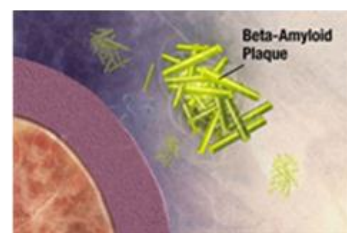
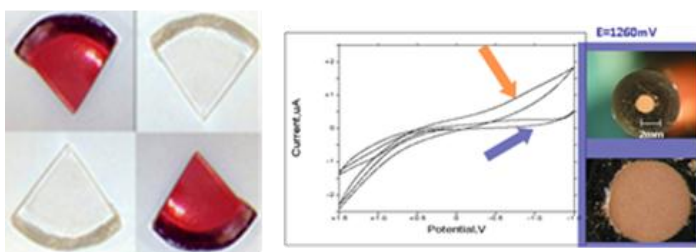


Chemical and Radiopharmaceutical Sciences Unit



Chemical and Radiopharmaceutical Sciences

Joaquim Marçalo and M. Isabel Prudêncio

The Chemical and Radiopharmaceutical Sciences Unit (CRSU) reinforced expertise in the synthesis and characterization of inactive and radioactive compounds with relevance in Health, Materials and Nuclear Sciences and Catalysis, and in the implementation and application of nuclear-based and related techniques in Cultural Heritage and Environmental and Earth Sciences. The research activities were performed by five research groups:

Applied Geochemistry & Luminescence on Cultural Heritage (GeoLuC) – dedicated to interdisciplinary studies of archaeological and geological contexts and materials, using nuclear methods in cultural and natural heritage. During 2010 a multidisciplinary project was initiated, on the diagnosis of pathologies and degradation mechanisms, and conservation strategies for Portuguese Cultural Heritage. Detailed geochemical studies of the lanthanides and actinides in superficial environments proceeded. Research activity in retrospective dosimetry is being developed through EURADOS. Collaboration for joint research proposals in luminescence processes has been established with CUDaM, UNIMIB, Italy.

Environmental and Analytical Chemistry – devoted to elemental and isotopic analysis applied to environmental geochemistry and oceanographic, isotope hydrology and archaeometallurgical research. Research focused in sedimentary geochemistry and radiocarbon dating aiming the palaeoenvironmental reconstruction on the Portuguese coastal area. Isotope hydrology investigations were carried out in different environments. During 2010 a new large research project was initiated aiming at the comprehension of the Early Metallurgy in the Portuguese Territory.

Inorganic and Organometallic Chemistry – committed to the synthesis of new actinide and lanthanide compounds and the study of their chemical properties and applications. The investigation of the partial oxidation of methane (as an important C1

feedstock) using lanthanide and actinide catalysts, obtained by intermetallic, sol – gel and molten salt routes, was expanded. A new project within ACTINET-I3, in Ln/An separation chemistry, was initiated in 2010.

Radiopharmaceutical Sciences – devoted to the development and implementation of 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. Worth of note in 2010 is a relevant publication describing a wealth of interesting structural and physicochemical properties of an entire series of lanthanide macrocyclic complexes. Such results helped to interpret kinetic data along the lanthanide series, an important issue for medical applications.

Solid State – dedicated to multidisciplinary studies of solid state science on selected new materials with unconventional electrical and magnetic properties. The replacement process of the old He liquefier by a new one, with expanded capacity and enhanced efficiency, was successfully completed in 2010. The combination of the preparative chemistry expertise with the specialised solid state physics techniques was applied in strategic selected type of materials, namely molecule based conducting and magnetic materials, and intermetallic compounds with *f*-elements.

Education and training at Undergraduate, MSc, PhD and Post-doctoral levels is one major achievement at CRSU. A strong participation of researchers of the Unit in advanced education activities in collaboration with universities is being done. National and international projects, many with the scientific coordination of the Unit, and mainly financed by the FCT, the EC and a pharmaceutical corporation proceeded. Additional funding was obtained through protocols, contracts and services with private and public institutions.

Staff

Researchers

M. ALMEIDA, Coord. (Agreg.)
I. SANTOS, Princ. (Agreg.)
M.I. PRUDÊNCIO, Princ. (Agreg.)
A. PAULO, Princ.
A.M.M. SOARES, Princ.
A.P. GONÇALVES, Princ.
J.C. WAERENBORGH, Princ.
J.D.G. CORREIA, Princ.
J. MARÇALO, Princ.
M.F. ARAÚJO, Princ.
V. GAMA, Princ.
C. BURBIDGE, Aux. (Contract)
C. FERNANDES, Aux.
C.C.L. PEREIRA, Aux. (Contract)
D. BELO, Aux. (Contract)

E.B. LOPES, Aux.
F. MARQUES, Aux.
F. MENDES, Aux. (Contract)
G. MORAIS, Aux. (Contract)
I.C. SANTOS, Aux.
J.B. BRANCO, Aux.
J.M. CARRETAS, Aux.
J.M. DE LA ROSA, Aux. (Contract)
J.P. LEAL, Aux.
L. MARIA, Aux. (Contract)
L.C.J. PEREIRA, Aux.
L.GANO, Aux.
M.C. OLIVEIRA, Aux.
M.I. DIAS, Aux. (Invited)
M.P.C. CAMPELLO, Aux.
P. CARREIRA, Aux.
P. RAPOSINHO, Aux.

S. RABAÇA, Aux. (Contract)
T. ALMEIDA GASCHE, Aux.

Admin. & Techn. Personnel

A. CRUZ
A. RODRIGUES
A.J. AMARO
A.J. SOARES
D. ANDRÉ
D. FRANCO
E. CORREIA
G. CARDOSO
I. FRAZÃO
L. FERNANDES
M. CORREIA
M.F. MARQUES
P. VALÉRIO
P.M. REIS
R. MARQUES

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 and geo-environmental contexts**, with a view to their characterization and/or conservation, through the **application of nuclear methods**.

The GeoLuC group has an interdisciplinary approach to the study of archaeological and geological contexts and materials, as well as of museum artworks. Provenance, production technology and chronology are the main goals of the archaeometric research. During 2010 an innovative multidisciplinary project was initiated, on the diagnosis of pathologies and mechanisms of degradation, and conservation strategies for Portuguese Cultural Heritage, using non-destructive techniques. Detailed geochemical studies for the understanding of the lanthanides, actinides and other trace element behaviour in superficial environments are another major research domain of the GeoLuC group. Geochemistry and luminescence were applied for the reconstruction of coastal palaeoenvironments of dune systems from Iberian Peninsula and Africa.

The main research activities of GeoLuC group during 2010 are summarised according to the following themes:

- kGy dosimetry using OSL and TTOSL signals from quartz.
- RADIART - Diagnosis, decontamination and conservation of cultural heritage: neutrons and ionizing radiation in artwork.
- Dating, authenticity, materials and pigments: Portuguese Faience and Chinese Porcelain produced for the Portuguese market (XVI to XVIII centuries).
- Application of luminescence dating to the understanding of Iberian cultural evolution.
- 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.
- Geochemistry, mineralogy and radiometric measurements of superficial environments in the Iberian Peninsula and Cape Verde islands - distinguishing geogenic and anthropogenic contributions.
- Nuclear methods for the characterization and preservation of cultural and natural heritage.

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 palaeoenvironmental 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 and luminescence analyses are an ongoing task, having the potential to obtain more detailed insights into the elemental composition and chronology/dosimetry of different types of materials 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 and post-doctoral programmes. 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 the participation and organization of national and international conferences.

Research Team

Researchers

M. I. PRUDÊNCIO, Princ. (Agreg.), Group Leader
M. I. DIAS, Invited Aux.
C. BURBIDGE, Aux. (Contract)
M. J. TRINDADE, Post-Doc, FCT grant

Students

A. JORGE, PhD student, U. Sheffield grant
S. VILELA, MSc student
J. MUNGUR-MEDHI, MSc student
A. L. RODRIGUES, FCT grant

Technical Personnel

L. FERNANDES
R. MARQUES, MSc
D. FRANCO
G. CARDOSO, MSc

Collaborators

M. A. GOUVEIA, Princ. (Retired)

kGy dosimetry using OSL and TTOSL signals from quartz

Burbidge, C.I., Cabo Verde, S.I., Fernandes, A.C.,

Prudêncio, M.I., Botelho, M.L., Dias, M.I., Marques, J.G., Cardoso, G.

Luminescence signals have been identified that permit the retrospective evaluation of absorbed doses in quartz up to tens of kGy: an order of magnitude beyond the maximum conventionally measured with this ubiquitous natural dosimeter. This work is part of a new project investigating the use of neutrons and ionizing radiation for diagnosis, decontamination and conservation of heritage materials (PTDC/HIS-HEC/101756/2008-RADIART).

Subsamples from historic ceramic tiles have been ^{60}Co gamma irradiated for the purposes of biological decontamination at CHIP (ITN), accompanied by Perspex dosimeters and quartz from a geological sample known to exhibit thermally-transferred optically-stimulated luminescence (TTOSL). OSL and TTOSL signals from quartz grains were measured (Fig. 1; -L1) using different preheats, and following re-irradiation with a $^{90}\text{Sr}/^{90}\text{Y}$ beta source at GeoLuC (-L2). OSL from 10 Gy test doses was measured following each high dose cycle (T1, T2). Reduction of the dynamic range of signal levels using linear modulation (LMOSL) was novelly applied for the avoidance of detector saturation effects without reducing detector sensitivity. Fits to gamma responses (Fig. 2) were interpolated through those to beta responses, to evaluate the effectiveness of retrospective dose evaluation for different signal integrals, preheat combinations, and dose intervals. OSL signals evident at short stimulation times, conventionally used for dosimetry and dating, exhibited inconsistent behaviour at high doses. High preheats reduced the significance of rapidly saturating and/or negative components in dose response (Fig. 2), and preferentially removed OSL and TTOSL signals evident at longer stimulation times (Fig. 1). Remaining signals yielded more accurate retrospective dose determinations. TTOSL signals evident at short stimulation times increased proportionally to dose between 1 and 30 kGy when a 300 °C preheat was applied (Fig. 2, arrow). Doses were underestimated by 13-20%: refinement of the measurement protocol should improve accuracy, but results already enable general assessment of radiation exposure.

This work has identified elements of OSL and TTOSL signals that can be used; following severe preheats, to retrospectively evaluate doses of tens of kGy.

GeoLuC is developing research in Retrospective Dosimetry with the European Radiation Dosimetry Group and with UPSR, ITN. Burbidge became a full EURADOS member in 2010: Working Group 10 is supporting attendance at meetings to develop the knowledge and contacts of GeoLuC. GeoLuC is contributing knowledge of luminescence dating and its research community. This has contributed to an international survey designed to stimulate knowledge exchange between physical and biological dosimetry practitioners.

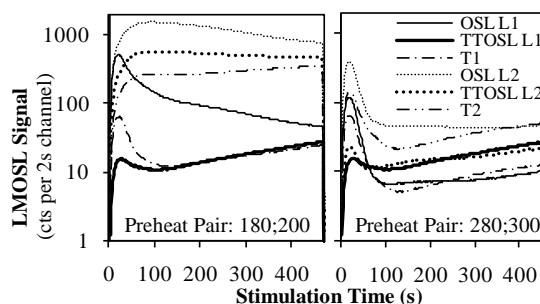


Fig. 1. LMOSL signals from quartz, for weak and severe preheats applied to -L1 and -L2 measurements, following doses of 1 kGy.

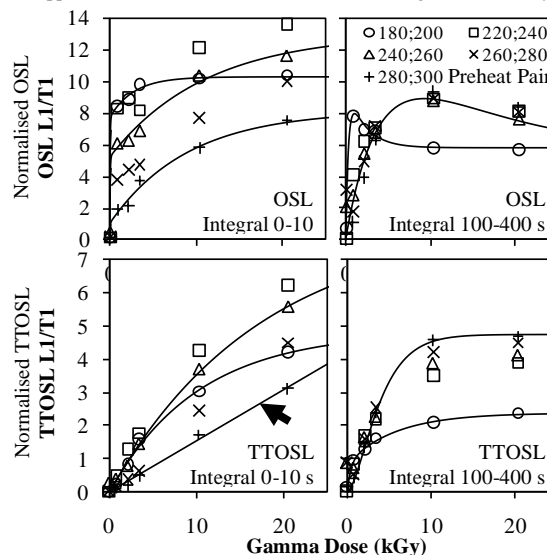


Fig. 2. Dose response characteristics of different OSL and TTOSL signal intervals for different preheats (OSL; TTOSL in °C/30 s).

Published work

Burbidge, C.I., Cabo Verde, S.I., Fernandes, A.C., Prudêncio, M.I., Botelho, M.L., Dias, M.I., Cardoso, G. (submitted) kGy dosimetry using OSL and TTOSL signals from quartz. Radiation Measurements.

Burbidge, C.I., Fernandes, A.C., Cabo Verde, S.I., Prudêncio, M.I., Botelho, M.L., Dias, M.I., Cardoso, G., Osvay, M. (2010) Retrospective dosimetry of ceramics irradiated for bio-decontamination and conservation of cultural heritage. In: EPRBioDose 2010, ISS and IRSN, Mandelieu La Napoule (France), pp. 170.

Burbidge, C.I., Fernandes, A.C., Cabo Verde, S.I., Prudêncio, M.I., Botelho, M.L., Dias, M.I., Cardoso, G., Osvay, M., Rocha, F. (2010) Comparison of OSL and TTOSL signals from quartz, for retrospective dosimetry in bio-decontamination and conservation of cultural heritage. In: UK Luminescence and ESR meeting 2010, University of Oxford, UK, pp. 27.

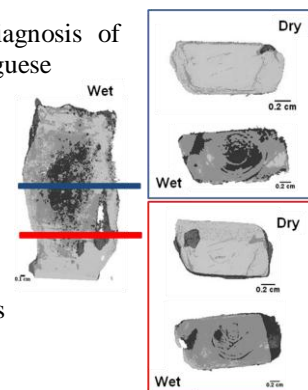
Prudêncio, M.I., Silva, T.P., Dias, M.I., Marques, J.G., Figueiredo, M.O., Esteves, L., Albuquerque, M.B., Botelho, M.L., Trindade, M.J., Burbidge, C.I., Marques, R. (2010) Non-destructive and micro-invasive techniques for cultural heritage diagnostics - a case study of glazed tiles from Portuguese historical buildings. In: 38th International Symposium on Archaeometry, Tampa, Florida.

Trompier, F., Ainsbury, L., Burbidge, C., Kulka, U., Romm, H., Rothkamm, K., Roy, L., Whitehouse, C.A., Fattibene P. EURADOS survey for physical dosimetry methods in emergency preparedness and population triage. In: EPRBioDose 2010, ISS and IRSN, Mandelieu La Napoule (France), pp. 1

RADIART - Diagnosis, decontamination and conservation of cultural heritage: neutrons and ionizing radiation in artwork

M.I. Prudêncio, T.P. Silva¹, M.I. Dias, J.G. Marques, M.A. Stanojev Pereira, M.O. Figueiredo¹, L. Esteves², M.B. Albuquerque³, S. Flor⁴, R. Carvalho⁴, M.L. Botelho, S.I. Cabo Verde, T. Silva, M.J. Trindade, C.I. Burbidge, R. Marques

This project consists of an innovative multidisciplinary approach to the diagnosis of pathologies and mechanisms of degradation, and to the conservation of Portuguese Cultural Heritage, by the use of non-destructive techniques. The main outputs expected are the establishment of procedure protocols for (1) inner structure visualization by NT and for (2) non-toxic radiation treatments of artworks. Compositional characterization of ceramic body and mortars (XRD and INAA) and of glazes (XRD and XRF) were performed in some types of glazed tiles from the XVII century, namely from the Madre de Deus church, Lisbon, and from the N. Sr^a dos Aflitos church, Elvas. Experiments of gamma irradiation for biological decontamination were performed. Visualization of physical structures in the interior of tile fragments was obtained by neutron tomography.



¹ Instituto Nacional de Engenharia, Tecnologia e Inovação, Estrada do Paço do Lumiar, 1649-038 Lisboa, Portugal

² Museu Nacional do Azulejo, Rua da Madre de Deus n° 4, 1900-312 Lisboa, Portugal

³ Conservar-Inovar, Lda, Av. Duque de Loulé n° 77, 4º Dto, 1055-088 Lisboa, Portugal

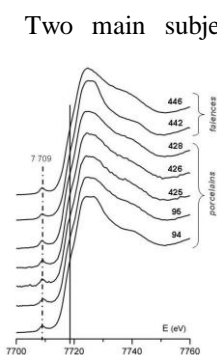
⁴ Rede Temática de Estudos de Azulejos (RTEACJMSS), Inst. de História de Arte (IHA-FLUL), Alameda da Universidade, Lisboa, Portugal

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. L. Rodrigues, A. Zink⁴

Co-K edge XANES spectra collected from blue glaze of PF and CPOPM

faience PF (XVII – 1st Portuguese market chemical and production technology established together was difficult to and hardness. rich blue glazes, XAFS and network-former in responsible for a blue ions occupy available coordination sites of the tetrahedral silica-rich glassy matrix.



Two main subjects were addressed in this FCT project through the same methodological approach applied to the early Portuguese half XVIII cent.) and to the Chinese porcelain ordered for the CPOPM (XVI-XVII cent.). For both cases a definition of mineralogical composition (INAA and XRD) and the (firing temperature and surface coating technique) was with a luminescence dating methodology. Still for CPOPM it establish TL and OSL dating due to their very thin thickness Regarding non-destructive characterization on selected cobalt-results confirm that cobalt plays the dual role of chromophore the blue glaze of CPOPM, the tetrahedral Co²⁺ ions being colouring, conversely non-colouring pseudo-octahedral Co²⁺ ions occupy available coordination sites of the tetrahedral silica-rich glassy matrix.

¹ CENIMAT, UNL. 2829-516 Caparica, Portugal; ² MNaz. Rua da Madre de Deus 4. 1900-312 Lisboa, Portugal.

³ IPCR. Rua das Janelas Verdes, 37. 1249-018 Lisboa, Portugal. 1; 4 CNRS, Musee du Louvre, Paris, France

Application of luminescence dating to the understanding of Iberian cultural evolution

M. I. Dias, M.I. Prudêncio, C. Burbidge, G. Cardoso, D. Franco, R. Marques, A.L. Rodrigues, A.C. Valera¹, C. Fabião², C. Odriozola³, V. Hurtado³, L. San Juan Garcia⁴, L. Osterbeek^{5,6}, J. Mungur-Medhi^{5,6}, C. Scarre⁷, J. Munghur Medhi^{6,8}, A. Cruz⁶, P. Cura⁶, J. Garcia Gazolaz⁹, J. Sesma⁹, D. Mosquera¹⁰, J. Sanjurjo¹⁰, S. M. Espino¹¹, C. Bento¹², A. Silva¹², T. Gomes¹²



Research activities including PhD thesis and post-graduation working programmes, in collaboration with national and international universities, regarding the study of Iberian cultural contexts of various chronologies and geological backgrounds, have been carried out. Several types of materials belonging to Portuguese and Spanish archaeological sites and museums have been studied by Luminescence methods, such as sediments, soils, mortars, heated clay structures, and ceramic and lithic artefacts. Special attention has been paid to the in situ measurements of gamma radiation within profiles of sedimentary/archaeological stratigraphy to provide additional information for the dating results, as well as to a better correlation with lithology.

¹ Era Arqueologia S.A. Portugal; ² Fac. Letras, Univ. Lisboa; ³ ISCME, CSIC, Seville, Spain; ⁴ Univ. Seville, Spain; 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; ⁹ Dep. de Cultura y Turismo, Pamplona, Navarra, Spain; ¹⁰ Inst. Universitario de Xeologia, Corunha, Spain; 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. An additional 17 samples are being dated from Mozambique. These represent a shift of focus between islands in the coastal dune cordon: now Bilene. Most of the samples contain relatively large doses for dating using conventional OSL signals from quartz. Methodology developed for the measurement of such samples is now stable: interest in extending the possible range of measurements to even higher doses/ages has fed into the work presented on kGy dosimetry. Work at Troia is now drawing to completion: an additional 24 samples received in 2010 are aimed at filling gaps in the chronological data obtained to date, and at achieving sedimentary levels predating the formation of the spit. It is aimed to develop Portuguese coastal studies on the neotectonics of older coastal formations.

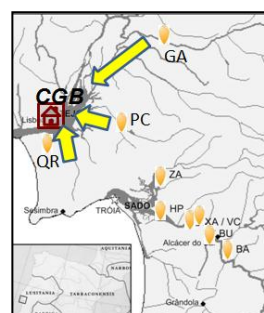


¹ IGM. LNEG, Portugal

² Inst. Universitario de Xeologia, Corunha, Spain

Casa do Governador da Torre de Belém (Tagus estuary): Halieutical 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



Several approaches were applied in this FCT interdisciplinary project: archaeometry, particularly compositional studies (chemical and mineralogical, INAA and XRD) of amphorae and luminescence dating; archaeozoology; archaeology, focusing specifically on the study of recovered artifacts, and building of the 3D virtual model of the unit. In 2010 we increased the number of classes to be sampled. New results highlight the strengthening of the trend previously observed, pointing most of the amphorae for a production in the Tagus basin. Having been most 20/21 = Dressel

Class 14 supplied by the river upstream kilns (Garrocheira), some Dressel 20/21 = 14 by the Tagus estuary kilns of P. Cacos, and other types distributed by P. Cacos and Q. Rouxinol kilns. Recent results suggest the existence of amphorae of unknown origin, with high contents of LREE, Hf and Th, pointing to the use of materials related to more acid lithologies (granites?).

Luminescence studies confirm the Roman age of the fish tank and indicate a Chalcolithic date for the paleosol on which it was built.

¹ Fac. Letras, Univ. Lisboa

² Era Arqueologia S.A. Portugal

Distribution of trace elements, especially lanthanides and actinides, in superficial environments of Portugal

M.J. Trindade, M.I. Prudêncio, M.I. Dias, R. Marques, M.A. Gouveia, D. Franco, J. Sanjurjo¹, D. Mosquera¹, J. R. Vidal Romani¹, F. Rocha²

Detailed geochemical studies on lanthanides, actinides (U and Th) and other trace elements' behaviours have been applied to superficial environments around Portugal. These studies have been complemented with mineralogical analysis and field radiometric measurements by portable gamma-ray detectors. This research contributes to the study of the post-depositional alteration processes (weathering) in vertical sedimentary profiles, with ultimate impact and application in soil formation and evolution studies, palaeoenvironmental investigations, and luminescence dating of Quaternary sediments. During 2010, our study was mostly focused on the variation of mineral and chemical composition in several size fractions (2 mm-63 µm, 63-20 µm, 20-2 µm and > 2 µm) of residual clays of dolerites, granites and slates from Central Portugal, a region known by its richness in uranium. The main aim was the understanding of the chemical changes that occur during the weathering of rocks in the formation of the various residual clays, especially the chemical patterns associated to uranium and other actinides and lanthanides mobilization.

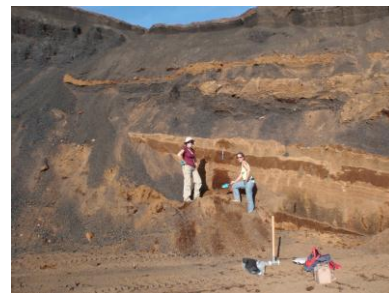


¹ Inst. Univ. de Xeologia, Corunha, Spain; ² Univ. Aveiro, GeoBioTec

Geochemistry, mineralogy and radiometric measurements 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, C. Burbidge, G. Cardoso, A.L. Rodrigues, F. Rui¹, M. Abad¹, F. Rocha², E. Silva², M.M.S. Cabral Pinto^{2,3}, M.M.V.G. Silva⁴

Geochemical, mineralogical and radiometric studies of superficial environments (soils and sediments) of the Iberian Peninsula and Cape Verde archipelago were performed. During 2010 a second field work campaign in the Fogo island was conducted. The results obtained so far showed that soils developed on carbonatites are clearly distinguished by high contents of K, Rb, Cs, W, Th and rare earth elements (REE). The main mineral compounds identified in Fogo topsoils are pyroxenes, feldspathoids, magnetite-maghemite, titanomagnetite, zeolites and phyllosilicates. The soil developed in carbonatites shows a distinct mineralogical association, with calcite, micas, phyllosilicates, and feldspars. Quartz and micas are found throughout the studied soils of this volcanic island, derived most probably from particulate deposition from the atmosphere, transported by wind from North Africa (Sahara).



¹ Univ. Huelva, Spain; ² Univ. Aveiro, GeoBioTec; ³ INIDA – Inst. Nac. Inv. Des. Ag., Santiago, Cabo Verde; ⁴ Univ. Coimbra

Nuclear methods for the characterization and preservation of cultural and natural heritage

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 cultural and natural heritage studies, most of them performed in the framework of master and doctoral theses, as well as post-doctoral programmes. Service work for public and private institutions also makes up a significant part of the work conducted by GeoLuC. Neutron activation analysis and luminescence methods are applied to palaeoenvironments and ancient materials studies, contributing to answering questions related with provenance, production technology, ancient recipes and alteration pathways, weathering processes, as well as absolute chronology, with an Iberian focus. Research work has also been conducted in the framework of the IAEA-TC Project RER/8/015 - Using Nuclear Techniques for the Characterization and Preservation of Cultural Heritage Artefacts in the European Region.

¹ Univ. of Sheffield – Dep. of Archaeology and Prehistory, England; ² Univ. Aveiro, GeoBioTec; ³ Univ. Bordeaux, France; ⁴ ISCME, CSIC, Seville, Spain; ⁵ Inst. Politécnico de Tomar, Portugal; ⁶ Inst. Univ. de Xeologia, Corunha, Spain; ⁷ Era Arqueologia S.A. Portugal; ⁸ Univ. Seville, Spain

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 Environmental Chemists, Geologists, Biologists and Conservation scientists. Different facilities have been implemented and are 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**.

Major achievements were obtained in the different research fields.

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 coastal lagoon of Pederneira and at the salt marshes of some main Portuguese estuaries. Particularly, new studies on Organic Geochemistry have contributed to evaluate the metal binding capacity of humic acids and to assess the origin of organic matter in sedimentary records related to sea level changes. Oceanographic studies concerning the marine reservoir effect, based on **Radiocarbon Dating** of pairs of samples (terrestrial and marine) were enlarged and new data were added the previously obtained allowing for the first time the quantification of ΔR for the Sotavento region of Algarve (Southern Portuguese coast), for the last 3000 yr.

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, mainly 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.

Archaeometallurgical research was focused on materials characterization, involving different analytical techniques (EDXRF, micro-XRF, optical metallography, XRD and SEM-EDS) of Cu based artefacts and other remains recovered in different archaeological sites from the whole 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. Obtained results could demonstrate the co-existence of both local and Orientalising signatures of bronze metallurgy during Early Iron Age. Study of the Macao Scientific and Cultural Center Museum Chinese copper cash was focused on the correlation of alloy elemental composition with metallic phases. Current observations showed that minor elements (Sn, Sb, Fe and As) are structurally significant in these coins since they tend to associate affecting the corrosion resistance of the alloy.

The EAC group continued 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.

Recently, in the sequence of the approval for financing by FCT a new large research project (resulting from the merging of 3 proposals) was initiated aiming at the comprehension of the Early Metallurgy in the Portuguese Territory (PTDC/HIS-ARQ/110442/2008). On the overall, the project main goal is to investigate the metallurgical evolution from Chalcolithic to Late Bronze Age and also during the Orientalizing period in the Portuguese territory.

Research Team

Researchers

M.F. ARAÚJO, Princ. Group Leader
A.M.M. SOARES, Princ
P. CARREIRA, Aux.
J.M. DE LA ROSA, Aux. (Contract)
M. G. SANTOS, Post-Doc, FCT grant (until September)

Students

E. FIGUEIREDO, PhD student, FCT grant
M. J. FURTADO, PhD student, FCT grant
J. MARTINS, PhD student, FCT grant
I. PEREIRA, Graduate student, FCT grant
P. PORTELA, Graduate student, FCT grant

Technical Personnel

D. NUNES, Graduate technician
P. VALÉRIO, Graduate technician
A. AMARO, Laboratory technician
M. CORREIA, Laboratory technician

Collaborators

P. ALVAREZ-IGLÉSIAS, Researcher, Univ. of Vigo, Spain
S. MOREIRA, PhD student, FCUL

Archaeometallurgy – Provenance, technology and use of metallic artefacts

M.F. Araújo, E. Figueiredo, P. Valério, M.J. Furtado, F. Pereira, A.M.M. Soares, R.J.C. Silva¹

Objectives

Archaeometallurgical research is being based on the chemical and structural characterization of archaeological metallic artefacts, tools and other materials employed in the metallurgical process as well as by-products that were originated during metallurgical operations. Studies have been mainly focused in archaeological materials from the Portuguese territory. Another current investigation in the archaeometallurgical field is being dedicated to the understanding of the production of ancient Chinese coins with diverse compositions, from the Macau Scientific and Cultural Centre collection.

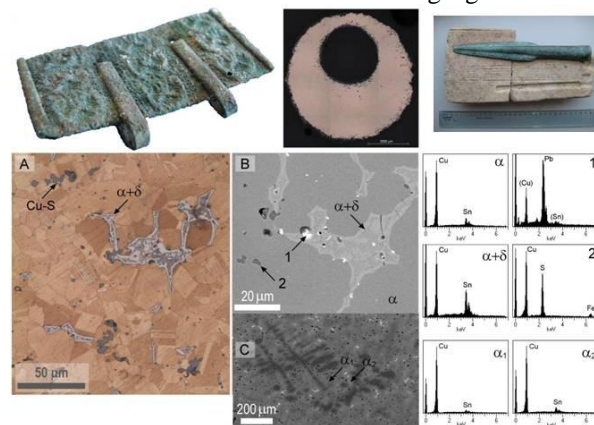
The main used techniques are EDXRF, optical metallography, XRD, SEM-EDS, digital X-radiography and radiocarbon dating aiming at the investigation of the evolution of ancient metallurgical operations, artefact production and corrosion processes (fundamental for conservation strategies).

Results

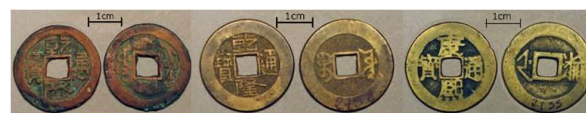
A large amount of archaeometallurgical data regarding metallic artefacts of various typologies and diverse materials related to metallurgical operations has been gathered and discussed. Artefacts and archaeological remains were recovered from diverse important archaeological sites (e.g. Baiões/Santa Luzia, Medronhal, Fraga dos Corvos, Escoural, Castro de Pragança). The overall results have shown that during the Chalcolithic period relatively pure coppers were at use (with exception for the presence of As), and that during Late Bronze age binary bronze with relatively constant tin contents (average of ~13wt.%) and impurities as Pb, As and Sb was the main material used. Unalloyed copper was used sporadically to produce particular items whenever the properties of this metal could be an advantage. Differing from other Western European regions, ternary bronzes seem to have a later appearance, i.e. during Iron Age. The shaping of large and more complex artefacts (e.g. spear heads, axes, closed rings) was made in moulds with only some final thermo-mechanical processing being needed. On the other hand, smaller and simpler items were produced by shaping pre-defined forms, as cast bars, through thermo-mechanical processes that could be very intense, as those that include various cycles of deformation and annealing.

Particular studies were dedicated to the important collection of copper-based artefacts belonging to the Orientalising settlement of Quinta do Almaraz. Its particular location (Tagus estuary) has favoured human occupation since the Neolithic period. Studied

artefacts were mainly composed by Cu-Sn alloys, systematically exhibiting rather low Sn contents (~2.2 to 8.8 %), despite the presence of few unalloyed coppers and leaded bronzes (Pb > 2 %). Relatively high Fe contents (~0.2 to 0.9 %) point to the use of efficient smelting furnaces. Manufacture operations consisted of hammering and annealing operations regardless of their typologies. Comparison with neighbouring Early Iron Age collections allows detection of both local and Orientalising signatures.



More recently the study of the emblematic collection of Vila Nova de S. Pedro settlement, internationally recognized has one of the most representative of metallurgical activities during Chalcolithic has been initiated in order to establish the first metallurgical steps in the prehistory of the Portuguese Estremadura.



Finally, the study of Chinese cash coins showed they are mainly brass and bronze coins with varied amounts of lead. Phase elemental composition and digital X-radiography allowed the observation of Pb globules susceptible to trans-globular corrosion in certain environments. Pb is immiscible in Cu-based alloys, being distributed in globules, which seem susceptible to trans-globular corrosion in certain environments. Preliminary-XRD analysis allowed to identify an Sb-rich phase (in some brass coins) similarly to previously identified Sn-rich phase; and the [Fe,As] rich phase. It was found these elements – Sb,Sn and Fe,As – tend to associate due to their similar properties and affect the corrosion resistance of the alloy. These results contribute to evaluate the importance of minor elements in the promotion of microstructural changes in Cu-based alloys, relevant to the conservation of this type of artefacts.

¹ Dep. de Ciências dos Materiais, FCT, Universidade Nova de Lisboa, Monte de Caparica, Portugal

Metal binding by humic acids in recent sediments from the SW Iberian coastal area*J.M. Rosa, M. Santos, M.F. Araújo, F.J. González-Vila¹*

The concentrations of Cu, Zn, Cr, Ni, Pb, As, Mn and Co were determined by ICP-MS in recent sediments from the Huelva littoral and in their humic acid (HA) fractions, in order to evaluate distribution and binding capacity of heavy metals to HAs. In addition, elemental composition and $\delta^{13}\text{C}$ values were determined to appraise the sources of organic matter in the area. The study involved the comparison of selected samples taken from different environments including the estuary of the Guadiana River, the main fluvial system of the region, the Tinto and Odiel system and shelf sediments. A significant positive correlation was found for Co, Zn, As and Pb in bulk sediments, suggesting a common origin of all of those elements, the mining activities and pyrite deposits located hinterland. On the other hand, results for Cr, Mn, Co and Ni pointed to the basic rocks from the low basin of the Guadiana River as their main source. Elemental (C, N) and isotopic ($\delta^{13}\text{C}$) analysis of sediments indicated a significant contribution of autochthonous plankton in coastal shelf sediments, whereas estuarine and riverine sediments showed major contribution of terrestrial biomass. Geochemical values for respective HAs suggested a greater terrestrial contribution in estuarine and marine OM than bulk sediments, which evidenced the influence of coastal currents and sediment fluxes. Concentration of trace metals in HAs followed the sequence $\text{Cu} \gg \text{Zn} > \text{Cr} > \text{Ni} \geq \text{Pb}$. Humic Acids sequester considerable amounts of Cu and Zn contributing to reduce the bioavailability of these contaminants. Low levels found in HAs for Mn and As suggested the formation of stable complexes with pyrite and the preferential binding of Cu and Zn in HAs.

¹ IRNAS, CSIC, Seville, Spain**Geochemical record of environmental changes in Portuguese estuaries and coastal area***M.F. Araújo, J.M. Rosa, S. Moreira¹, A.M.M. Soares, M.C. Freitas¹, F. Fatela¹, F.J. González-Vila²*

The overall objectives of this current work are the recognition of recent environmental changes which have occurred at the main Portuguese estuaries and coastal lagoons, by multidisciplinary approaches to trace the history of the sedimentary record. Geochemical and sedimentological data of a sedimentary sequence (Lagoa da Pederneira) allowed its palaeoenvironmental reconstruction and four stratigraphic units have been identified related to diverse environments mainly related to climate and sea level rise. Final lipidic extracts of dried sections of cores (1 m depth) collected in the estuaries (Minho, Lima and Mira) were analysed by gas chromatography-mass spectrometry (GC-MS). The variability observed in the biomarkers downcore distribution allowed to identify the origin in the organic matter supply (terrestrial/marine). Sections of top-most cores were characterized by the presence of a complex mixture of polysaccharides, lignin derived compounds, fatty acids and a greater abundance of n-alkanes. The dominance of n-alkanes with a distribution biased toward higher chain lengths (n-C25 to n-C33) together with an odd-over-even predominance and the presence of lignin compounds indicate of a terrestrial higher plant origin. However, this dominance of terrestrial markers disappears in the deeper sections (e.g. Minho river) suggesting a greater marine contribution in ancient times.

¹ Laboratório de Processos Costeiros, Centro e Departamento de Geologia da FCUL, Lisboa, Portugal² IRNAS, CSIC, Seville, Spain**The variability of the marine radiocarbon reservoir effect in Southern Atlantic Iberian Coast***A.M. Monge Soares, J.M. Matos Martins, P. Portela, A. M. Arruda¹*

The quantification of the marine radiocarbon reservoir effect (ΔR) is essential in order to calibrate conventional radiocarbon dates from marine shell samples with reliability. Also, the quantification of this parameter can provide information concerning the intensity of coastal upwelling in marine regions influenced by this phenomenon.

Previous research regarding these issues has been done for the Atlantic Iberian coast. Nevertheless, new data were added to these research allowing for the first time the quantification of ΔR for the Sotavento region of Algarve (Southern Portuguese coast), for the last 3000 yr. A ΔR weighted mean value of -65 ± 30 ^{14}C yr was obtained for the Sotavento region. This area can be considered as a transition zone between an area influenced by the prolongation of the western coastal upwelling system in the southern Portuguese coast, the Barlavento region of Algarve ($\Delta R = +65 \pm 20$ ^{14}C yr), and an area where the upwelling regime is absent, the Andalusian coast ($\Delta R = -135 \pm 20$ ^{14}C yr).

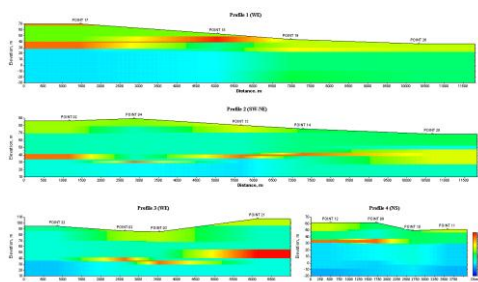
These values are in accordance with the oceanographic conditions present in Southern Atlantic Iberian coast, and suggest a consistent oceanographic pattern in the region for the last 3000 yr.

¹ Faculdade de Letras, Universidade de Lisboa, Lisboa, Portugal

Arid /semi arid zones hydrology

P.M. Carreira, D. Nunes, F. Monteiro Santos¹, J.M. Marques², Hans Eggenkamp², M. F. Ben Hamouda³

Overexploitation of coastal aquifers and pollution are among the main problems related to groundwater resources assessment and management in Tunisia. Brackish groundwater for agriculture and human supply is being provided to numerous parts of the region, as the only type of available water. The salts income to the groundwater systems could be derived from seawater intrusion (overexploitation of the systems- very touristic area), from salt dissolution (evaporitic minerals within the basin sediments), and from marine aerosols. A field work campaign was carried out in order to sample groundwater to determine ²H, ¹³C, ¹⁸O, ³⁵Cl and ³H content. The isotopic results obtained together with geophysical survey will help to clarify this problem.



¹ Instituto de Ciência da Terra e do Espaço / Dep. Física da Faculdade de Ciências da Universidade de Lisboa, Lisboa, Portugal

² Dep. de Engenharia de Minas e Georrecursos, Instituto Superior Técnico, Lisboa, Portugal

³ Faculty of Sciences of Semlalia, Hydrogeology Laboratory, Marrakech, Morocco

⁴ Isotope Hydrology and Geochemistry Unit Technopole de Sidi Thabet, Tunisia

Groundwater isotopic geochemistry applied in 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 analyses δ¹⁵N 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 N₂ concentration; based on the simultaneously determined N₂/³⁶Ar ratios and assuming that ³⁶Ar content in crustal and mantle-derived fluids is negligible with respect to ³⁶Ar concentration in the atmosphere. Besides, ³⁵Cl sampling campaign was performed in order to identify the origin of Cl in the groundwater systems (mantle or sea water mixing).



¹ Dep. de Engenharia de Minas e Georrecursos, Instituto Superior Técnico, Lisboa, Portugal

² Dep. de Geologia, Faculdade de Ciências da Universidade de Lisboa, Lisboa, Portugal

³ Istituto Nazionale di Geofisica e Vulcanologia, Palermo, Italy

⁴ Departamento de Geociências, Universidade dos Açores, Ponta Delgada, Portugal

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. The main goals of the work are to understand the influence of the electronic structure and the size of the f-elements in the properties of their compounds, and to find new applications for these elements. Chemical properties are 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 goal.

Important facilities maintained by the Group are a laboratory for catalytic studies, a laboratory for handling 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).

We continued to study important environmental issues such as the activation and valorisation of methane as C1 feedstock, namely through the catalytic partial oxidation of CH₄ (POM reaction) using O₂ or N₂O as oxidant. The lanthanide and actinide catalysts were obtained by three routes: i) an intermetallic route, ii) a sol – gel route and iii) a molten salt route. Under O₂, the molten salt approach allowed the production of hydrocarbons, particularly C3, with an unusual high selectivity (>70%). Under N₂O, the main products were C2 hydrocarbons and the increase of the CH₄/N₂O molar ratio had a significant influence on the selectivity. The selective catalytic reduction of N₂O by CH₄ is not only as an effective method of N₂O abatement but, in particular, an effective method of N₂O and CH₄ valorisation. To our knowledge, this is the first time that such results are reported over molten salts and bimetallic lanthanide or actinide oxides.

The investigation of the coordination chemistry of actinides and lanthanides with O- and N-donor ligands continued. The multidentate aminophenolate ligands

{(Ar^tBu₂O)₂-cyclam} and {Salan-^tBu₂} were successively used in the preparation of new Ln(III), U(III) and An(IV) (An = Th, U) complexes with varied structural features.

Gas-phase chemistry/mass spectrometry studies expanded in 2010. New uranium species, namely, the sulfur analogue of uranyl and several uranium carbide cluster ions were produced. The complexation of heterocyclic N-donor bases (building blocks of ligands used in Ln/An separations) towards Ln(III) and An(III) ions was investigated. Key d-transition metal species involved in catalytic processes, namely, Re and Mo complexes, and Ta oxides, were also studied.

Molecular energetics studies continued. An affinity scale of cations commonly used in ionic liquids started to be determined using the NTF₂ anion as a reference. The gas-phase acidity of chromanol was determined, on the way to obtaining the acidity of vitamin-E.

In a collaboration with FCT/UNL, new lanthanide-based luminescent materials were prepared using compounds of the type Ln₈(OH)₂₀Cl₄·nH₂O as intercalators.

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

Joint projects with the Research Unit “Glass and Ceramic for the Arts” (a collaboration between ITN, FBAUL and FCT/UNL) on lanthanide-containing glasses and ruby glass were pursued.

A relevant part of the activity of the Group is the training of research students, which had a significant increase in 2010. Some of the Group members continue to be involved in undergraduate and post-graduate university teaching. The financial support for the work is mainly from FCT, via research projects and PhD and Post-doc grants. A new project within ACTINET-I3, in Ln/An separation chemistry, was initiated in 2010.

Research Team

Researchers

J. MARÇALO, Princ., Group Leader
J.B. BRANCO, Aux.
J.P. LEAL, Aux.
T. ALMEIDA GASCHE, Aux.
J.M. CARRETAS, Aux.
C.C.L. PEREIRA, Aux., (Contract)
L. MARIA, Aux., (Contract)
N. MARQUES, Retired Princ.
A. PIRES DE MATOS, Retired Coord.
B. MONTEIRO, Post-Doc, FCT Grant

Technical Personnel

A. CRUZ
A.J. SOARES

Students

R. MELO, PhD student, FCT grant
A.F. LUCENA, Research student, (Jan.-Oct.); PhD student, FCT grant (Since Oct.)
J.M. VITORINO, Research student, FFCUL/FCT grant (Jan.-Nov.); PhD student, FCT grant (Since Dec.)
S.C. LEAL, PhD student, FCT grant
M.M. VARELA, PhD student
A.C. FERREIRA, Research student, ITN grant
E. MORA, Research student, ITN grant
C. LOURENÇO, Research student, ITN grant (Since Mar.)
V. SOUSA, Research/Technical student, FCT grant (Since Oct.)
L. SILVA, Research student, ITN grant (Until Nov.)
G. LOPES, Research student, ITN grant (Until Aug.)

f- Block Elements as Catalysts

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

Objectives

The main objectives of this research are: (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 to the resolution of key environmental issues.

Introduction

We continue to study the activation and valorisation of methane and carbon dioxide as valuable C1 feedstock's, namely through the catalytic partial oxidation of CH₄ (POM reaction) using O₂ or N₂O as oxidant. 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 - lanthanide chlorides molten salts. The catalytic reactions were followed on-line by gas chromatography.

Results

The intermetallic and sol – gel routes allowed the production of syngas with the appropriate H₂/CO mol ratio and high conversion of methane over the bimetallic nickel based oxide catalysts, which are cheaper materials with an activity, selectivity and stability comparable to that of the noble metal based catalysts, e.g. 5 wt. % M/Al₂O₃ (M = Rh, Pt) (Fig. 1). The good catalytic behaviour of this nickel based catalysts and its high stability is a major achievement since the known and widely studied noble metal based catalysts are limited by their high cost, whereas the deactivation of other catalysts is the major drawback of this reaction that limit a widespread industrial application.

On the other hand, 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 main products are now C2 hydrocarbons (except for Ce and Eu) and the best results were those obtained over the lanthanum and samarium catalysts (Sel.C2 ~ 70 %) (Fig. 2). The results obtained for the partial oxidation of CH₄ by N₂O confirm this unusual behaviour of the molten salts (Conv. CH₄ > 10 %; Sel. C2 ~ 70-80 %). To our knowledge, this is a novelty over molten salts catalysts containing f-block elements.

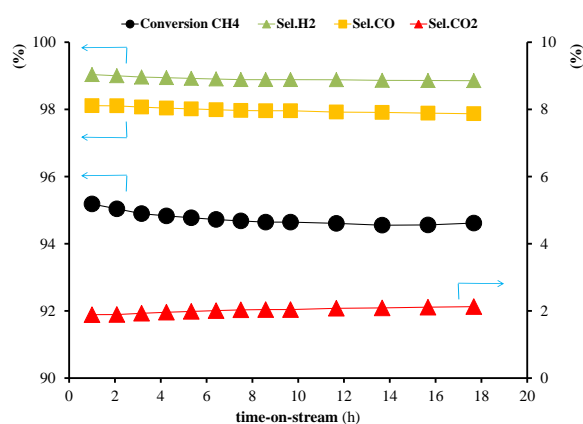


Fig. 1. Bimetallic Ni-U oxide (2NiO-UO₃) catalytic activity and selectivity as a function of time on stream at 800 °C for the partial oxidation of methane by O₂.

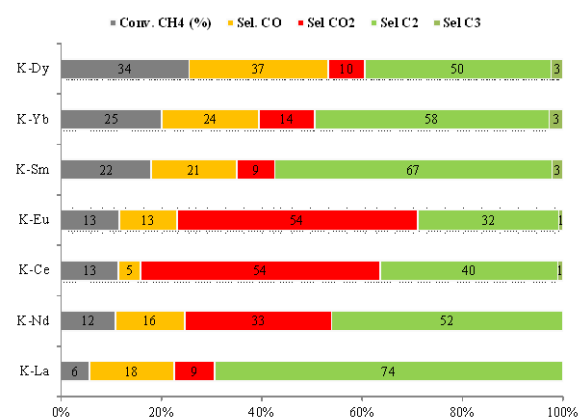


Fig. 2. K-Ln chlorine molten salt catalysts activity and selectivity at 750 °C for the partial oxidation of methane by O₂.

Published work

A.C. Ferreira, A.M. Ferraria, A.M. Botelho do Rego, A.P. Gonçalves, A.V. Girão, M.R. Correia, T. Almeida Gasche, J.B. Branco, Partial oxidation of methane over bimetallic copper–cerium oxide catalysts, *J. Mol. Catal. A-Chem.* 320 (2010) 47–55.

A.C. Ferreira, A.P. Gonçalves, T. Almeida Gasche, A.M. Ferraria, A.M. Botelho do Rego, M.R. Correia, A.M. Bola, J.B. Branco, Partial oxidation of methane over bimetallic copper- and nickel-actinide oxides (Th, U), *J. Alloys Comp.* 497 (2010) 249–258.

A.C. Ferreira, A.M. Ferraria, A.M. Botelho do Rego, A.P. Gonçalves, M.R. Correia, T. Almeida Gasche, J.B. Branco, Partial oxidation of methane over bimetallic nickel–lanthanide oxides, *J. Alloys Comp.* 489 (2010) 316–323.

¹ University of Aveiro, I3N and Physics Department.

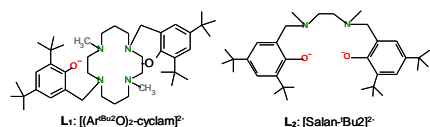
² Technical University of Lisbon / IST, IN and Centre for Molecular Physical Chemistry.

³ ITN/UCQR, Solid State Group.

f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

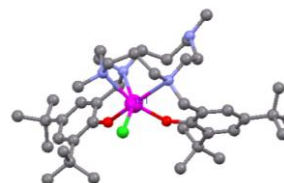
 L. Maria, E. Mora, A. Cruz, J. M. Carretas, J. Marçalo, N. Marques, I. C. Santos¹, A. M. Martins², M. Mazzanti³

The main goal of this research work is to develop new coordination environments for the f-elements and to synthesize new compounds with potential interest in organic synthesis and catalysis. We continued the



Scheme 1

investigation of the coordination chemistry of actinides (Th and U) and lanthanides based on O- and N-donor ligands, namely, with the multidentate aminophenolate ligands L¹ and L² (Scheme 1). The reaction of the trans-N,N'-bis(phenolate)-cyclam ligand L¹ with LnCl₃(THF)_x (Ln = La, Sm, Yb) and U₃(THF)₄ led to the formation of the neutral compounds [Ln{(Ar^tBu₂O)₂-cyclam}Cl] and [U{(Ar^tBu₂O)₂-cyclam}] in good yields. The solid-state structures of the La, Sm and U complexes showed that the metal centers are seven coordinated and L¹ acts as a hexadentate ligand. The smaller ionic radius of Yb(III) led to the formation of a six-coordinated compound with the macrocycle acting as pentadentate, with one of the nitrogens uncoordinated (Fig.1). The reactions of the tetradentate ligand L² with AnCl₄ (An = Th, U) showed that this bis(aminophenolate) is a good anchor for An(IV) complexes. The new eight coordinated complexes [An{Salan-tBu₂}Cl₂L] (An = Th, L = dme, bipy; An = U, L = bipy) and [Th{Salan-tBu₂}₂] were synthesised and characterised by NMR experiments, ESI/QITMS and X-ray diffraction analysis.

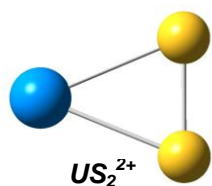

 Fig.1 - [Yb{(Ar^tBu₂O)₂-cyclam}Cl]

¹SS Group/UCQR-ITN. ²Centro de Química Estrutural, IST. ³INAC, CEA-Grenoble (France).

Gas-Phase Chemistry and Thermochemistry of Elementary Actinide Molecules

 J. Marçalo, C. C. L. Pereira, A. F. Lucena, A. Pires de Matos, A. P. Gonçalves¹, L. Andrews², J. K. Gibson³

Gas-phase chemistry studies, using advanced mass-spectrometry techniques (LDI/FTICRMS and ESI/QITMS), are conducted to search for new elementary actinide species and reactions, and investigate their chemical and thermochemical properties. In 2010, we were able to produce the first synthesis and theoretical description of bare US₂²⁺ (the sulfur analogue of uranyl) in the gas phase. We used FTICRMS to study the reaction of U²⁺ ions with COS in which we observed the sequential, efficient formation of US²⁺ and US₂²⁺.



Theoretical studies performed by C.J. Marsden (Univ. Paul Sabatier, Toulouse, France) showed that, in contrast to linear uranyl (O=U²⁺=O), US₂²⁺ has a strongly bent structure at both B3LYP and CCSD(T) levels of theory, with the linear isomer being some 100 kJ/mol higher in energy. Also in 2010, UC_n and USi_n compounds, obtained by high-temperature synthesis techniques, were investigated by LDI/FTICRMS. UC_n showed to be an efficient precursor for the formation of new UC_x⁺ and U₂C_x⁺ (x = 2-14) ions, with UC₂⁺ being especially abundant; no Si analogues could be obtained from USi_n. These LDI studies of UC_n and USi_n samples were accompanied by matrix-isolation spectroscopy experiments with similar samples at the U. Virginia in which new neutral UC_x species could be identified; USi_n is currently under study.

¹SS Group/UCQR-ITN. ²U. Virginia (Chalottesville, VA, USA). ³Lawrence Berkeley National Lab. (Berkeley, CA, USA).

Mass Spectrometry Studies of the Coordination Chemistry of Lanthanides and Actinides

 J. Marçalo, C. Lourenço, J. M. Carretas, B. Monteiro, J. P. Leal, I. Paiva¹, L. Berthon², J. K. Gibson³

The coordination chemistry of the lanthanides (Ln) and actinides (An) with N-donor ligands is a topic of current interest, as associated to Ln/An separations within advanced nuclear fuel cycles. Some of the ligands used have simple heterocyclic N-donor bases as building blocks. Within the ACTINET-I3/JRP-17 project, we have been using mass spectrometry (ESI/QITMS and LDI/FTICRMS) in the investigation of the complexation properties of different N-donor bases and simple N-donor ligands towards Ln(III) and An(III) ions. The relative affinity of a representative number of N-donor bases towards Ln(III) ions was studied by ESI/QITMS. These experiments indicated that the relative gas-phase affinities of the N-donor molecules followed their gas-phase basicities, with the notable exception of pyridazine for which a η² coordination mode seems to prevail, leading to a stronger bonding. The coordination of the new neutral tetradentate ligand L = bis[3-(2-pyridyl)pyrazolyl]methane (Fig. 1) towards Ln(III) and Y(III) in solution was also studied using ESI/QITMS. Experiments with different M/L ratios as well as CID indicated that the 1:1 stoichiometry was preferred. Comparative studies of the gas-phase affinities of different bases and ligands towards early Ln(III) and Am(III) ions by ESI/QITMS and LDI/FTICRMS are currently under way.

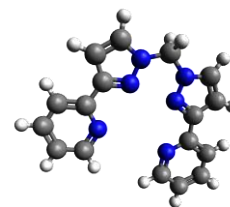


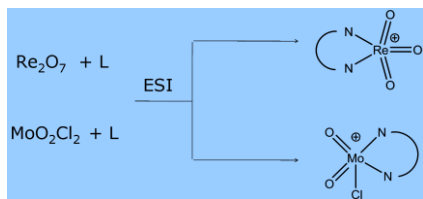
Fig.1 - Bis[3-(2-pyridyl)pyrazolyl]methane

¹RRW Group/UPSR-ITN. ²CEA-Atalante (Marcoule, France). ³Lawrence Berkeley National Lab. (Berkeley, CA, USA).

Mass Spectrometry Studies of d-Transition Metal Species

J. Marçalo, A. F. Lucena, J. M. Carretas, B. Monteiro, M. C. Oliveira¹, J. K. Gibson²

Mass spectrometry can be a useful tool in the study of different aspects of the chemistry of metal compounds. We have been using ESI/QITMS and LDI/FTICRMS in the investigation of key d-transition metal species involved in catalytic processes.



The catalytic activity in olefin epoxidation of $[\text{Re}(\text{CH}_3\text{O}_3\text{L})]$ and $[\text{MoO}_2\text{Cl}_2\text{L}]$ complexes, where L is a bidentate N-donor ligand, is strongly influenced by the electronic and steric nature of L. The relative stability of mono- and bidentate N-donor adducts of $[\text{ReO}_3]^+$ and $[\text{MoO}_2\text{Cl}]^+$ (as models for the neutral complexes) was investigated by ESI/QITMS, to probe the technique as a simple alternative to standard

methods (spectrophotometry, NMR) of solution characterization. The results were in overall agreement with spectrophotometric studies of the stability of N-donor adducts of $[\text{Re}(\text{CH}_3\text{O}_3)]$ and $[\text{MoO}_2\text{Cl}_2]$.

Transition metal oxides have numerous applications as heterogeneous catalysts, support materials, etc., and are present in the reaction centers of many enzymes. To provide fundamental chemical models to rationalize the chemistry in complex multi-charged systems and to obtain new thermodynamic data of ionic and neutral species containing these elements, we have been examining the gas-phase chemistry and thermochemistry of singly and doubly charged transition metal oxide ions by FTICRMS. The ionization energies of TaO and TaO₂ have been determined by a bracketing method, employing a selected set of organic compounds of known ionization energies. The oxygen-dissociation energies of singly and doubly charged TaO and TaO₂ have also been determined via reactions with several oxidants with different oxygen affinities.

¹ Centro de Química Estrutural, IST. ² Lawrence Berkeley National Lab. (Berkeley, CA, USA).

Molecular Energetics of Organic, Inorganic and Organometallic Compounds

J. P. Leal¹, J. B. Branco, T. Almeida Gasche, J. M. Vitorino¹, L. Silva, M. T. Fernandez², M. E. Minas da Piedade², J. A. Martinho Simões², R. Borges Santos²

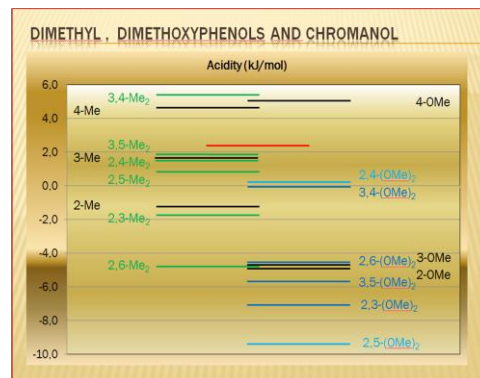
The main objective is to collect energetics data, rationalize it in a systematic way and explore connections between energetics and structure of molecules (both inorganic and organic compounds). Special importance was given to f-element compounds (both on solid state and in solution). To achieve this goal, lanthanide and actinide (organometallic and intermetallic), alkaline and alkaline-earth compounds, hydrocarbons and ionic liquids were studied.

During 2010, an extended version of an already published empirical model for the prediction of the enthalpies of formation of hydrocarbons was enlarged to accommodate CHO compounds. The site www.therminfo.com, online in 2010, allows the retrieving of existing enthalpies of formation (critically analyzed) and the estimation of non existing values for hydrocarbon compounds.

The nature of ionic liquids in the gas phase continued to be studied and the kinetic 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. Also, an affinity scale of cations usually used in ionic liquids formulation started to be determined using the NTf₂ anion as a reference.

After conclusion of the gas-phase acidity measurements of dimethoxy and di-methyl-substituted phenols, the gas-phase acidity of chromanol was determined, on the way to obtaining the vitamin-E acidity.

The study of polyalkoxides of alkaline and alkaline-earth metals had new developments: some of the already synthesised compound where calorimetrically measured and the corresponding enthalpies of formation obtained.



¹ IOC Group/UCQR-ITN & Centro de Química e Bioquímica, FCUL. ² Centro de Química e Bioquímica, FCUL.

Decomposition of Recalcitrant Effluents

J. P. Leal, R. Melo¹, M. L. Botelho²

The degradation/decomposition mechanism of gallic acid was elucidated by using pulse-radiolysis studies to unveil the initial steps and mass spectrometry (ESI-QIT/MS) to identify the major intermediates. New studies are on the way with some other recalcitrant compounds (acetovanilone and sculetol) to see if the decomposition mechanism is similar to the one proposed for gallic acid.

¹ IOC Group/UCQR-ITN & RTPP Group/UFA-ITN. ² RTPP Group/UFA-ITN.

Lanthanide-Based Luminescent Materials

C. C. L. Pereira, B. Monteiro, J. P. Leal, T. Almeida Gasche, L. C. Branco¹, C. A. T. Laia¹, P. Viana Baptista²

The synthesis of new lanthanide-based luminescent materials was pursued. Compounds of the type $\text{Ln}_8(\text{OH})_{20}\text{Cl}_4 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu, Tb, Dy}$) were prepared and used as precursors for the synthesis of new materials by intercalation, via chloride ion exchange, of ligands of the beta-diketone and chalcone families and of DNA fragments. The synthesis and characterization of ionic liquids involving anionic Ln complexes ($\text{Ln} = \text{Eu, Gd, Tb, Dy}$) with beta-diketonate ligands was continued. The photophysical and photochemical properties of the new materials were studied at FCT/UNL.

¹REQUIMTE, FCT/UNL. ²CIGMH, FCT/UNL.

Glass Science with Applications in Art Studies

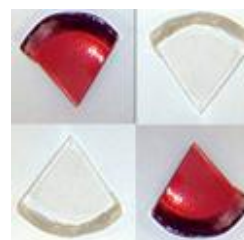
A. Pires de Matos¹, C. Queiroz², A. Ruivo^{2,3}, J. Marçalo¹, M. L. Botelho⁴

In 2010, A. Pires de Matos continued as coordinator of the Research Unit “VICARTE-Glass and Ceramics for the Arts”. Work was carried out by members of ITN and FCT/UNL mainly in the development of new materials for artistic applications.

Gold ruby glass doped with lanthanide oxides obtained by gamma irradiation: To sodalime silicate glasses containing different concentrations of gold, cerium, europium and samarium oxides were added. The samples were irradiated with gamma rays in order to obtain nanoparticles of gold. The influence of the lanthanide oxides in the colour striking was studied. The effect of the investigated lanthanide oxides on the reduction of the gold ions to metal was interpreted considering pertinent redox equilibria and the Ellingham diagrams for the lanthanide oxides.

Synthesis of copper ruby glass using gamma radiation: To a batch of raw materials used to prepare soda lime silicate glass, cuprous oxide was added. After irradiation with gamma rays and thermal treatment at about 600°C a red colour was obtained which was due to nanoparticles of copper. When cupric oxide was used no reduction was observed.

Following the objectives of the project “Glass in Art: Light and Colour” (POCI/EAT/60496/2004), thin-layer deposition on glass was made using the spray-pyrolysis technique. The first experiments with copper acetate in methanol and water gave origin to a thin layer deposition of copper oxide which after heating at about 600°C gave origin to nanoparticles of copper.



¹IOC Group/UCQR-ITN & VICARTE, FCT-UNL. ² VICARTE, FCT-UNL. ³REQUIMTE, FCT/UNL. ⁴ RTPP Group/UFA-ITN.

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 with expertise on organic and coordination chemistry, bioconjugation, radiochemistry, animal and cell studies, and molecular biology. Such expertise and facilities enable the RS group to deal with problems of modern Radiopharmaceutical Sciences and to provide education and training at different levels.

The main achievements during 2010:

Research:

1 – Publication of a masterpiece describing a wealth of interesting structural and physicochemical properties of an entire series of lanthanide macrocyclic complexes. Such results helped to interpret kinetic data along the lanthanide series, an important issue for medical applications.

2- Based on the bone-seeking/imaging properties of $^{99m}\text{Tc}(\text{CO})_3$ -alendronate, a new project between the Group and the Clinical and Translational Oncology Research Unit/IMM/U. Lisbon has started, aiming at the design of multifunctional compounds for the imaging/treatment of bone metastases.

3 - In close cooperation with the Group of Theoretical and Computational Biochemistry/ Faculty of Sciences/U. Porto, molecular docking and molecular dynamic studies were initiated to get insight into the structural parameters responsible for the increased inhibitory effects of Re(I)-complexes towards iNOS

4 – The first ^{99m}Tc -organometallic complex combining specific cell targeting with nuclear internalization has been isolated. This result opens new avenues for the design of Auger therapeutic agents.

5 - Within the framework of a wide cooperation involving our Group, the Cell and Molecular Neuroscience Unit/IMM/U. Lisbon and the ICNAS/U. Coimbra, we have introduced a set of fluorinated

azole derivatives aiming at the targeting of amyloid aggregation.

6 - The radiotracer ^{99m}Tc -TMEOP, designed by our Group for myocardial imaging, localizes in the mitochondria, being potentially useful for *in vivo* tumour multidrug resistance (MDR) detection.

Education and Training

1-Graduation:

Radiopharmacy teaching at ESTSeL and at Faculty of Pharmacy/University of Lisbon.

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 2nd Cycle of Chemistry, Faculty of Sciences/UL

d) Teaching at the Master in Pharmaceutical Sciences, Lusófona University.

e) Teaching at the Master in Human Molecular Biology, Faculty of Sciences/UL

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

Expertise Provided:

Nuclear Medicine Centers, Portuguese Medicines Evaluation Agency, IAEA, Foreigner Science Foundations (Canada and Uruguay), International Conferences and International Journals.

Publications:

Peer-Review International Journals – 19; Reports - 8; Proceedings – 11; Communications – 24; Invited Lectures and Seminars: 14.

Research Team

Researchers

I. SANTOS, Princ., (Agreg.) 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.
G. MORAIS, Aux.

Students

S. GAMA, Post-Doc, FCT grant
P. S. ANTUNES, Post-Doc, FCT grant
M. K. S. BATISTA, Post-Doc, FCT grant

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
R. GOMES, Undergraduate student
M.ANTUNES, Undergraduate student
A. NEVES, Undergraduate student
H. BATISTA, Undergraduate student

Technical Personnel

RODRIGUES
E. CORREIA

Lanthanide(III) Complexes of *trans*-H₆do2a2p: Structural Studies Along the Series

M. Paula C. Campello, Sara Lacerda, Isabel C. Santos, Giovannia A. Pereira,¹ Carlos F. G. C. Geraldés,¹ Jan Kotek,² Petr Hermann,² Jakub Vaněk,³ Přemysl Lubal,³ Vojtěch Kubiček,⁴ Éva Tóth,⁴ Isabel Santos

The main goal of this project is the design of Ln-based bone-seeking agents. To get a better insight in the biological behaviour of the radiolanthanide complexes and to improve their pharmacokinetics, complexes of *trans*-H₆do2a2p- H₆L with Ln(III) ions were investigated at the macroscopic level.

Results

The tetraazamacrocyclic 1,4,7,10-tetraazacyclododecane-1,7-bis(acetic acid)-4,10-bis(methylenephosphonic acid), *trans*-H₆do2a2p-H₆L (Fig. 1), reacts with ¹⁵³Sm/¹⁶⁶Ho nitrates yielding very stable radiolanthanide complexes with similar biological profile. Trying to explain these results, the complexation properties of *trans*-H₆do2a2p along the lanthanide series were investigated.

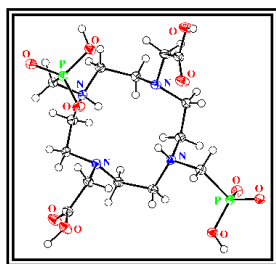
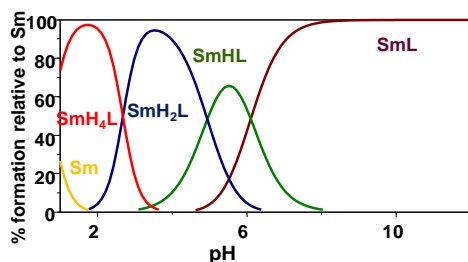


Fig. 1. Molecular structure of H₆L.

Potentiometric and ¹H/³¹P NMR studies have shown the formation of very stable and kinetically inert complexes, being the [LnL] species the only one present in solution at pH ≥ 8 (Fig. 2).

Fig. 2. Species Distribution Diagram for Sm-H₆L.



In the solid state the [LnL] complexes (Ln = Ce, Nd, Sm, Eu, Tb, Dy, Er, Yb) are present as twisted square antiprismatic isomers. However, a change from nonacoordinated complexes, with one water molecule in the coordination sphere (Ce→Sm), to anhydrous octacoordinated complexes (Sm→Yb) occurs.

The central ions move more deeply inside the ligand cavity in the Ce–Sm series and then almost do not move further up to Yb. The water coordination has also a strong effect on the opening angle OP–Ln–OP

and on the twist angle of the phosphonic/acetic pendant arms (Fig 3).

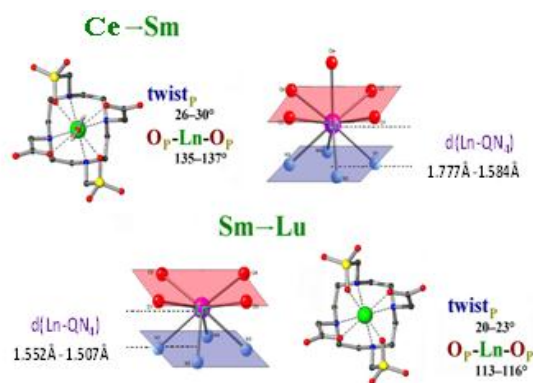


Fig. 3 Structural parameters of LnL complexes.

The structures are maintained in solution, as indicated by ¹H/³¹P NMR analysis. The lanthanide induced shifts (LIS) data reflect more the gradual geometrical change of the metal coordination sphere than the change of the hydration number of the complexes which occurs at Sm.

The structural data found for the lanthanide complexes in solution and in the solid state agree with the biological profile found for the [¹⁵³Sm-do2a2p] and [¹⁶⁶Ho-do2a2p] complexes.

Published work:

M. P. C. Campello, S. Lacerda, I. C. Santos, G.A. Pereira,¹ C.F.G.C. Geraldés,¹ J. Kotek,² P. Hermann,² J. Vaněk,³ P. Lubal,³ V. Kubiček,⁴ É. Tóth,⁵ I. Santos, Lanthanide(III) Complexes of *trans*-H₆do2a2p in Solution and in the Solid State: Structural Studies Along the Series, *Chem. Eur. J.* **16** (2010) 8446-8465.

M. P. C. Campello, S. Lacerda, I. C. Santos, G.A. Pereira,¹ C.F.G.C. Geraldés,¹ J. Kotek,² P. Hermann,² J. Vaněk,³ P. Lubal,³ V. Kubiček,⁴ É. Tóth,⁴ I. Santos, Lanthanide(III) Complexes of *trans*-H₆do2a2p: Synthesis, Structural Studies, Labelling and Biological Evaluation, Cost D38 Action Annual Meeting, 20-22th June, Thessaloniki, Greece.

¹ Dep. Life Sciences and Center of Neurosciences and Cell Biology, Univ. Coimbra, Portugal

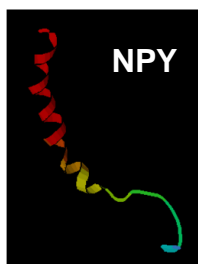
² Dep. Inorg. Chemistry, Charles University in Prague, Czech Republic

³ Dep. Chemistry, Masaryk University, Brno Czech Republic

⁴ Centre de Biophysique Moléculaire, CNRS, Orléans, France

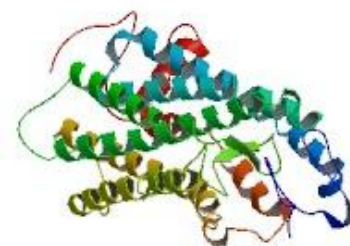
Radiolabeled neuropeptide Y (NPY) analogs for Y1 receptor-targeting in breast cancer

P. Antunes, P. Raposinho, C. Fernandes, I. Santos



The extremely high expression and incidence of neuropeptide Y1 receptors (NPYY1R) in breast cancer make them a promising target for molecular imaging and therapy of this type of tumors. Based on the selective Y1R agonist [Pro³⁰, Nle³¹, Bpa³², Leu³⁴]NPY(28-36) (NPY1), several short peptides were synthesized and conjugated to DOTA and to a pyrazolyl-based bifunctional chelator (pzNN). DOTA- and pzNN-conjugates were quantitatively labeled with ⁶⁷Ga and ^{99m}Tc, respectively. These new radiometallated peptides were characterized by comparing their

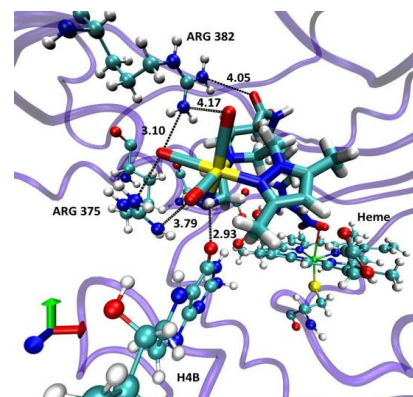
HPLC profiles with the ones obtained for the corresponding *cold* complexes. *In vitro* stability, lipophilicity, and pharmacokinetic profile of the labeled peptides were determined. Binding affinity determination, internalization studies and biological assessment in tumor bearing mice are underway.



Y1 Receptor model

Insight into the high affinity of Re(I)/^{99m}Tc(I) complexes for the iNOS enzymeB. L. Oliveira, F. Mendes, P. D. Raposinho, I. Santos, J. D. G. Correia, A. Ferreira,¹ C. Cordeiro,¹ A. P. Freire,¹ I. S. Moreira,² P. A. Fernandes,² M. J. Ramos²

Aiming to find radioactive probes for *in vivo* targeting of Nitric Oxide Synthase (NOS), we have recently introduced a set of Re/^{99m}Tc(CO)₃-complexes containing L-arginine derivatives with high *in vitro* (enzymatic assay) and *in vivo* (LPS-induced RAW 264.7 macrophages) affinity for the enzyme. These results prompted us to perform molecular docking and molecular dynamic studies to get an insight into the structural parameters of the Re complexes responsible for their increased inhibitory effect towards iNOS, when compared to the free bioconjugates. Preliminary results showed that the Re(I) complexes really fit into the predicted cavity and interact strongly with the enzyme.

¹ Centro de Química e Bioquímica, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, Portugal.² Requite/Departamento de Química, Faculdade de Ciências da Universidade do Porto, Portugal.**^{99m}Tc(CO)₃-labeled alendronate for bone imaging**

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

We have synthesized and characterized the novel complexes *fac*-[M(CO)₃(*k*³-pz-alendronate)] (M = Re or ^{99m}Tc), and evaluated the biodistribution profile of the ^{99m}Tc(I) complex. This compound is stable at physiological conditions, presents a fast rate of blood clearance, high rate of total radioactivity excretion and high bone uptake.

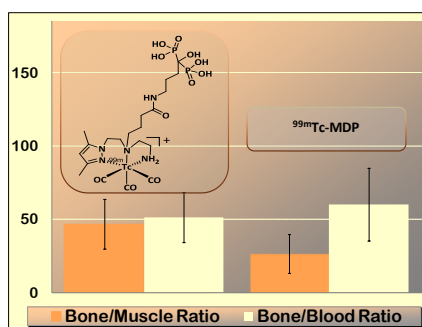


Fig. 1 Target/non target organs ratios.

The target to non target ratios at 4 h p.i. (Fig. 1) were high and comparable to the ones obtained for ^{99m}Tc-MDP, which is the radiopharmaceutical for bone imaging in current clinical use. This biodistribution profile was confirmed by SPECT imaging in Sprague Dawley rats (Fig.2).

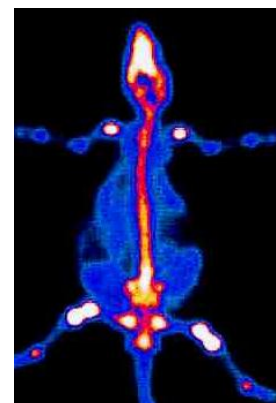
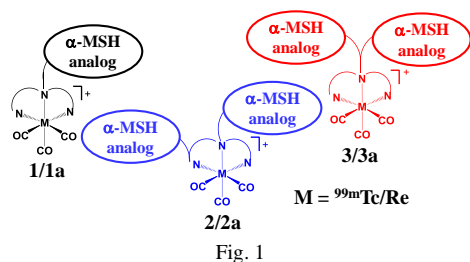


Fig. 2 SPECT imaging in Sprague Dawley rats at 2 h post-injection.

Homodimeric conjugates of a linear α -MSH analog for melanoma imaging

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



2/2a and **3/3a** (Fig. 1). The rhenium surrogates **1a** and **2a** displayed excellent receptor binding affinities in the subnanomolar range. Cell uptake studies have shown that **3** displayed the highest cellular uptake, when compared to the homodimeric and monomeric derivatives **2** and **1**, respectively (Fig. 2). Complex **3** holds promise as a radioactive probe for melanoma imaging, and is currently under biological evaluation.

Aiming to investigate the Melanocortin 1 receptor-targeting properties of $^{99m}\text{Tc}(\text{CO})_3$ -labeled homodimeric conjugates based on a linear α -MSH analog (NAPamide), we have synthesized the metallated peptides **1/1a**,

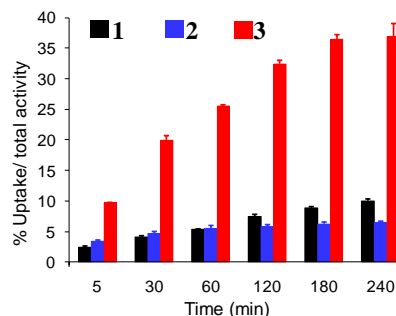
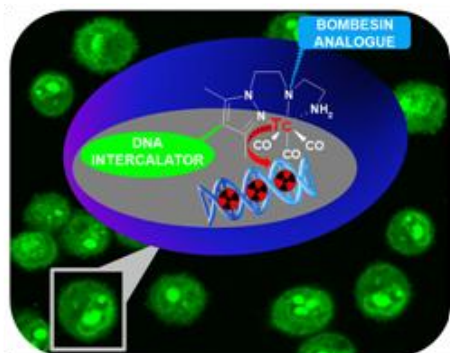


Fig. 2 Uptake in B16F1 melanoma cells (37°C).

Cell-specific and nuclear targeting with multifunctional $^{99m}\text{Tc}(\text{I})$ complexes

 T. Esteves, F. Marques, A. Paulo, J. Rino,¹ P. Nanda,² C. Smith,² I. Santos


To explore the usefulness of ^{99m}Tc as an Auger emitter, we have introduced and biologically evaluated novel multifunctional structures comprising: i) a pyrazolyl-diamine framework (pz*NN) bearing a set of donor atoms to stabilize the $[\text{M}(\text{CO})_3]^+$ ($\text{M} = \text{Re}, ^{99m}\text{Tc}$) core; ii) a DNA intercalating moiety of the acridine orange (AO) type; iii) and a bombesin (BBN) analogue of the type X-BBN[7-14] (where X = SGS, GGG) to provide specificity. Cell uptake studies have shown that the presence of the AO intercalator and metallation did not compromise the capability of the BBN metalloconjugates to accumulate specifically in GRPr-positive PC3 human tumor cells, targeting the nucleus. To the best of our knowledge, these compounds are the first examples of ^{99m}Tc

bioconjugates that combine specific cell targeting with nuclear internalization, which are crucial issues for the usefulness of ^{99m}Tc in Auger therapy.

¹ IMM, Faculdade de Medicina da Universidade de Lisboa, Lisboa, Portugal

²Research Division, Harry S. Truman Memorial Veterans Hospital, University of Columbia, USA.

PEGylated DOTA- α -MSH analogues for *in vivo* targeting of melanoma

F. Silva, M. P. Campello, M. Baptista, A. Paulo, I. Santos

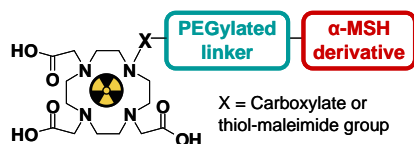
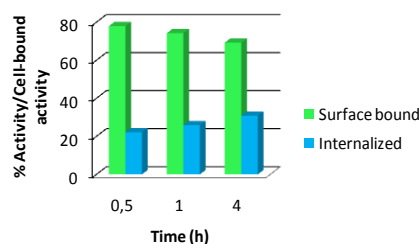


Fig.1 – PEGylated DOTA-NAPamide

radiopeptides, which were characterized by HPLC comparison with the cold Ga congeners and evaluated in B16F1 murine melanoma cells (Fig. 2). Biodistribution studies of these novel radiometallated peptides in tumor-bearing mice are currently underway to assess their ability to target melanoma *in vivo*.

In an effort to develop new tools for *in vivo* melanoma imaging, we have synthesized α -MSH derivatives having PEGylated linkers bound to a DOTA chelator (Fig.1).

Some of these derivatives were labeled with ^{67}Ga , affording novel


 Fig.2 – Cellular uptake of ^{67}Ga -DOTA-PEG2-NAPamide at 37°C in B16F1 cells.

Radiolabeled benzazole derivatives for *in vivo* imaging of amyloid aggregation

G. Morais, A. Paulo, I. Santos, H. Miranda,¹ T. Outeiro¹

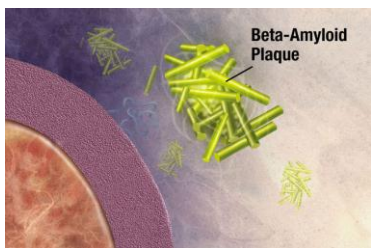


Fig. 1 Schematic drawing of β -amyloid aggregates.

Aiming to prepare compounds exhibiting high affinity and selectivity to amyloid aggregates (Fig. 1), the histopathological feature of neurodegenerative diseases, we have designed and synthesized a number of fluorinated styryl heteroaromatic derivatives (Fig. 2). These compounds were obtained using novel synthetic strategies and fully characterized. Profiting from their intrinsic fluorescence, the *in vitro* affinity of the synthesized compounds towards aggregates of insulin, beta-amyloid ($A\beta_{1-42}$) and α -synuclein was also assessed (Fig. 2). The synthesis and biological evaluation of radiofluorinated congeners are currently underway.

¹ IMM, Faculdade de Medicina da Universidade de Lisboa, Lisboa, Portugal

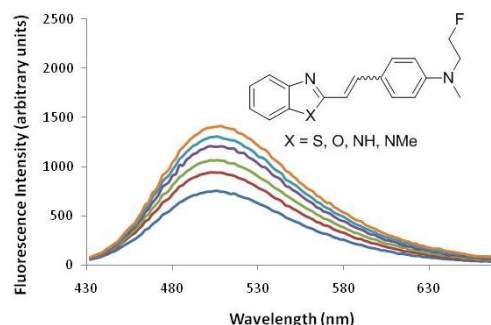
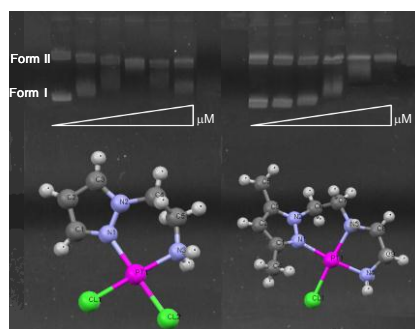


Fig. 2 – Styryl heteroaromatic derivatives and their enhancement of fluorescence upon interaction with $A\beta_{1-42}$ fibers.

Design of novel anticancer drugs based on Pt(II) complexes with pyrazolyl-containing chelators

S. Gama, F. Mendes, F. Marques, Isabel C. Santos, A. Paulo, I. Santos, E. Gabano,¹ M. Ravera¹



A series of Pt(II) complexes anchored by bidentate or tridentate pyrazolyl-alkylamine chelators bearing different substituents at the azolyl rings has been prepared to assess their interest as anticancer drugs. The complexes have been fully characterized by classical analytical methods, and in some cases also by X-ray diffraction analysis. Cell uptake, antiproliferative properties and DNA interaction were evaluated. These studies have shown that the complexes were less active than cisplatin on the ovarian carcinoma A2780 cell line. Nevertheless they kept their activity in the cisplatin-resistant A2780cisR cell line and presented a lower resistance factor compared to cisplatin.

¹ DiSAV, Università del Piemonte Orientale “Amedeo Avogadro”, Alessandria, Italy

^{99m}Tc(I) Tricarbonyl complexes for targeting melanotic melanoma

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

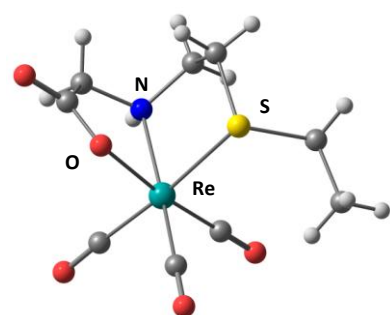


Fig 1

Within our interest on ^{99m}Tc-labeled small-molecules for targeting tumoral tissues, we have pursued with the search of new radioactive probes suitable for the early detection of melanotic melanoma. To achieve this goal we have synthesized and evaluated a series of Re(I)/^{99m}Tc(I) tricarbonyl complexes anchored by (N,N,O) or (S,N,O)-tridentate chelators (Fig. 1) bearing different melanin-avid pharmacophores. In general, the synthesized complexes have shown a moderate to high *in vitro* affinity for melanin, and in some cases were able to target *in vivo* murine melanoma tumors with favorable target/non-target ratios (Fig. 2).

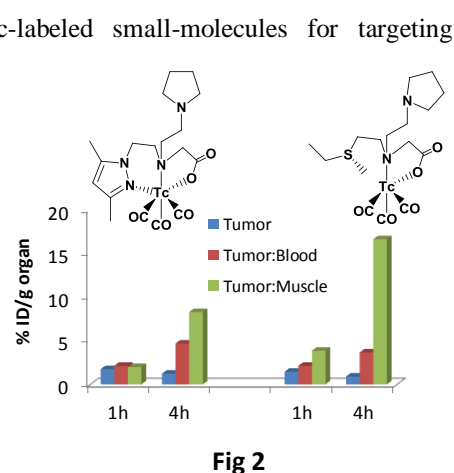
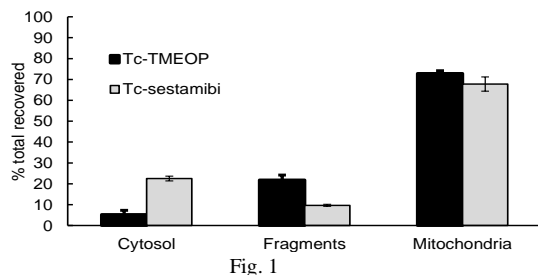


Fig 2

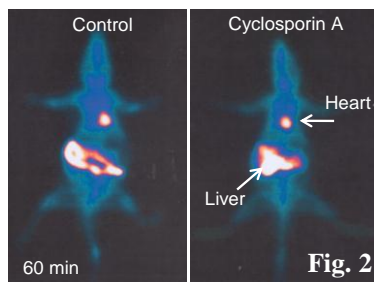
Myocardial localization and excretion mechanism of a novel ^{99m}Tc radiotracer for heart imaging

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

We developed a ^{99m}Tc organometallic complex, ^{99m}Tc-TMEOP, which exhibits a high initial and persistent heart uptake associated to rapid blood and liver clearance. More detailed studies in isolated rat hearts were performed for this complex and compared with ^{99m}Tc-sestamibi. Subcellular distribution studies showed that ca. 70% of ^{99m}Tc-TMEOP accumulates in the mitochondria, similarly to ^{99m}Tc-sestamibi (Fig. 1).



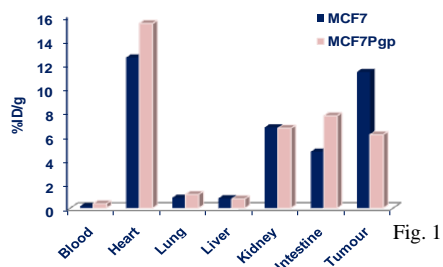
Biodistribution studies in rats in the presence of cyclosporin A revealed an increase in kidney and liver uptake of ^{99m}Tc-TMEOP, suggesting the involvement of multidrug resistance transporters in the pharmacokinetic profile of this complex (Fig. 2).



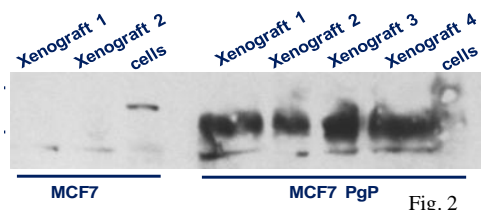
Evaluation of novel ^{99m}Tc(I) cationic complexes as probes for multidrug resistance (MDR)

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

The cationic radiotracer ^{99m}Tc-TMEOP, originally developed as a myocardial perfusion agent, was evaluated for cancer early detection and non-invasive monitoring of multidrug resistance (MDR) by SPECT. The usefulness of ^{99m}Tc-TMEOP for functional assessment of MDR was studied using nude mice bearing MDR negative and positive tumour xenografts. The biodistribution profile of ^{99m}Tc-TMEOP showed a tumour uptake almost 2 times higher in the MCF7 xenografts compared to the MCF7 PgP tumours (Fig. 1).

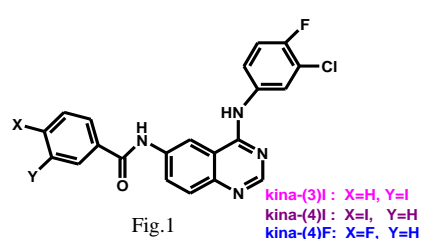


The *in vivo* MDR phenotype of the tumours was confirmed by detection of protein expression levels (Fig. 2). All together these data indicate that this new complex has potential for *in vivo* tumour MDR detection.

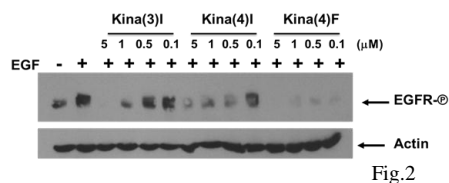


Novel radiolabeled receptor tyrosine kinase inhibitors for *in vivo* targeting of EGFR

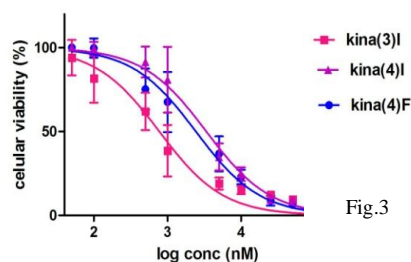
C. Neto, M. C. Oliveira, L. Gano, C. Fernandes, F. Mendes, I. Santos, M. Kuchar¹, T. Kniess¹



Aiming at the development of new tyrosine kinase inhibitors (TKI) for EGFR tumor imaging, novel anilinoquinazoline derivatives were synthesized and characterized (Fig.1). Western blot analysis



showed that all compounds inhibit EGFR autophosphorylation at low micromolar level, being compound kina(4)F the most potent inhibitor (Fig. 2). MTT assay indicates that all compounds are potent inhibitors of A431 cells proliferation (Fig. 3). These data suggest further evaluation of these compounds as SPECT/PET biomarkers for molecular imaging of EGFR positive tumors.



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

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 remained the only one operational in Portugal, serving also many users outside ITN. The replacement process of the old He liquefier by a new one, with expanded capacity and enhanced efficiency, was successfully completed in July after a 4 month period of interruption in the liquid helium supply.

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.

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 an important topic of research due to their unique properties. This research become now focused on a new fundamental aspects of crystallogenesi studied with AFM. The chemistry of bisdithiolene complexes and related TTF donors, namely substituted with coordinating groups as building blocks for multifunctional materials is a another topic of research that has been pursued.

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 and presently the combination of spin crossover compounds with other conducting and magnetic functionalities is being explored.

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 recently 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

M. ALMEIDA, Coord., Group Leader
V. GAMA, Princ.
J. C. WAERENBORGH, Princ.
A. P. GONÇALVES, Princ.
E. B. LOPES, Aux.
L. C. J. PEREIRA, Aux.
I. C. SANTOS, Aux.
D. BELO, Aux. contract
S. RABAÇA, Aux. contract

M. AFONSO, Post-Doc, ITN grant
S. DIAS, Post-Doc, FCT grant
M. F. LU, Post-Doc, FCT grant (since September)
P. I. GIRGINOVA, Post-Doc, ITN grant (since October)

E. TSIPIS, Post-Doc, FCT grant
Y. VERBOVYTSKYI, Post-Doc, FCT grant

Students

M. DIAS, PhD Student, FCT grant
A. NEVES, PhD Student, FCT grant.
A. CERDEIRA, PhD Student, FCT grant.
M. HENRIQUES, PhD Student, FCT grant
B. VIEIRA, PhD Student, FCT grant
R. SILVA, BIC grant
S. OLIVEIRA, BIC grant
L. RIBEIRO, ITN grant (since July)

Collaborators

A. CASACA, Adjunct Professor, ISEL
R. T. HENRIQUES, Assoc. Professor, IST

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. Verbovytsky, P. A. Carvalho¹, A. Ferro¹, O. Tougait², H. Noël²

Objectives

The major objective of this research line is to study (*f*-element)-(*d*-metal)-X ternary systems in order to establish the phase relations, and to identify, synthesise and characterise new ternary compounds. Basic information for the synthesis of pure samples and growth of single crystals is also expected to be obtained here.

Results

The work is focused on several unexplored or only partially explored ternary systems. Our previous results on the U-Fe-B system indicate the existence of five ternary borides, UFeB₄, UFe₂B₆, UFe₃B₂, UFe₄B and U₂Fe₂₁B₆, but it was not possible to obtain these phases as pure compounds and further studies were needed. Therefore, results of the *liquidus* projection for the B-rich corner were achieved, and in this region six ternary reactions were revealed. The two compounds belonging to it, UFeB₄ and UFe₂B₆, are confirmed to be formed by ternary peritectic reactions, but UFeB₄ has a considerably larger primary crystallization field, which points to an easier preparation of single crystals of this boride, when compare with UFe₂B₆. The study will be expanded in the near future to the remaining regions of this system.

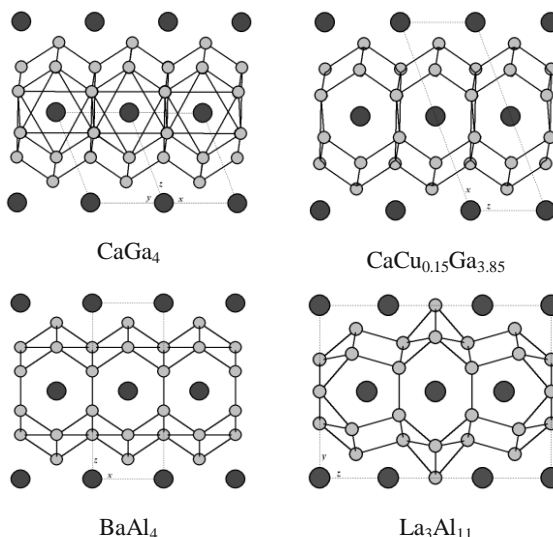
Ternary systems containing *f*-elements and zinc were almost not explored up to the beginning of our studies, with only some crystal structures of selected R_xZn_yX_z compounds being reported.

The systematic investigation of the phase relations in the (*f*-element)-Zn-X systems was continued. The Yb-Zn-Ga and Eu-Zn-Al systems, in the 0-33.3 at.% R concentration range at 400°C, were completely explored and seven ternary compounds (the last six new) were found and their crystal structures were assigned:

YbZn_{0.75-2}Ga_{3.25-2}, (BaAl₄-type),
 YbZn_{0.25-0.5}Ga_{3.75-3.5}, (CaCu_{0.15}Ga_{3.85}-type),
 Yb₃Zn_{7.5-6.8}Ga_{3.5-4.2}, (La₃Al₁₁-type),
 YbZn_{9.2-8.3}Ga_{1.8-2.7} (BaHg₁₁-type),
 Eu₂Zn_{13.9-14.3}Al_{3.1-2.7} (Th₂Zn₁₇-type),
 Eu₃Zn₁₈Al₄ (Ce₃Zn₂₂-type) and
 EuZn₁₋₂Al₃₋₂ (BaAl₄-type).

A relationship between the crystal structures existing along the “row” CaGa₄ (YbGa₄) – CaCu_{0.15}Ga_{3.85} (YbZn_xGa_{4-x}) – BaAl₄ (YbZn_xGa_{4-x}) – La₃Al₁₁ (Yb₃Zn_{11-x}Ga_x) has been established. The CaGa₄ and CaCu_{0.15}Ga_{3.85} are distorted variants of the BaAl₄ structure type and the La₃Al₁₁ structure can be obtained from BaAl₄ considering three unit cells and merging part of the 4*e* positions from this last structure type into the 2*d* positions of the La₃Al₁₁ structure. An extended solid solution, YbZn_{2-x}Ga_x (0 ≤ x ≤ 1), was also identified in the Yb-Zn-Ga system.

Preliminary results on the U-Fe-Ge and U-Fe-Sb isothermal sections were also obtained. These studies indicated a very rich U-Fe-Ge system, with more than 10 ternary phases (8 of them being new compounds) stable at 900°C. In the U-Fe-Sb system only 2 phases, UFe_{1-x}Sb₂ and U₃Fe_{1-x}Sb₄ (both new), were identified until now.



Published or in press work (selected)

M. Dias, I.C. Santos, P.A. Carvalho, M. Bohn, O. Tougait, H. Noël, A.P. Gonçalves, Considerations on the U-Fe-B ternary system, *40^{èmes} Journées des Actinides & 2nd Workshop on Actinide Targets*, CERN, Geneva, Switzerland, March 27 – April 1, 2010.

Yu. Verbovytsky, A.P. Gonçalves, The Yb-Zn-Ga system: partial isothermal section at 400°C with 0–33.3 at.%, *Intermetallics* **18** 655-665 (2010).

Y. Verbovytsky, L.C. Alves, A.P. Gonçalves, Phase relations of the Eu-Zn-Al system at 400 degrees C from 0 to 33.3 at.% Eu, *J. Alloys Compd.* **495** 39-44 (2010).

M.S. Henriques, D. Berthebaud, A. Lignie, O. Tougait, H. Noël, A.C. Ferro, A.P. Gonçalves, The study of the U-Fe-Ge system at 900°C, *16th Workshop on Magnetism and Intermetallics*, IFIMUP-IN and Departamento de Física e Astronomia, Universidade do Porto, Porto, Portugal, 4 – 5 March, 2010, C3.

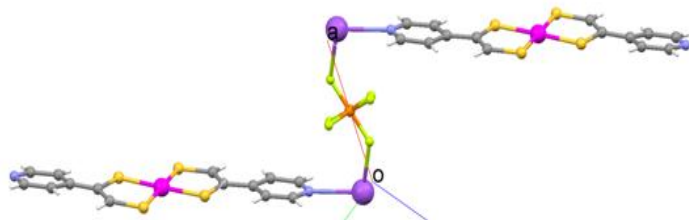
M.S. Henriques, A.C. Ferro, O.Tougait, H.Noel, A.P Gonçalves, The study of the isothermal section of the U-Fe-Sb ternary system at 700°C, *17th International Conference on Solid Compounds of Transition Elements*, Annecy, France, September 5-10, 2010.

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

Neutral Pyridine-functionalized Bisdithiolene Complexes

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

Transition metal bisdithiolene complexes stable in their neutral state are not so frequent but they are currently attracting increasing interest due to a large potential interest as active components in optical, electrical and magnetic materials. Recently we have focused our attention on bisdithiolene complexes functionalized with pyridine groups which could coordinate other metals through the N atoms and lead to novel heterobimetallic magnetic networks. Under such effort the neutral complexes $[\text{Ni}(4\text{-pedt})_2]$ and $[\text{Au}(4\text{-pedt})_2]$ were prepared and characterised. The nickel complex was obtained as a single molecular compound while the gold one was



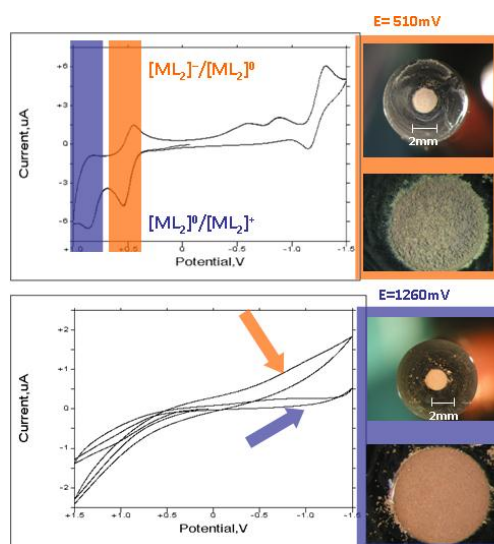
obtained incorporated in a NaPF_6 salt with, the pyridine nitrogen atom coordinating the sodium atom. None of these compounds is a good electrical conductor. The Ni complex is diamagnetic, but the paramagnetic gold complexes are connected only by short $\text{S}\cdots\text{S}$ contacts in chains responsible for weak antiferromagnetic interactions.

Electrodepositable Materials from Bisdithiolene Complexes Containing Pyridine Groups.

S. Rabaça, S. Oliveira, M. Afonso, M. Almeida

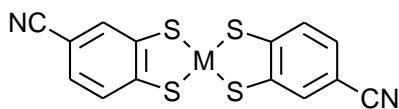
From the viewpoint of technological applications the processability of crystalline molecular materials is difficult, and conducting polymers have been more attractive for the development of technological devices. To fully utilize the properties of molecular species such as metal transition bisdithiolene complexes it is important to find ways of increasing the processability of these materials.

We have found that some transition metal bisdithiolene complexes substituted with pyridine groups are excellent candidates to be used as precursors to electrodepositable materials. Our group have already develop a significant synthetic effort with pyridine substituted metal transition bisdithiolene complexes and within this project explored and study the better conditions and bisdithiolene precursor to be used as precursors of electrodepositable materials. The electrodeposition from solutions of anionic complexes $[\text{Au}(4\text{-pddt})_2]^-$, depending on the potential yields two different materials. In the range 0.51 V vs. Ag/Ag^+ a greenish deposit corresponding to the neutral complex was obtained, while above 1V it was formed a brownish deposit with metallic shine and higher conductivity corresponding to the cationic complex.



The series of transition metal cianobenzenodtiolate complexes $[\text{M}(\text{cbdt})_2]$

A. Cerdeira, S. Rabaça, P. I. Girginova, I. C. Santos, L. C. J. Pereira, R. T. Henriques, D. Simão,¹ M. Almeida



The redox properties of dithiolene complexes are quite sensitive to the ligand nature and their relative contribution, compared to the transition metal, to the frontier orbitals. Following the recent synthesis in our group of the new ligand $\text{cbdt} = 4\text{-cyanobenzene-1,2-dithiolate}$ an extended series of complexes $[\text{M}(\text{cbdt})_2]$ with different transition metals ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Au}, \text{Cu}, \text{Pd}$) could be obtained and characterised. These complexes were found to be mainly in the trans configuration except the Fe one which adopts a transoid dimerised arrangement of cis-bisdithiolene $[\text{Fe}(\text{cbdt})_2]$ units. The redox behaviour of these complexes is intermediate between those based on unsubstituted benzenedithiolate (bdt) and dicyanobenzene (dcbdt). However at variance with some $[\text{M}(\text{dcbdt})_2]$ complexes no stable partially oxidised states could be obtained. The magnetic susceptibility of the $[\text{Co}(\text{cbdt})_2]$ complex is consistent with an undimerised arrangement of units in a high spin configuration. The use of these complexes as building blocks for conducting and magnetic materials and the secondary coordination through the N atom is currently being explored.

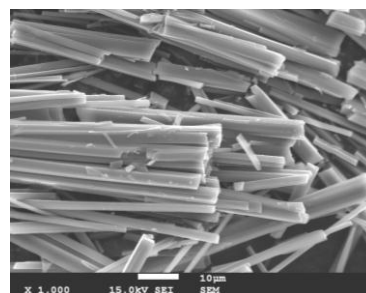
¹ Inst. Superior de Engenharia de Lisboa, Lisboa, Portugal.

Electrocrystallisation of the series of charge transfer salts (Per)_n[M (mnt)₂].

M. Afonso, R. Silva, L. Ribeiro, M. Matos,^{1,2} Q. Ferreira,² M. Almeida

The series of charge transfer salts (Per)_n[M (mnt)₂] presents still unique features among molecular conductors calling for further studies requiring high quality single crystals. The electrocrystallisation has been in general a procedure with large success to obtain single crystals of many charge transfer salts. However the application of this technique to this series of perylene compounds has several limitations. Therefore a systematic study was initiated aiming at both obtaining higher quality single crystals and understanding the factor governing the crystallogenes and determining the obtention of different phases.

Using high resolution AFM, performed both in-situ and ex-situ, the early stages of electrocrystallisation over different substrates were monitored and limiting nucleation and growth steps and mechanism could be identified. The systematic electrocrystallisation studies enabled for the first time (Per)₂[Pd(mnt)₂] single crystals to be obtained by electrocrystallisation. However these crystals were found to be mainly of the β-type semiconducting polymorph.



¹ Instituto Superior de Engenharia de Lisboa, Lisboa, Portugal and.

² Instituto de Telecomunicações, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal

Infrared properties of the one-dimensional organic conductors (perylene)₂ M (mnt)₂, M = Au, Pt.

N. Drichko¹, S. Kaiser¹, R. Shewmon¹, J. Eckstein¹, M. Dressel¹, M. Matos, R.T. Henriques, and M. Almeida M. Afonso, R. Silva S. Oliveira M. Almeida

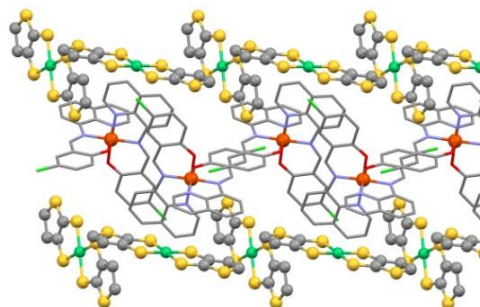
In spite of the large interest in the α-(perylene)₂[M(mnt)₂] compounds and extensive studies that have been performed in these compounds their optical properties have remained so far largely unexplored in part by the difficulty in obtaining suitable samples with large enough crystal faces. As a first step aiming at filling this lack of basic characterization, the optical properties of the one-dimensional organic conductors (perylene)₂[Pt(mnt)₂] and (perylene)₂[Au(mnt)₂] analogue have been investigated at ambient and low temperatures using the largest single crystals selected from several crystallization essays. The spectra with polarization along the molecular stacks show a simple Drude behavior with no detectable influence of electron-electron interactions. Based on the spectra for different polarizations an assignment of the vibrational modes was made. With polarization perpendicular to the stacks, a wide band observed in the mid-infrared range evidences a charge transfer between perylene and anion stacks. These electronic properties could be analyzed in comparison with other quasi-one-dimensional synthetic metals.

¹ Physikalisches Institut, Universität Stuttgart, D- 70550 Stuttgart, Germany

A new hybrid exhibiting room temperature spin-crossover and ferromagnetic cluster-glass behavior.

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

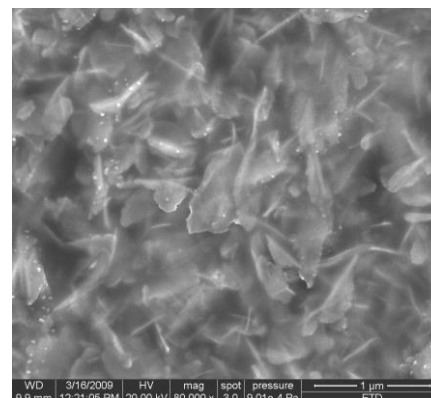
Spin-crossover (SCO) compounds have been systematically studied for more than 20 years but recently there was a renewal interest and the possibility of combining, in the same material, the SCO properties with other physical or chemical properties. In these context transition metal dithiolates appear as suitable anions to combine with SCO cations. Our experience on new dithiophene complexes lead to the selection of the [Ni(α-tpdt)₂]⁻ paramagnetic anion (tpdt= 2,3-thiophenedithiolate) and to a hybrid material, [Fe(5-Cl-qsal)₂][Ni(α-tpdt)₂]CH₃CN (H5-Cl-qsal = N-(8-Quinoly)-5-chlorosalicylaldimine) where the SCO phenomena is combined with the magnetic network of [Ni(α-tpdt)₂]⁻. The crystal structure is based on alternated layers of [Fe(5-Cl-qsal)₂]⁺ cations and of [Ni(α-tpdt)₂]⁻ anions. The hybrid magnetic behaviour in this compound arises from the ferromagnetic cluster-glass behaviour, ascribed to the anions network, and from the spin crossover (SCO) of the [Fe(5-Cl-qsal)₂]⁺ cations. The SCO process with $T_{1/2} = 298$ K (high spin fraction = 0.5) was found to be rather sluggish, which is attributed to the effect of the anions that seem to restrict the structural distortions of the cations associated with the SCO process.



Single Component Molecular Conductors Processed as thin films

E. Laukhina,¹ V. Lebedev,¹ V. Laukhin,¹ A.P. Pino,¹ E.B. Lopes, A.I.S. Neves, D. Belo, M. Almeida, J. Veciana,¹ C. Rovira¹

A simple procedure to cover a polycarbonate film with a metallic or a semiconductor-like layer of the single component conductor $[\text{Au}(\alpha\text{-tpdt})_2]^0$ (tpdt=2,3-thiophenedithiolate) was established. These new organic bi-layer films are of technical interest due to the unusual combination of low crystallinity and high conductivity. This feature is unprecedented and an advantage within molecular conductor materials, whose electrical transport properties have been, so far, depended and directly controlled by their supramolecular structures. The low crystalline character of the $[\text{Au}(\alpha\text{-tpdt})_2]^0$ -based layer not only decreases the grain boundary resistance, allowing $[\text{Au}(\alpha\text{-tpdt})_2]^0$ to behave as a metallic system, but also makes these low values of electrical resistance highly reproducible. The processing characteristics of polycarbonate films coated with a highly conductive $[\text{Au}(\alpha\text{-tpdt})_2]^0$ -based layer make them potentially useful for electronic applications where lightweight, large area coverage and flexibility are required (the figure shows SEM images from the metallic conducting layer of $[\text{Au}(\alpha\text{-tpdt})_2]^0$ covering an organic polycarbonate film).



¹ Institut de Ciència des Materials de Barcelona (CSIC), Campus Universitari de Bellaterra, E-08193 Cerdanyola, Spain.

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, M.F.Lu^{1,3}

Materials based on iron-containing oxides with perovskite-derived structures attract significant attention for energy-related electrochemical technologies, such as electrodes of solid oxide fuel cells or ceramic membranes for conversion of natural gas and biogas.

Transition metal-containing oxides are usually active for total combustion of hydrocarbons. High catalytic activities towards partial oxidation of methane have however been reported for perovskite-related ferrites. Explanations proposed for this phenomenon are: strongly-bonded lattice oxygen with low mobility, presence of carbonate species on the surface, or formation of catalytically active species such as iron carbide or metallic Fe. In order to obtain experimental information on the surface states of ferrite-based mixed conductors and on their role in CH_4 oxidation processes, which is still very scarce, a study by conversion electron Mössbauer spectroscopy started in 2010. The incorporation of Mo in $\text{S}_3\text{Fe}_2\text{O}_7$ was also investigated. A raise of the n-type electronic conductivity was observed although it remains insufficient to provide a high anodic performance in reducing atmospheres. On the other hand the incorporation of Mo leads to decreasing p-type charge carrier concentration and mobility, in agreement with Mössbauer data which showed an increased hole localization. Further enhancement of the dimensional stability and n-type electronic transport in $\text{Sr}_3(\text{Fe},\text{Mo})_2\text{O}_{7-\delta}$ is unlikely due to the relatively low Mo solubility, close to approximately 5% per f.u. in oxidizing conditions.

¹ Dept. de Engenharia Cerâmica e do Vidro, UIMC, Universidade Aveiro, 3810-193 Aveiro, Portugal.

² Institute of Physicochemical Problems, Belarus St. University, Minsk, Rep. of Belarus.

³ Key Laboratory of Rare Earth Chem. Physics, Changchun Institute of Applied Chemistry, Changchun 130022, People's Republic of China

Mössbauer spectroscopy in Materials Science

J.C. Waerenborgh, E. Tsipis

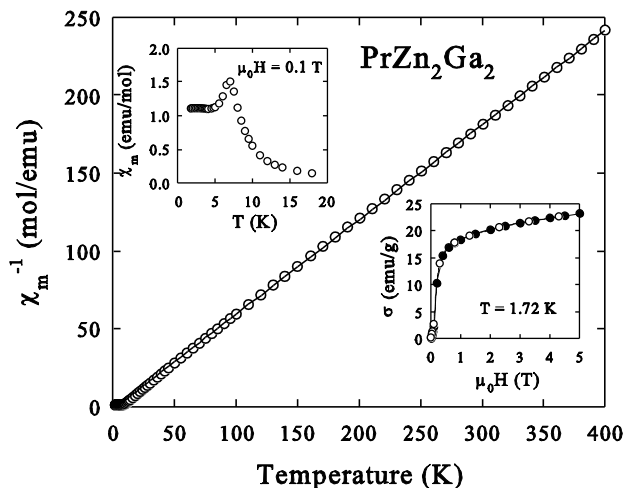
In 2010 the Mössbauer spectroscopy laboratory was kept running by one permanent and one post-doctoral researcher. This facility has been developed in ITN for 30 years and presently assists other national or foreign research institutions in the frame of joint research projects. In 2010 the application of the conversion electron technique in collaboration with CENIMAT/I3N, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa is emphasized. This study allowed the evaluation of the structure, phase composition and SnO/SnO₂ ratio on p-type tin oxide thin film transistors prepared in different atmospheres and annealed at different temperatures. The high performance of the films prepared in CENIMAT will enable the production of fully transparent metal oxide semiconductors, associated with all the main advantages offered by transparent/oxide electronics. Other studies have also been performed such as characterization of the Fe-containing phases in environmental samples, a calcrete profile on the top of a calcareous consolidate dune, on multifunctional magnetic materials obtained by insertion of a spin crossover Fe^{III} complex into bimetallic oxalate-based ferromagnetic lattices, on UFe_{2+x} Laves phases prepared by ultrafast cooling in collaboration with the Univ. of Valencia, Spain; Charles University, Prague, Czech Republic; Dept. of Physics, Florida State University, USA.

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. Sérgio, M. Almeida, L. Havela¹, O. Tougaard², H. Noël²

The understanding of the magnetic and strongly correlated electron behaviour of intermetallics containing *f*-elements, in particular the role of the *f*-orbitals, has been the major subject of a long-term project in the Solid State group.

The study of the U₂Fe₃Ge compound was continued in 2010 in order to identify the origin of the magnetic ordering. High-pressure X-ray diffraction measurements evidence no structural transition up to 25 GPa. Electrical resistivity measurements under pressure show that the Curie temperature decreases with the increasing pressure. The observed behaviour is similar to that observed in the UNi₂ and UFe₂ Laves phases, pointing to an itinerant magnetism for U₂Fe₃Ge. Novel RZn₂Ga₂ (R= La, Ce, Pr, Nd, Sm) intermetallics have been synthesized and their crystal structures and magnetic properties were characterized. All compounds crystallize in the tetragonal BaAl₄ type structure. The CeZn₂Ga₂ compound remains paramagnetic down to 1.7 K but the Pr-, Nd- and Sm-based intermetallics order antiferromagnetically at low temperatures, with likely contribution of some ferromagnetic components.



¹ Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, 12116 Prague, Czech Republic.

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

New materials for thermoelectric applications

E.B. Lopes, A.P. Gonçalves, G. Delaizir¹, O. Rouleau¹, C. Godart¹

The identification, preparation and characterization of new thermoelectric systems with high figure of merit are of fundamental importance to their potential application in environment friendly energy applications. During 2010 we continued the studies on 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) and started to explore the glasses in the Cu-Te-As system. Our preliminary results show that the melt spinning technique allows us to extend the Cu-Te-As glassy domain and leads to T_g values that permit the use of these glasses in applications up to 100°C. A maximum S²/ρ value of ~100 μW K² m⁻¹ was obtained for the Cu₃₀As₁₅Te₅₅ composition, a power factor twice that of the best value obtained for the Cu-Ge-Te system and at a much lower cost of As compared to Ge. Further work is on the way to make bulk glass for these systems, more suitable for practical applications purposes.

¹ Lab. de Chimie Metallurgique des Terres Rares, ISCSA-CNRS UPR209, F- 94320 Thiais, France.

Superconductivity in TiNiSi-type structure compounds

A.P. Gonçalves, J.C. Waerenborgh, L.C.J. Pereira, E.B. Lopes, M.S. Henriques, M. Almeida, L. Havela¹, O. Tougaard², H. Noël², J.S. Brooks³, A. Kiswandi³, E. Steven³

The coexistence of superconductivity and ferromagnetism in UGe₂, UIr, URhGe and UCoGe is an hot topic which raised the question about the dominant mechanism responsible for the pairing. Both URhGe and UCoGe belong to the uranium family of compounds with TiNiSi-type structure and it is expected that a similar behaviour can exist in analogous compounds.

Electrical transport measurements were performed on a UFeGe sample. Superconductivity was observed at T_C ~ 1 K, with a critical field > 4 T. However, SEM observations show that the sample has several phases and EDS measurements indicate Zr as impurity. Therefore, Zr-Fe alloys, which become superconductor below 1 K, can be the reason for the observed superconductivity and further studies are need to determine the its origin.

¹ Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, 12116 Prague, Czech Republic.

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

³ National High Magnetic Field Laboratory, USA.

High magnetic field facility*E. B. Lopes, A. Casaca¹, M. Almeida*

The ITN high magnetic field facility permits the study of electrical transport properties under magnetic fields with different orientations up to 18 T and for temperatures in the range 0.3-300 K, using both AC and DC techniques. During 2010 the 18T cryostat was used to pursue the research activities in different magnetotransport characterisation projects with emphasis on heavy fermion and non-Fermi liquid behaviour in intermetallics.

Several intermetallic compounds were characterized: In the continuation of the study of the interesting itinerant ferromagnet U_2Fe_3Ge this material was measured as a single crystal, and it was found a sharper transition in the resistivity at the Curie temperature T_C followed by a Fermi Liquid behaviour at low temperatures; $U_3Fe_4Ge_4$ which from the coefficient of T^2 dependence of the resistivity at low temperature was found to be a moderate heavy fermion; $U_9Fe_7Ge_{24}$ compound that is metallic, nonmagnetic and follows the expected Bloch-Gruneisen law; and some members of the $YbZn_xGa_{4-x}$ family of compounds that are also nonmagnetic and follow the expected Bloch-Gruneisen law for the resistivity at low temperatures.

¹ Inst. Superior de Engenharia de Lisboa, Lisboa, Portugal.