig. 1). Therefore, this type of complexes emerged as promising building blocks to develop site-directed radioprobes for *in vivo* imaging and/or Auger radiotherapy. To achieve such goal, multifunctional complexes bearing bombesin analogs (Fig. 2) and/or NLS (Nuclear Localization Signal) peptides have been isolated and fully characterized. The *in vitro* evaluation of these radioconjugates is underway in order to assess their specificity for tumor cells, ability to accumulate in the nucleus and suitability for Auger targeted radiotherapy.

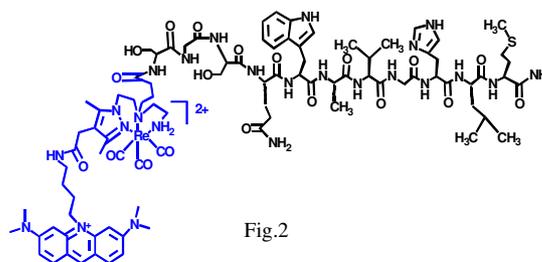
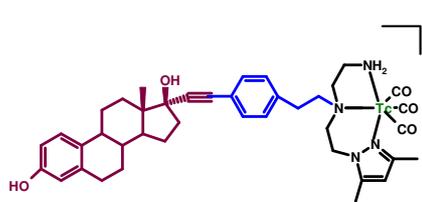


Fig.2

¹ Research Division, Harry S Truman Memorial Veterans' Hospital, Columbia, MO 65201, Missouri, USA

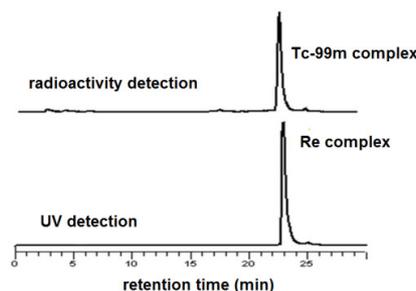
Estradiol-based metal complexes for breast cancer diagnosis.

C. Neto, M. C. Oliveira, L. Gano, F. Marques, I. Santos, T. Thiemann¹.



Following our previous work on the design and evaluation of new probes for targeting estrogen receptor (ER), a novel estradiol derivative labeled with *fac*-[^{99m}Tc(CO)₃] has

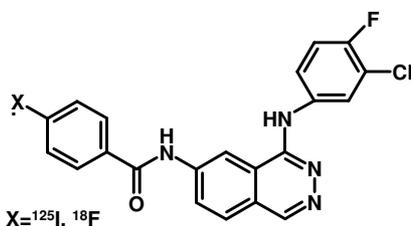
been synthesized and characterized by HPLC comparison with its rhenium surrogate. The ^{99m}Tc(I)-complex, obtained in high radiochemical yield and purity, is stable in total blood, human serum and liver homogenate up to 4h incubation at 37°C. Receptor binding affinity, cell studies and *in vivo* evaluation of this ^{99m}Tc-complex as a biomarker for the molecular imaging of ER expressing tumors are in progress.



¹ Dep. of Chemistry, Fac. of Sciences, United Arab Emirates Univ., United Arab Emirates

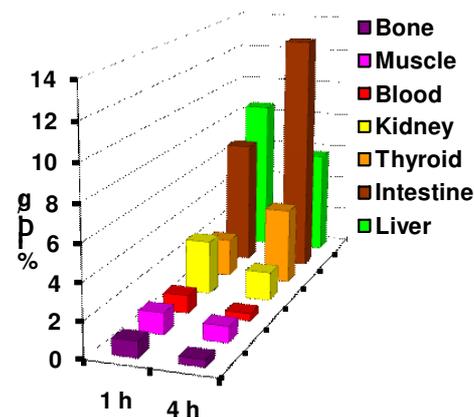
Novel radiolabeled receptor tyrosine kinase inhibitors for *in vivo* targeting of EGFR

C. Neto, M. C. Oliveira, L. Gano, C. Fernandes, I. Santos, M. Kuchar¹, T. Kniess¹



Searching for SPECT/PET radiotracers for *in vivo* imaging of EGFR tumors, novel anilinoquinazoline-based compounds were synthesized, characterized and labeled with ¹²⁵I and ¹⁸F.

The radioiodinated compounds were obtained in high yield and with high specific activity. *In vitro* cellular assays have shown high uptake by A431 cells. For some of the iodinated compounds, biodistribution studies revealed low accumulation in most organs and a small thyroid uptake. The radiofluorination using the [¹⁸F]KF/Kryptofix complex are still under optimization.



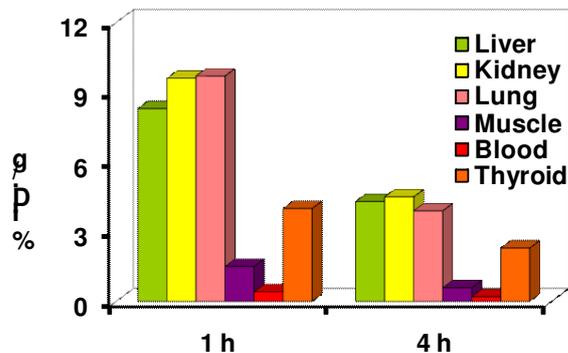
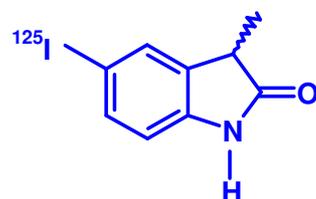
¹ PET-Tracer Group, Institute of Radiopharmacy, FZD, Germany

Radiolabeled VEGFR tyrosine kinase inhibitors as potential SPECT tracers for angiogenesis imaging

M. C. Oliveira, L. Gano, I. Santos, M. Kuchar¹, T. Kniess¹

Oxindole-based molecules, used as lead structures for VEGFR-TK inhibitors, were synthesized, characterized and labeled with ¹²⁵I. The radiocompounds were obtained in high radiochemical yield and their purity (≥ 98%) and identity were confirmed by HPLC. High radiochemical stability in saline solution and in human serum was found up to 24h when kept in the dark at 37°C. The lipophilic

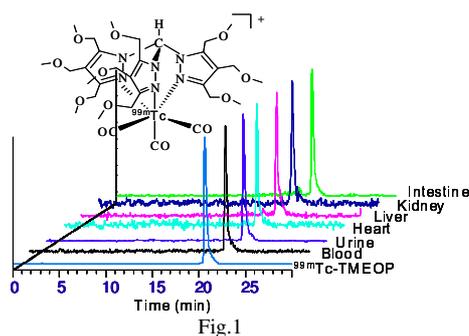
compounds (logP ≈ 2.25) present a low plasma protein binding (5-10%), and biodistribution studies in healthy CD-1 mice indicated a rapid clearance from most organs, including blood, as well as a high *in vivo* stability. Based on these lead compounds further studies are underway.



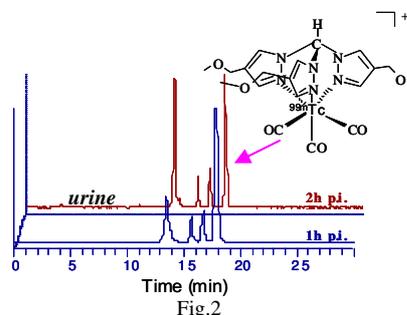
¹ PET-Tracer Group, Institute of Radiopharmacy, FZD, Germany

Metabolic Studies of Ether-Containing Tris(pyrazolyl)methane $^{99m}\text{Tc(I)}$ Complexes

C. Fernandes, L. Gano, A. Paulo, I. Santos

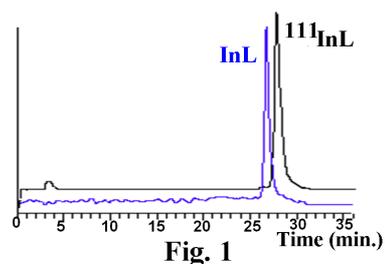


Tris(pyrazolyl)methane $^{99m}\text{Tc(I)}$ -complexes with ether substituents at the 3-, 4- and 5- positions presented a remarkable *in vivo* stability (Fig. 1) and hold potential as myocardial imaging agents. By contrast, complexes with tris(pyrazolyl)methane bearing ether substituents uniquely at the 4-position did not accumulate in the myocardium and showed extensive metabolism (Fig. 2). The *in vivo* behavior of these chelators, together with the possibility of their derivatization through the central carbon atom,

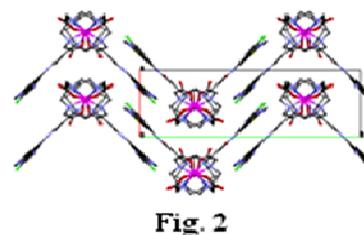


make them promising as bifunctional chelators. As the observed metabolism is expected to improve the biological performance (e.g. blood clearance and overall excretion) bioconjugates with adequate biomolecules are being explored.

Bifunctional DOTA-like chelators for biomolecules radiolabeling

 R. Garcia, F. Silva, S. Lacerda, M. Batista, L. Gano, R. Frago, M. P. C. Campello, P. Fousková¹, E. Toth¹, A. Paulo, I. Santos


Within our interest on macrocyclic complexes of trivalent radiometals for molecular imaging, we have evaluated new $\text{In}/^{111}\text{In}$ complexes of a DOTA-like chelator bearing a quinazoline pendant arm (Figs. 1 and 2) and a ^{67}Ga radiocomplex



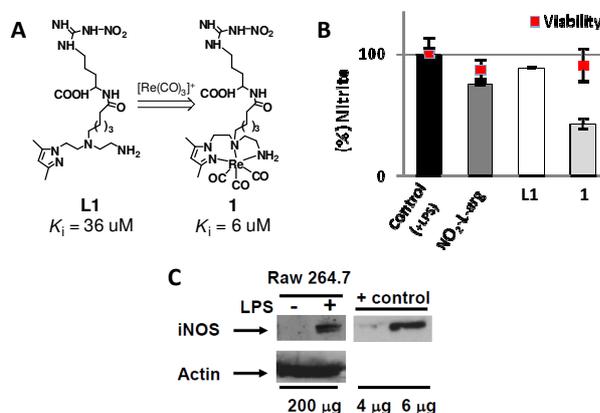
of DO3ASH. ^{111}InL , an hydrophilic neutral radiocomplex, exhibits high stability under physiological conditions, presenting a very low cell internalization level. By contrast, the ^{67}Ga -DO3ASH complex, also prepared in high yield, presents a favourable biological profile, being in progress the functionalization of DO3ASH with clinically relevant biomolecules.

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

Re(I)-complexes as potent inhibitors of iNOS

 B. L. Oliveira, F. Mendes, F. Figueira, J. D. G. Correia, P. D. Raposo, I. Santos, A. Ferreira¹, C. Cordeiro,¹ A. P. Freire¹

Aiming to find new $^{99m}\text{Tc(I)}$ compounds for probing inducible Nitric Oxide Synthase (iNOS) *in vivo*, we synthesized $\text{Re(I)}/^{99m}\text{Tc(I)}$ complexes containing pendant L-arginine analogs. *In vitro* enzymatic studies with iNOS have shown that the affinity to the enzyme of the inhibitor-containing conjugates is improved upon metallation with " $\text{Re}(\text{CO})_3$ " (A). The most remarkable result was obtained with the complex containing $\text{NO}_2\text{-L-arg}$ (1) coupled to the chelator through a 6 carbon linker. This complex presented a considerable inhibitory action ($K_i = 6 \mu\text{M}$), comparable to that of the free inhibitor ($\text{NO}_2\text{-L-arg}$; $K_i = 3 \mu\text{M}$). Complex 1 was also able to inhibit NO production ($\sim 46\%$) in LPS-stimulated RAW 264.7 macrophages (B, C).


¹ Centro de Química e Bioquímica, Dep. de Química e Bioquímica, Fac. de Ciências da Univ. de Lisboa, Portugal.

Novel multi-functional bone-seeking agents

E. Palma, J. D. G. Correia, L. Gano, S. Casimiro¹, L. Costa,¹ I. Santos

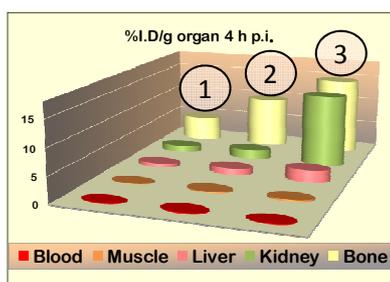


Fig.1

The discovery of a synergistic cytotoxic effect of bisphosphonates combined with antitumoral agents has been well demonstrated in both pre-clinical and clinical setting. This fact prompted us to propose new multifunctional compounds for simultaneous delivery of radiation, chemotherapy and bisphosphonate units to bone metastatic lesions. Therefore, we have introduced novel complexes of the type $fac-[M(CO)_3(k^3-L)]^+$ ($M = Re$ or ^{99m}Tc ; $L = pz$ -pamidronate, **1**; $L = pz$ -alendronate, **2**; $L = pz$ -Glu-alendronate, **3**) and evaluated the biodistribution profile of the ^{99m}Tc complexes in mice (Fig. 1). The compounds were stable at physiological conditions and presented high bone uptake and high target to non target ratio, 4 h p.i. (Fig. 2). Their conjugation to cytotoxic units and evaluation is in progress.

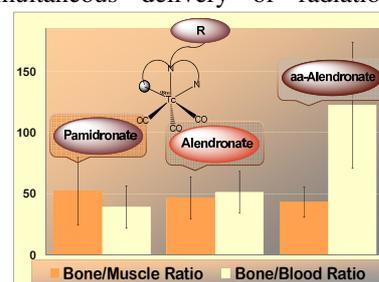


Fig.2

¹ Inst. de Medicina Molecular, Fac. de Medicina, Lisboa, Portugal

New ^{99m}Tc probes for monitoring multidrug resistance: From cardiology to oncology

F. Mendes, L. Gano, C. Fernandes, A. Paulo, I. Santos

Lipophilic cationic myocardial perfusion radiopharmaceuticals have been used for cancer detection and monitoring of tumour Multi Drug Resistance (MDR). The complexes ^{99m}Tc -TMEOP and ^{99m}Tc -DMEOP, promising myocardial SPECT imaging agents, were evaluated for MDR imaging. The uptake and efflux kinetics of ^{99m}Tc -TMEOP were assessed in human cancer cells and in derivative drug-resistant lines, which overexpress Pgp1 (responsible for MDR) (Fig. 1). The uptake of ^{99m}Tc -TMEOP is comparable with ^{99m}Tc -Sestamibi, being greatly reduced in cells over-expressing Pgp (Fig. 2). ^{99m}Tc -TMEOP was further evaluated *in vivo* and it was showed that it could act as a substrate of Pgp.

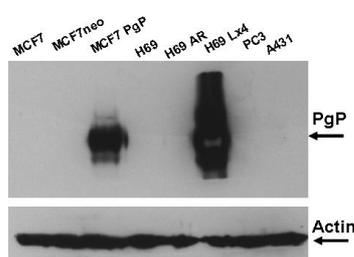


Fig. 1

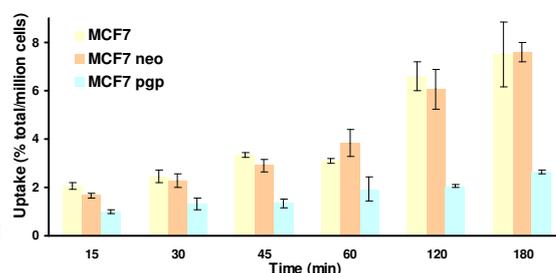
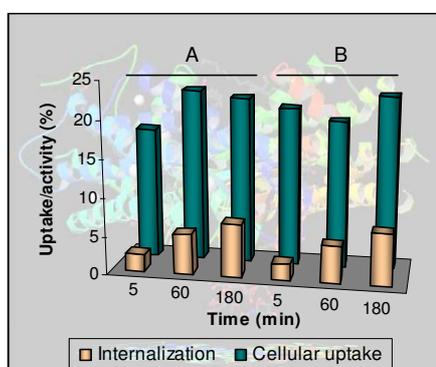


Fig. 2

Melanoma MC1R-targeting with $^{99m}Tc(CO)_3$ -labeled cyclic α -MSH analogs.

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



Following our work on MC1R-targeting, with cyclic radiolabeled α -melanocyte-stimulating hormone (α -MSH) analogs for melanoma imaging, two new cyclic compounds were synthesized and conjugated to a pyrazolyl-based bifunctional chelator (pz). The binding affinity of the peptide-pz conjugates pz - β Ala-Nle- c [Asp-His-D-Nal(2')-Arg-Trp-Lys]-NH₂ ($IC_{50} = 0.3$ nM) and c [CO- p -C₆H₄-CO-His-D-Nal(2')-Arg-Trp-Lys]Lys(pz)-NH₂ ($IC_{50} = 11.9$ μ M) to the MC1R has been determined by competitive binding assays using ^{125}I -(Tyr²)-NDP, and a significant loss of affinity for the second conjugate was found. Both compounds were labeled with fac - $^{99m}Tc(CO)_3^+$ and the radiocomplexes (**A** and **B**) evaluated *in vitro* and *in vivo*. For both, a rapid and significant cellular uptake was found (Fig. 1), but their tumor uptake was negligible in melanoma-bearing mice.

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. After a lengthy bureaucratic process the contract for a new He liquefier, with expanded capacity, was signed and it is expected to be commissioned in May 2010.

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 as a source of important discoveries as model quasi-1D CDW systems. Recent achievements include the analysis of the angular dependent magnetoresistance of the Au compound under pressure in terms of the Fermi surface geometry. The Mössbauer spectroscopy was successfully applied to the study of the λ -(BETS)₂FeClO₄ metal to insulator and AFM transition.

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 multifunctional 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.

The application of Mössbauer spectroscopy to different fields was pursued with large emphasis in the development of novel ferrite with mixed ionic-electronic conductivity for applications in alternative energy sources

A significant output of the group continued 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.

Research Team

Researchers

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Multifunctional conducting materials with Spin Cross Over behaviour

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

Objectives

The main goal of this project is the development of new multifunctional hybrid molecular materials that display the coexistence or synergism of spin crossover (SCO) with other properties, such as magnetism or electrical conductivity.

Results

We focused our work on hybrid materials based on cationic Fe(III) SCO complexes with a FeN_4O_2 coordination and, in order to achieve electrical conductivity or magnetism, either nickel bisdithiolate anionic complexes, $[\text{Ni}(\text{dmit})_2]^{z-}$ ($0 < z \leq 1$) or $[\text{Ni}(\alpha\text{-tpdt})_2]$. In the Fe(III) SCO complexes a variety of ligands, mainly derivatives of the tridentate qsal or hexadentate sal_2 -trien were used. These include ligands with extended aromatic fragments and a variety of substituents (Cl, Br, NO_2 , OH, OMe). Different new salts with smaller anions (Cl, SCN, NO_3 , BF_4 , ClO_4 , PF_6 , BPh_4), were also prepared.

The crystal structures of the compounds with Cl or Br substituents consist in alternating layers of cations and anions, where the cationic layers are based on stacks with sizable intrachain π - π interactions, through the aromatic ligands. [1-5].

The compounds with aromatic ligands lead to sharper SCO transitions. Furthermore in most cases the SCO processes occurs near room temperature (RT), which is favourable to possible applications of these materials.

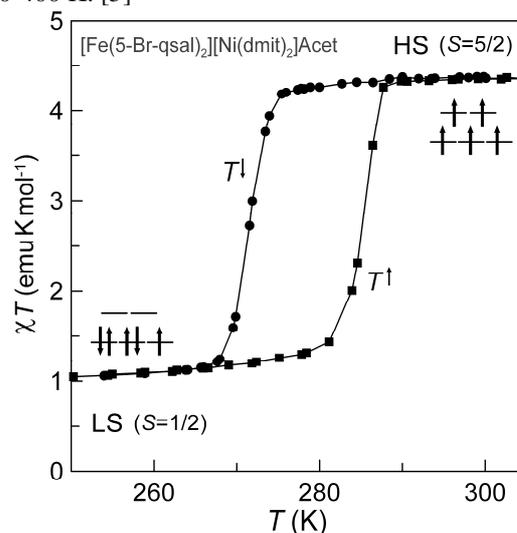
$[\text{Fe}(\text{Cl-qsal})_2][\text{Ni}(\alpha\text{-tpdt})_2] \cdot \text{MeCN}$ shows a SCO process at RT and a FM spin-glass behavior at 8 K, assigned to the cationic and anionic networks respectively [2]. The related compound obtained with the Br-qsal ligand, showed also a spin transition but no magnetic ordering process was observed at low temperature.

With $[\text{Ni}(\text{dmit})_2]^-$, it was possible to prepare a variety of new compounds, often with solvent in the crystal structure as $[\text{Fe}(x\text{-qsal})_2][\text{Ni}(\text{dmit})_2] \cdot 0.5\text{H}_2\text{O} \cdot 0.5\text{MeCN}$ [$\text{Fe}(\text{Cl-qsal})_2][\text{Ni}(\text{dmit})_2] \cdot x\text{MeCN}$ ($x=0, 1, 2$), $[\text{Fe}(\text{Br-qsal})_2][\text{Ni}(\text{dmit})_2] \cdot \text{Solv}$ (Solv = DCM, Acet) [3,4] which induces drastic changes in the SCO processes.

$[\text{Fe}(\text{Br-qsal})_2][\text{Ni}(\text{dmit})_2] \cdot \text{Acet}$ showed a 1st order SCO process with hysteresis of ~13 K ($T_{1/2} \uparrow = 285$ K, $T_{1/2} \downarrow = 272$ K) and it is a semiconductor, ($\sigma_{\text{RT}} \sim 1 \times 10^{-5}$ S/cm, $E_a \sim 340$ meV), with the SCO process inducing an effective modulation of electrical conductivity, with higher conductivity in the HS state [3,4].

The compounds based on partially oxidized anions ($[\text{Ni}(\text{dmit})_2]^{z-}$, $0 < z < 1$), showed a significant enhancement of the electrical conductivity, and for $[\text{Fe}(\text{Cl-qsal})_2][\text{Ni}(\text{dmit})_2]_{3.3}(\text{CH}_3)_2\text{CO}$ $\sigma_{\text{RT}} \sim 0.2$ S/cm ($E_a \sim 100$ meV), with a modulation in $\sigma(T)$ with hysteresis below 265 K [3,4].

In compounds based on the sal_2 -trien ligand the work was devoted to the "nst" ligand, where the aromaticity was extended. The crystal structures of these compounds are similar to the qsal based compounds. $[\text{Fe}(\text{nst})\text{SCN}]$ exhibits a two step spin transition, with a sharp at $T_{1/2} = 140$ K and a gradual one at $T_{1/2} \sim 260$ K. $[\text{Fe}(\text{nst})] \text{BPh}_4$ shows a gradual process at $T_{1/2} \sim 350$ K. The magnetic behavior of these salts is sensitive to the incorporation of solvent molecules in the lattice, exhibiting gradual SCO processes at $T_{1/2} \sim 350$ -400 K. [5]



$[\text{Fe}(\text{nst})][\text{Ni}(\text{dmit})_2]$ and $[\text{Fe}(\text{nst})][\text{Ni}(\text{dmit})_2]_3$ were found in the HS state without SCO. The second compound with a partially oxidized anion is a semiconductor ($\sigma_{\text{RT}} = 0.74$ S/cm, $E_a = 170$ meV) [5]. Solutions of this cation revealed thermochromic effects, related with the SCO process [5].

Published or in press work (selected)

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A.I.S. Neves, J.C. Dias, D. Belo, B.C.J. Vieira, L.C.J. Pereira, I.C. Santos, J.C. Waerenborgh, M. Almeida, D. Belo, V. Gama, *Cryst. Eng. Comm.* **11**, 2160-2168 (2009).

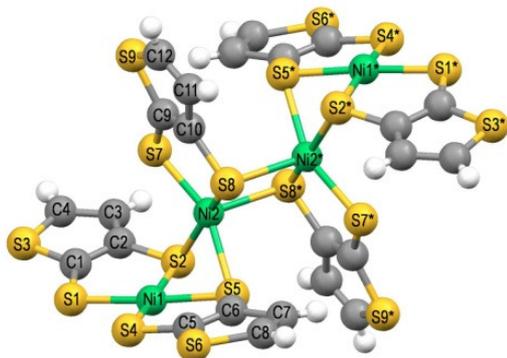
J.C. Dias, J.C. Nunes, B. Vieira, I.C. Santos, L.C.J. Pereira, J.C. Waerenborgh, V. Gama, 8th Inorganic Chemistry Conference, Curia, Portugal, 16-17 October 2009.

J.C. Dias, J.C. Nunes, B. Vieira, I.C. Santos, L.C.J. Pereira, J.C. Waerenborgh, V. Gama, European Conference on Molecular Magnetism, ECMM2009, Wroclaw, Poland, 4-7 October 2009.

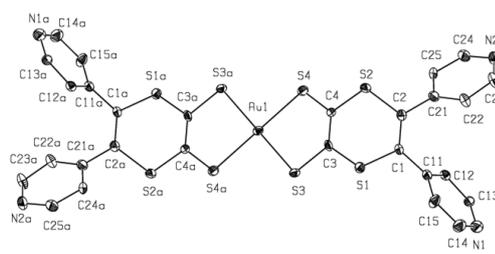
B.J.C. Vieira, L.C.J. Pereira, I.C. Santos, V. Gama, 8th Inorganic Chemistry Conference, Curia, Portugal, 16-17 October 2009.

[Ni₄(α-tpdt)₆]²⁻: a linear mixed valence Ni dithiolene (Ni₄-S₁₂) clusterA.I.S. Neves, I.C. Santos, D. Belo, M. Almeida, E. Ruiz¹, C. Rovira²

Transition metal dithiolene (dt) complexes, M(dt)_n, are known to display a variety of coordination geometries depending on the metal, but metal clusters are rare. With the [Ni(α-tpdt)₂]⁻ paramagnetic anion (tpdt = 2,3-thiophenedithiolate) that has been intensively used by us during last years we could isolate and characterise as single crystal the salt [K(15-crown-5)₂][Ni₄(α-tpdt)₆] which is the first example of a linear Ni₄-S₁₂ cluster, a molecular geometry unprecedented among metal-dithiolenes. This cluster presents relatively short Ni-Ni distances and it results from an unstable equilibrium between regular square planar monoanionic and dianionic bi-dithiolenes. The DFT calculations show that in spite the short distances (2.756 and 3.142 Å) there is no direct Ni-Ni interaction, the outer nickel atoms being Ni^{II} while the central ones Ni^{III} in a class 1 mixed-valence complex according to the Robin-Day classification.

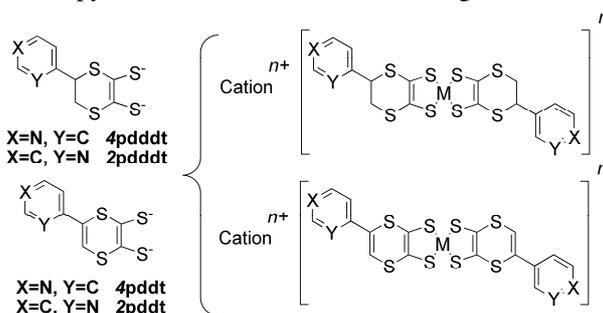
¹ Dept. Química Inorgànica, Univ. de Barcelona, Diagonal 647, Barcelona E-08028 Spain..² Inst. de Ciència des Materials de Barcelona (CSIC), Campus Univ. de Bellaterra, E-08193 Cerdanyola, Spain.**Pyridine-functionalized TTF derivatives and their Dithiolene Complexes**S. Rabaça, S. Dias, A. Cerdeira, S. Oliveira, I. C. Santos, M. Almeida, A.C. Brooks¹, J.D. Wallis¹,

Recently some TTF derivatives substituted with functional groups that can coordinate to transition metals, especially containing N coordinating atoms and their complexes have been described. This synthetic effort has been also extended to the preparation of similarly substituted dithiolene transition metal complexes, which can be seen as the inorganic analogues of TTF where the central C=C bond is replaced by a transition metal. Under this project we focussed our attention on pyridine-substitution in the fully unsaturated version of BEDT-TTF, bis(vinylenedithio)tetrathiafulvalene, since there is a π system linking the metal ion binding site and the electroactive organosulfur system. New pyridine-substituted BEDT-TTF, namely the tetra(pyridyl) substituted symmetrical donors, the di(pyridyl) substituted unsymmetrical and their Ni and Au dithiolene complexes have been synthesized and characterized. These molecules are being explored in molecular materials, and are expected to lead to stronger synergy between electrical and magnetic properties.

¹ School of Science and Technology, Nottingham Trent Univ., Nottingham NG11 8NS, UK.**New Asymmetrically Substituted Dithiolene Complexes with Secondary Coordination Ability**

S. Rabaça, S. Oliveira, S. Dias, I. C. Santos, R.T. Henriques, M. Almeida

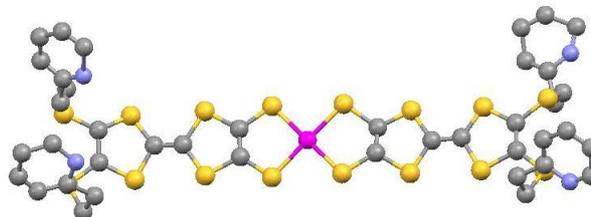
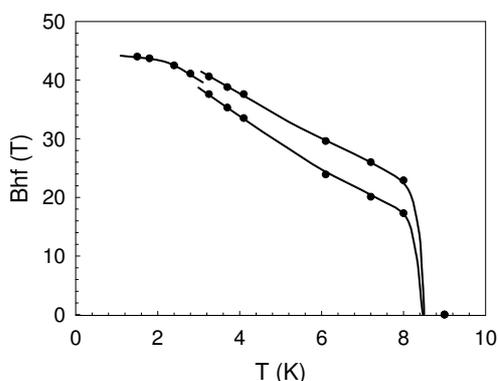
Transition metal bisdithiolene complexes substituted with pyridine groups are excellent candidates to be used as bridging coordinating centers and in particular the asymmetrically substituted ones. Extended and sulphur-rich ligands have already been reported with the introduction of a pyridine functionalized dithiine ring fused to the dithiolene group. However the corresponding asymmetrically substituted dithiolene complexes have been unexplored. Our group have already develop a significant synthetic effort with metal transition dithiolene complexes based on divalent ligands containing both sulphur and nitrogen coordinating atoms within pyridine groups and within this project developed the synthesis of a variety of new asymmetrically substituted dithiolene complexes which have been isolated with different cations; [M(L)₂]ⁿ⁺ L=2pdddt, 4pdddt, 2pddt, 4pddt; M = Ni, Au and Cu.



Bisdithiolene complexes based on an extended ligand with TTF and pyridine moieties

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

Square planar neutral complexes with extended dithiolene ligands have attracted increasing interest due to their extended π -conjugation system and possibility of displaying high electrical conductivity. In these metal complexes with extended TTF-dithiolene ligands, the side groups on the TTF moiety have been so far restricted to alkyl groups or conjugated rings. Another recent trend in dithiolene and TTF chemistry has been the incorporation of functional groups containing N atoms able to coordinate transition metals, in order to explore new coordination structures relevant in the field of magnetic conductors or magnetic coordination polymers. With this work it was developed the synthesis which enabled the preparation and characterization of the first pyridine substituted extended dithiolene ligand with TTF moieties and the corresponding anionic Au dithiolene complex $[n\text{Bu}_4\text{N}][\text{Au}(\text{pesdt})_2]$.

**Mössbauer spectroscopy study of the magnetic transition in λ -(BETS) $_2$ FeCl $_4$** J. C. Waerenborgh, S. Rabaça, M. Almeida, E. B. Lopes, A. Kobayashi¹, B. Zhou¹, J.S. Brooks²

The compound λ -(BETS) $_2$ FeCl $_4$ has been regarded as an effective demonstration of the interaction of π conduction electron and d -electron localized magnetic moment systems in molecular crystalline materials, where antiferromagnetic insulating and magnetic field induced superconducting states can be realized. The 8.3 K metal-insulator (M-I) and antiferromagnetic (AF) transition in this compound has been thought to be cooperative, involving both the itinerant π -electron and localized d -electron spins with AF order appearing in both systems simultaneously. However, recent specific heat data has indicated otherwise [Akiba *et al.*, J. Phys. Soc. Japan 78 (2009) 033601]; although the π -electron system orders antiferromagnetically and produces a M-I transition, a "mysterious" paramagnetic d -electron state remains. ^{57}Fe

Mössbauer measurements support the paramagnetic model, provided the d -electron spins remain in a fast relaxation state below the transition, but they show an additional transition at 3 K. From the measured hyperfine fields, the temperature dependence of the π - d electron exchange field was also determined.

¹ Dept. of Chemistry, College of Humanities and Sciences, Nihon Univ., Sakurajosui 3-25-40, Setagaya-Ku, Tokyo 156-8550, Japan.² Dept. of Physics and National High Magnetic Field Laboratory, Florida State Univ., Tallahassee, FL 32310, USA.**Two-Chain Compounds under High Magnetic Field**M. Almeida, J.C. Dias, R.T. Henriques, M. Matos¹, J. S. Brooks², E. S. Choi,² D. Graf²,

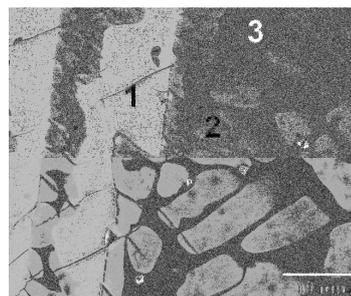
(Perylene) $_2$ M(mnt) $_2$ compounds with M=Au, Pt, ... initially reported by our group more than 20 year ago still offer a unique chance to investigate the coupling between two types of chains (conducting and magnetic) in the same solid and to test the theoretical predictions for the behaviour of quasi 1D CDW systems under large magnetic fields. In these compounds it was recently discovered that under moderate pressures (4-6 kBar) the CDW state is suppressed and a metallic regime is recovered at low temperatures, showing quantum oscillations previously interpreted as due to Stark interference between orbits in closely spaced open Fermi surfaces. The analysis of the complex behaviour of the angular dependent magnetoresistance of (Per) $_2$ [Au(mnt) $_2$] under pressure was completed in 2009. By a careful analysis of both magnetic field and orientation dependence of the magnetoresistance it was possible to independently identify the orbital and geometrical effects, the so called Lebedev magic angles associated with the crystallographic lattice plane parameters. The orbital effects were surprisingly found in excellent agreement with the results of the Fermi surface calculations based on room temperature ambient pressure structure, demonstrating that the suppression of the CDW recovers a metallic state comparable to that at high temperature and ambient pressure. These results could be also compared with previous studies of the well-known Bechgaard salts, emphasising the more extreme 1D character of the perylene compounds.

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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. Verbovitsky, O. Sologub, P.A. Carvalho¹, A. Ferro¹, 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. In 2009 the study of the U-Fe-B system was continued. The solidification paths for UFe₄B, UFe₃B₂ and UFe₄B, situated along the U:(Fe,B)=1:5 line, were determined. All compounds melt incongruently, being formed by peritectic reactions, and a cascade of peritectic reactions exists along this line. The phase equilibria in the Ce-Au-Sb system was also investigated in the 0-50 at.% Ce concentration range at 870 K. Five ternary compounds were found to exist: CeAu_{1-x}Sb₂, Ce₃Au₃Sb₄, Ce(Au_{1-x}Sb_x)₂, CeAuSb and the new Ce₃Au₂Sb₃. The phase relations in the ternary system Yb-Zn-In have been established for the partial isothermal section in the 0-33.3 at.% Yb concentration range at 400°C. This Yb-Zn-In partial section is characterized by the presence of three extended homogeneity ranges, In solubility in Yb₁₃Zn₅₈ and YbZn₂, and Zn solubility in YbIn₂, and the existence of one ternary compound, YbZn_{1-x}In_{1+x}, x~0.3.



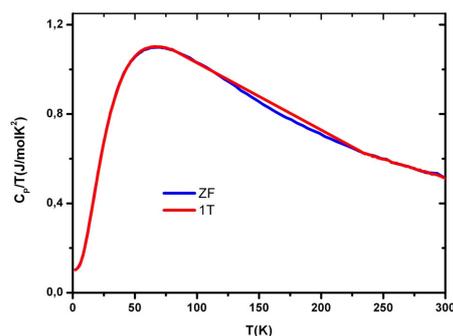
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Magnetic and strongly correlated electron behaviour in intermetallics

A.P. Gonçalves, J.C. Waerenborgh, L.C.J. Pereira, E.B. Lopes, M. Dias, M.S. Henriques, O. Sologub, S. Sério, P. Gaczynski, M. Almeida, L. Havela¹, O. Tougaard², H. Noël², M.M. Cruz³

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. The most significant results obtained during 2009 concern the study of the U₂Fe₃Ge compound, discovered last year U₉Fe₇Ge₂₄. U₂Fe₃Ge is one of the few exceptions to the Hill's rule. Specific heat measurements don't show any prominent anomaly close to the magnetic transition, pointing to an itinerant magnetism, and the Sommerfeld coefficient was found to be $\gamma \sim 46$ mJmol⁻¹ U K⁻² at zero magnetic field. The new U₉Fe₇Ge₂₄ compound was found to crystallize in a new structure type, with U-U closest distances larger than 4Å. No magnetic transition is observed down to 2K, probably due to a sizable hybridization between the U *f*-electrons and the *p*-electrons from Ge. This compound has a Sommerfeld coefficient of $\gamma \sim 66$ mJmol⁻¹ K⁻², being a moderate heavy fermion.



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New materials for thermoelectric applications

E.B. Lopes, A.P. Gonçalves, E. Alleno¹, O. Rouleau¹, C. Godart¹

The identification, synthesis and characterization of new thermoelectric systems with high figure of merit are of fundamental importance to their potential application in environment friendly energy sources. During 2009 we focused our attention in the family of electrically conducting glasses with general compositions in the range Cu_{x+y}Ge_{20-x}Te_{80-y} (0 ≤ x ≤ 20; 0 ≤ y ≤ 10). The samples have been prepared by melt spinning and used to test the possibility of obtaining conducting glasses for thermoelectric applications. These amorphous materials were found to have in general very small thermal conductivity and a large Seebeck coefficient that is relatively insensitive to changes in composition. However as the Cu content is increased they become progressively more conducting. ZT values of the order of 0.2 were obtained, indicating that these materials are potential candidates for high performance thermoelectric materials.

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Materials for solid oxide fuel cells and dense ceramic membranes

J C Waerenborgh, E. Tsipis, V. V. Kharton¹, A. Yaremchenko¹, E.N. Naumovich¹, M. V. Patrakeev²

Development of novel materials based on iron-containing oxide phases with perovskite or perovskite-derived structures, with mixed oxygen-ionic and electronic conductivity and high oxygen permeability, attract significant attention for energy-related electrochemical technologies, such as electrodes of solid oxide fuel cells (SOFCs) and ceramic membranes for conversion of natural gas and biogas. Information on the point-defect interaction mechanisms in these materials with multiple oxygen sublattices is still scarce. It is however necessary for the analysis and prediction of the anion migration parameters, chemical and thermal expansion, and defect ordering phenomena. In 2009, in addition to the preparation of new compounds, atomistic modeling techniques, often used to probe defect formation and reactions in oxide materials, were applied to investigate the p-type electronic charge carriers in the RP ferrites. These atomistic computer simulations together with ⁵⁷Fe transmission Mössbauer spectroscopy analysis of Sr₃LaFe_{3-x}Al_xO_{10-δ} (x = 0.3 – 0.6, δ = 0 – 0.28) provided evidence that the introduction of point defects, such as Al³⁺ and oxygen vacancies, into the central perovskite layers of n = 3 RP ferrite structure may lead to a complete reconfiguration of the electronic sublattice. Namely, the local lattice distortions near Al³⁺ and the repulsion between the positively charged vacancies and holes, induce massive hole displacement out of the energetically-favorable equatorial planes to the edge octahedra, accompanied with progressive localization. Increasing oxygen deficiency up to δ ≈ 1 results in the formation of relatively stable aluminum-oxygen tetrahedra in the central perovskite-type blocks. These phenomena are expected to increase two-dimensional character of the ionic and electronic conduction in the n = 3 RP ferrites, and to decrease their stability.

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Mössbauer spectroscopy in Materials Science

J C Waerenborgh, E. Tsipis

A Mössbauer spectroscopy laboratory has been developed in ITN for more than 30 years in order to support local research projects. In 2009 the researcher responsible for the facility and one post-doc assured the maintenance and running of the equipment. Presently the expertise developed in ITN assists other national or foreign research institutions in the frame of joint research projects. Several *PhD* or *MSc* students used the facility. Work performed include the characterization of the Fe-containing phases in soils and sediments of a coastal lagoon in a semi-arid area, studies on clay minerals and iron oxides as fingerprints of fire effects in limestone monuments, on molecular conductors, on multifunctional magnetic materials obtained by insertion of a spin crossover Fe^{III} complex into bimetallic oxalate-based ferromagnets, on UCu_xFe_{5-x}Al₇ intermetallics with heavy-fermion-like behaviour and on YFe_xAl_{12-x} (4 ≤ x ≤ 5) where uncorrelated iron-rich nanoclusters with short-range ferromagnetic-like order were confirmed above T_c, in collaboration, respectively, with the Petrology and Geochemical Center of the Technical Univ. Lisbon; Dept. of Physics, Florida State University, USA; Univ. of Valencia, Spain; Lab. Chim. du Solide et de Matériaux, Univ. Rennes, France; Charles University, Prague, Czech Republic; W. Trzebiatowski Inst. of Low Temp. and Struct. Res., Wrocław, Poland.

High magnetic field facility

A. Casaca¹, E. B. Lopes, M. Almeida, V. Laukhin², J. S. Brooks³

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. During 2009, there was a focus on the ³He insert used to pursue the research activities in different magnetotransport characterisation projects.

1. Single component molecular metals Au(α-tpdt)₂ processed as thin films on polymeric surfaces and as a bulk powder (compressed pellet). Both type of samples show at very low field a peculiar behaviour which could be due to a reentrant superconducting phase (partial). The magnetoresistance below 8K is relatively large and follows the behaviour of a paramagnetic conductor. This comparison allowed to conclude that the complex magnetotransport properties observed on the processed thin films reflect in fact the intrinsic properties of the single component molecular metal Au(α-tpdt)₂.
2. λ-(BETS)₂⁵⁷FeCl₄ to confirm the 8K antiferromagnetic and metal-insulator transitions.
3. Several intermetallic compounds heavy fermion candidates like the U Laves phase U₂Fe₃Ge and U₉Fe₇Ge₂₄ which is a moderate heavy fermion.

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