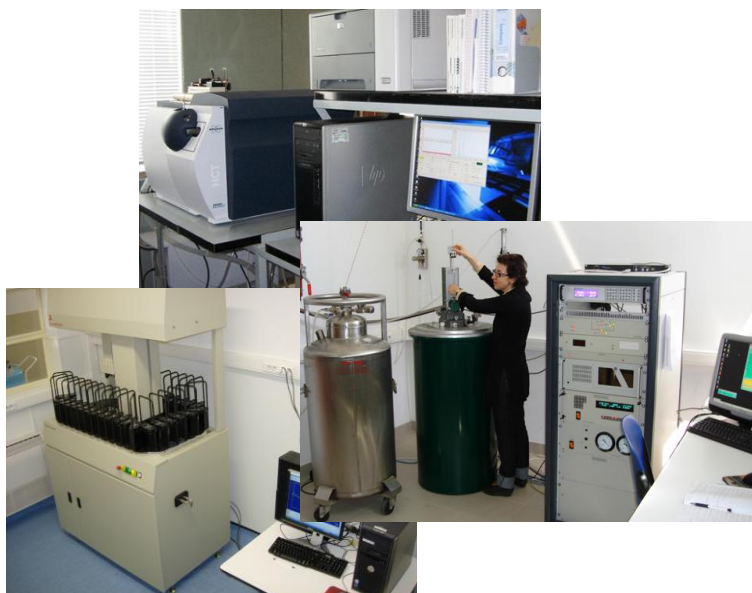


Chemistry Sector



Chemistry

Maria de Fátima Araújo

The policy followed at the Chemistry Department was the reinforcement of its competence skills on: the synthesis and characterization of inactive and radioactive compounds with relevance in Health, Materials and Nuclear Sciences and Catalysis; and the implementation and use of nuclear-based and related analytical techniques to Environmental and Earth Sciences and Cultural Heritage.

Activities are organized in five research teams:

Solid State – the group centres its research activity in complementary areas of solid state science focused on new materials with unconventional electrical and magnetic properties. It combines a high expertise on preparative chemistry of molecule based conducting and magnetic materials and of intermetallic compounds with a wide range of specialized solid state techniques. The expertise in high temperature preparation techniques allowed an industrial contract to be carried out with nuclear fuel industry.

Inorganic and Organometallic Chemistry – the activities of the group comprise the synthesis, characterization and chemical reactivity studies of inorganic, organometallic and intermetallic compounds of actinides and lanthanides aiming at understanding the influence of the electronic structure of these elements in the chemical properties of their compounds. Studies using the new ESI/QITMS facility were initiated and several ionic species generated from thorium, uranyl and lanthanide nitrates were characterized in the gas phase.

Inorganic and Radiopharmaceutical Chemistry – The group is involved in basic/applied-oriented research and technology transfer to find radioactive probes for molecular imaging and/or targeted radiotherapy. Research is based on innovative organic and coordination chemistry, bioconjugation, radiochemistry, radiopharmacy and cellular biology. Some of the major achievements were the implementation of a new technique - Western Blot and the selection of the ISATechII complex by a

pharmaceutical company to enter into clinical evaluation as a myocardial imaging probe.

Environment and Analytical Chemistry – the group is committed to the comprehension of the biogeochemical cycles of chemical elements and light isotopes in the Environment. Nuclear-related analytical techniques, mass spectrometry for light isotopes, tritium and radiocarbon dating are applied in: Environmental Geochemistry, Isotope Hydrology, Oceanography, and Archaeometry. Studies on coastal upwelling, coastal palaeoenvironmental evolution, water resources, radiocarbon dating and archaeometallurgy were pursued and strengthened.

Cultural Heritage and Sciences – research team is especially dedicated to the study of Portuguese cultural assets and corresponding environment contexts, through the application of nuclear analytical methods and absolute dating. Geochemistry, mineralogy and chronology are the main research domains, applied to archaeometry, environmental geology and palaeoenvironmental reconstruction. Luminescence laboratory activities have progressed to new research projects in archaeometry and geology.

During 2007 some laboratories were rebuilt and new facilities/equipments installed. Under the National Scientific Infrastructure Programme, an OSL dating reader system with a dual laser single grain OSL attachment, a gamma Spectrometer with automatic sample changer, a SQUID magnetometer and an ESI/QITMS (part of the National Mass Spectrometry Network) were installed and put in operation. Besides, a HPLC coupled with an ICP/MS were purchased.

Chemistry researchers maintained its recognized tradition on high level education and training by student's supervision (MSc, PhD and Post-doc) and participation in advanced training activities.

National and international projects financed by the FCT and EC most with the scientific coordination of the Department are in progress. Further funds were obtained by Protocols, Contracts and Services with different Institutions and Industries.

Chemistry Staff

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Cultural Heritage and Sciences

M. Isabel Prudêncio

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

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

The CHS research activities during 2007 were developed as follows:

- Portuguese clays: geochemical and mineralogical characterization with a view to technological applications
- Luminescence applied to dating geological and archaeological contexts and artefacts
- Luminescence applied to faiences and porcelains: Dating, authenticity, materials, pigments
- Archaeometry of ceramic, metal and lithic materials
- Geochemistry of the earth surface: natural background and evaluation of anthropogenic inputs
- Nuclear methods of analysis: development and application of luminescence techniques and neutron activation analysis

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

The application of these methodologies unique in Portugal, is crucial for solving archaeological and geological problems. The research is developed

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

This group is specialized in trace-element analysis and geochemistry (i.e., geochemical fingerprinting) and mineralogy of geological and archaeological materials. We are an archaeometrically oriented lab in Portugal with powerful analytical techniques in a single location. We also support geochemical research mainly concerning superficial environments, related with weathering and sedimentary processes, as well as environmental studies.

Research of CHS group also comprises luminescence techniques applied to archaeology and geology, including the study of natural radioactivity. The luminescence laboratory has incremented the number of financed research projects in geology and archaeology: (i) coastal dunes and fluvial sediments; (ii) archaeological contexts; (iii) dating and authenticity of pottery from various chronologies (from pre-historical to contemporaneous materials).

Under the National Scientific Infrastructure Programme, an automated combined TL/IRSL/Blue-light OSL dating reader system, Risø TL/OSL-DA-15C/D, with a dual laser single grain OSL attachment, and a Integrated Gamma Spectrometer with automatic sample changer were installed and are fully running, increasing the analytical capabilities of the group.

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

Research Team

Researchers

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M. I. DIAS, Invited Aux.

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L. PENG, MSc student
A. CALADO, MSc student
P. FRANCISCO, graduation student

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R. MARQUES
D. FRANCO
G. CARDOSO

Collaborators

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

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

M.I. Dias, M.J. Trindade, R. Marques, M.I. Prudêncio, D. Franco, M.A. Gouveia, F. Rocha¹

The characterization of clay raw materials from the Meso-Cenozoic southern and western borders of Portugal was performed using three approaches: granulometric, mineralogical and geochemical. The study of the behaviour of raw materials with firing (at temperatures from 300 to 1200° C) was also performed in laboratory experiments simulating the ceramics manufacture process, in order to enable future archaeometric studies. The main goals are: (i) better understanding the mineralogy and geochemistry of sediments, particularly of clayey levels, and (ii) a more detailed knowledge of the distribution of trace elements, namely rare earth elements (REE), in sediments and their correlation with mineralogy, particularly the clay minerals.



Fig. 1. Bustos clay pit in Aveiro region (Upper Cretaceous level of the occidental border)

Mineralogy allowed distinguishing different types of materials, as well as a better understanding of the paleoenvironment and evolutionary history of the depositional environments. Elemental composition and ratios of immobile elements of both felsic and mafic sources contribute to establish the origin of the deposits, the degree of chemical weathering and the recycling of material coming from the upper continental crust. The major elements, certain trace elemental ratios (Th/Sc, Zr/Sc, La/Sc) and the rare earth elements patterns showed variations on sediments source areas and have evidenced the importance and responsibility of weathering, sedimentary calibration and diagenesis processes on the variation observed among and inside groups. After Sc normalization, it was possible to evaluate the geochemical nature of different units.

Temperature-induced mineralogical transformations of Algarve region clays were found to be dependent on the composition of the materials, particularly the type and content of carbonates (calcite and dolomite).

Detailed studies of fine fractions allowed identifying the trace elements incorporated in clay minerals by absorption / adsorption and/or substituting major elements.

The results obtained enabled to establish geochemical and mineralogical reference groups and fingerprinting clay raw materials, essential for contemporaneous and ancient ceramics applications.

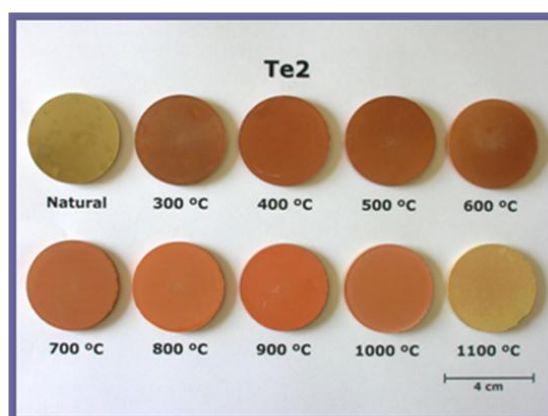


Fig. 2. Probes of powdered clay sample after firing at different temperatures.

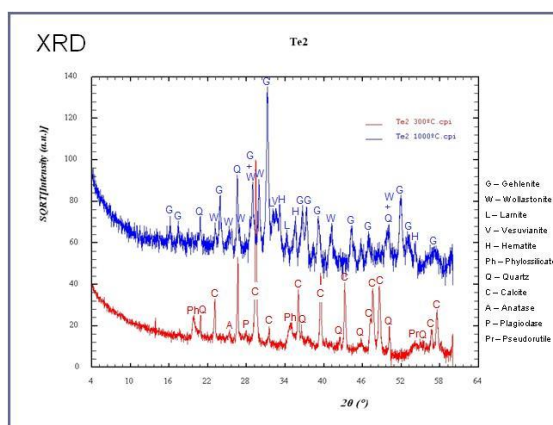


Fig. 3. XRD patterns of fired clays (300°C and 1000°C)

Published work:

M. I. Dias, M. I. Prudêncio (2007), On the importance of using scandium to normalize geochemical data preceding multivariate analyses applied to archaeometric pottery studies, *Microchem. J.* (2007), 136-141, doi:10.1016/j.microc.2007.11.009

¹ Univ. Aveiro

Optically stimulated luminescence applied to dating geological and archaeological contexts

M.I. Dias, M.I. Prudêncio, D. Franco, G. Cardoso, R. Marques, D. Mosquera¹, J. Sanjurjo¹, L. Rebelo², A. Martins³, L. Osterbeek⁴



An international intercalibration was done in order to validate analytical methods and results comparability, including uncertainties about luminescence mechanisms, measures reproducibility and precision, sample heterogeneity, humidity content and nuclide migration. In the case of a climbing dune, results on grain variations in burial dose rates were mainly due to spatial heterogeneity of radioisotopes contributing to the β -dose field and to non-uniform shielding of grains from relatively low activity. The effect of such heterogeneity is an increase in the scatter of equivalent dose values. The application of OSL to geology has contributed to a better knowledge of the Quaternary climate change scenario, based on multi-proxy investigations of paleosols, sediments and dunes. The TL-OSL absolute dating of archaeological contexts and related artefacts (ceramics and lithics) contributes to a better definition of the chrono-stratigraphic sequence of human occupation.



¹ Instituto Universitario de Xeologia, Corunha, Spain

² IGM. INETI

³ Univ. Évora

⁴ Instituto Politécnico de Tomar, Portugal.

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

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

This project focus on Portuguese faience and Chinese porcelain produced for the Portuguese market (XVI to XVIII centuries), aiming to contribute for a better knowledge of chronology precision, identification and, if possible, differentiation of production centers and technologies of ceramic production, as well as to characterize surface coatings (glazes and pigments). The main methodological approaches are INAA and XRF for chemical characterization, along with XRD for phase identification.



Considering that another main goal consists in accurately dating the ceramics, also TL was done to pastes. TL has an important impact in the field of authenticity, contributing to well judge genuine and imitative objects. These approaches have contributed to ascertain chemical and mineralogical composition of pastes, to outline the technological features and to define the nature of coatings and pigments.



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⁴ CNRS, Musée du Louvre, Paris, France

“Material Cultural Science”: Dating and provenance of archaeological ceramics from the Portuguese and Spanish Guadiana basin

M.I. Dias, M.I. Prudêncio, R. Marques, D. Franco, M.A. Gouveia, G. Cardoso, A.C. Valera¹, C. Odriozola², V. Hurtado³, L. San Juan Garcia³

This research project concerns a more accurate chronology establishment of Copper Age ceramics, as well as, a detailed study of production technology and consumption of artefacts from the Portuguese and Spanish Guadiana basin archaeological sites, namely Perdigões, Porto Torrão, Monte do Tosco and Mercador, and San Blas, La Pijotilla, Palacio III and Molino Perdido, respectively. Methodology involved includes physical and chemical characterization techniques (INAA, XRF and XRD), AMS and luminescence dating techniques. Compositional groups and categorization of productions as well as ritual and votive patterns were established. An important correlation between compositional grouping and the way these categories show a relationship with the spatial and chronological variations recorded in the use of archaeological materials was obtained.

¹ Era Arqueologia S.A. Portugal

² ISCME, CSIC, Seville, Spain

³ Univ. Seville, Spain

Archaeometry of ceramic, metal and lithic materials

M.I. Dias, M.I. Prudêncio, M.A. Gouveia, D. Franco, R. Marques, A. Jorge¹, P. Day¹, C. Capitão-Mor², P. Francisco², F. Rocha³

Nuclear methods of analyses were applied to several archaeometry studies, including ceramics, metal and lithic artifacts. The technological procedures during the manufacture process of making ancient pots, and its provenance were established for pre-historic ceramics from settlements and necropolis contexts of Beira Alta archaeological sites, contributing to a better understanding of continuities or innovations in ceramic production in a diachronic point of view.



Similar studies were done to other chronologies and regions, such as the Islamic ceramics from Silves, Algarve. Also ceramic and lithic raw materials resources exploitation strategies at local/regional scale were studied for several national archaeological sites, like silex artifacts characterization from Lisbon region.

¹ University of Sheffield – Department of Archaeology and Prehistory, England; ² Univ. Aveiro

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. Fabião¹, S. Gabriel², M. Coelho², I. Filipe²

This project aims to understand one of the most important economic activities of the coastal areas of the former Roman Province of Lusitania, the salted fish and *salsamenta* production, exported in amphorae to other areas of the Roman Empire. By the study of the archaeological site “Casa do Governador da Torre de Belém” (Tagus estuary) and related contextual evidence, the aim is to provide a solid understanding of its organization and chronology. The archaeozoological study is done with a view to better understand the nature of the products and the kind of fishing activity involved. The archaeometric approach, using the ITN database of Lusitanian amphorae production centers, aims to identify the amphorae production center that supplied that fish industry. This running project also makes available data that can be used by researchers working in other areas of the Roman Empire, contributing to the establishment of the final destination of the Tagus estuary products.

¹ Fac. Letras, Univ. Lisboa; ² Era Arqueologia S.A. Portugal

Geochemistry of the Earth surface: natural background and evaluation of anthropogenic inputs

M.I. Prudêncio, M.I. Dias, R. Marques, D. Franco, M.J. Trindade, J.C. Waerenborgh¹, F. Ruiz², M. Abad², V. Cruz³, M.O. Oliveira⁴

Geochemistry, crystal chemistry and mineralogy studies are applied to environmental projects. The expertise on geochemistry of the earth surface of CHS group researchers enables a detailed and complete overview in this kind of studies, with the characterization of the natural background and the evaluation of anthropogenic inputs. The CHS running projects, concerning the quality control and identification of pollutants of geological environments, refer mainly to lagoon environments. The geochemistry of the earth surface, particularly the geochemistry of trace elements in secondary natural systems, and the alterations due to pollution actions in sediments and soils, was applied to two case studies: the “Lagoa das Sete Cidades”, Açores, Portugal and the “El Melah” lagoon, Tunisia.



¹ Solid State Group, ITN; ² Univ. Huelva, Spain; ³ Univ. Açores; ⁴ Fac. Ciências, Univ. Lisboa

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

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

The luminescence and neutron activation laboratories were reinforced with new equipment on behalf of the national Re-equipment Program by FCT (CONC-REEQ/590/2001).

Instrumental neutron activation analysis is a well-established method within this group since the seventies. Based on the use of the RPI (nuclear research reactor unique in the Iberian Peninsula), this analytical method together with luminescence techniques (complemented with other methods) supports most of the research activities of the CHS group. Public and private institutions often requested CHS group for services of both laboratories. The quality of the analytical procedures of INAA is periodically controlled through the analyses of international standards and inter-calibrations with other laboratories, in order to maintain and increment the good performance of the laboratories. The Luminescence Dating Laboratory participates in international comparisons, particularly with the Musée du Louvre (CNRS), France and IUX, Spain.

Environment and Analytical Chemistry

Maria de Fátima Araújo

Activities within the Environment and Analytical Chemistry Group mainly involve the study of the Biogeochemical Cycles of Chemical Elements and Light Isotopes in the Environment. Our expertise is in the fields of **Instrumental Analytical Chemistry**, **Environmental Geochemistry**, **Isotope Hydrology**, **Oceanography**, **¹⁴C Dating** and **Archaeometallurgy**.

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

During the current year the clean laboratory for the ICP-MS (Inductively Coupled Plasma Mass Spectrometer) for isotopic and trace element research, financed by the “*Programa Nacional de Re-Equipamento Científico*” was installed. Also, a laboratory dedicated to the sample preparation for AMS (Accelerator Mass Spectrometry) measurements is underway.

Environmental Geochemistry and **Oceanographic** research was developed under a multidisciplinary approach, including sedimentology, geochronology, absolute dating, meteorology and paleoecology. Research was focused in Sedimentary Geochemistry: to evaluate environmental changes (natural and man-induced) occurred during the Holocene on the Portuguese coastal area. Moreover, studies concerning the marine reservoir effect off the W margin of Iberian Peninsula, based on **Radiocarbon Dating** of pairs of samples (terrestrial and marine) allowed the study of the variability of the coastal upwelling off Atlantic Iberia during the Holocene and its correlation with palaeoclimatic change.

Isotope Hydrology research studies were implemented taking into account the sustainable regional development and the appropriate use of the water resources and coastal management based on several European and national directives. Investigations in different environments namely: Urban Areas; High Mountain Areas; Arid and Semi Arid Zones and Gas Geochemistry in CO₂-rich Thermomineral Waters, were reinforced. Besides, a new research area was initiated on the contribution of environmental isotopes hydrology to the geothermal potential evaluation and the seismo-volcanic hazard assessment at Azores archipelago. Their characterisation is being addressed to the exploitation and future development of regional water resources and the delimitation of protection areas.

Further works in **Archaeometallurgy** were implemented on the characterization of the technological and social conditions of Copper and Bronze Age metal production and circulation in Portugal. Cu and Au-based artefacts collections from the N and SW archaeological sites have been studied. Corrosion processes in archaeological Cu-based materials and surface enrichment processes were also investigated using optical metallography, micro-fluorescence and scanning electron microprobe. A study of the largest Portuguese collection of Cu-based Chinese coins was initiated in order to infer about its authenticity and the metallurgical development that they represent in its relation with the economic History of China. The EAC group is highly engaged in education and training of students from different Universities preparing their MSc and PhD thesis under our supervision.

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

Research Team

Researchers

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P. ALVAREZ-IGLESIAS, Post-Doc., FCT grant

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Environmental Geochemistry – Elemental and Isotopic Research

*M.F. Araújo, P. Carreira, A.M. Monge Soares, P.G. Fernandes, C. Correadeira,
P. Alvarez-Iglésias, D. Nunes, P. Valério, R. Cardoso, J. Martins, A. Amaro, M. Correia*

Objectives

The development and promotion of coordinate research on Earth and Environmental Sciences by implementing analytical and absolute dating techniques:

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

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

- 1) to establish the evolutionary patterns of coastal environments since the Holocene; identify sediment sources and evaluate the major driving factors controlling its distribution and composition; setting up regional backgrounds and the beginning and origin of anthropogenic inputs;
- 2) to determine the origin of different groundwater systems, definition of recharge areas and in the identification of mixture between different water bodies; assess the vulnerability of groundwater to surface pollution; understand and determine the origin of pollution in hydric systems;
- 3) to assess the variability of the W Iberian coastal upwelling; identify episodes of abrupt shifts in oceanic circulation, probably coupled with abrupt climatic changes.

Results

Geochemical and dating studies carried out in shelf, estuarine and lagoon sediments revealed to be essential tools in the study of transitional and marine environments, providing indication about the marine/terrestrial origin of the deposited materials and allowing to recognise and evaluate changes occurred during the Holocene. During this year, studies were mainly focused on: the SW Iberian shelf sediments (Gulf of Cadiz); the Minho estuary; the SW coastal lagoons and salt marshes of the Lima, Tagus and Mira estuaries. Geochemical and geochronological studies demonstrate that SW Iberian shelf sediments exhibit signatures of a continental origin. Main sources of pollution were identified as the mineral wastes resulting from the ore exploitation along the Iberian Pyrite Belt. A clear record of the beginning of "pollution" was detected in shelf sediments coincident with the mining exploitation reactivation during the XIX century. Palaeoenvironmental analysis on the Holocene evolution in Portuguese coastal zone

(Minho estuary and SW lagoons) reveal the existence of several sedimentary units identified as sequences of fluvial, marine and estuarine facies. These correspond mostly to the Holocene record influenced by climatic changes. Geochemistry of salt marsh sediments of different estuaries has permitted the establishment of regional background levels and to derive the enrichment caused by man induced factors.

Environmental isotope techniques applied to Caldas de Manteigas Spa thermal waters show that the upper valley of Zêzere river, should be faced as a potential catchment area of this system, where the main recharge seems to occur laterally. Besides, the $\delta^{13}\text{C}$ of the CO_2 gas measured in the thermomineral waters (NE of Portugal) indicate a mantellic origin, supported by the $^3\text{He}/^4\text{He}$ ratio measured in the gas phase. Also, isotope methods have allowed the identification of pollution sources: natural, industrial, agricultural, and domestic respectively inside Santa Margarida Military Training Campus, at Porto urban area and within Aveiro and Beja regions. Agricultural practices and high industrial areas with over exploitation of the systems were identified as sources of pollution to the environment: sediment and hydrological domains.



Foto R. Cardoso

Radiocarbon dating has been used as a tool to set up chronological frameworks for the past environmental changes identified in our research. Besides this, the regional marine reservoir effect values, ΔR , for the 5th, 4th and 3rd Millennium BC were determined. Results enable a better clarification of the variability of the coastal upwelling off Atlantic Iberia, namely off western Portuguese coast. Also, a ΔR value was determined for an estuarine reservoir (of the river Tagus, near Muge, c. 7000BP), which allows a reliable and precise calibration of conventional radiocarbon dates from human skeletal material from the famous Mesolithic shell middens of Muge. Radiocarbon dating was also applied to aeolianite samples in order to set up a geochronologic framework to aeolian carbonate-rich sand deposits from the Lisbon region.

Geochemical record of environmental changes in the coastal zone (Portugal) since the Holocene*M.F. Araújo, C. Corredeira, P. Alvarez-Iglésias, S. Moreira¹, M.C. Freitas¹, C. Andrade¹, T. Drago²*

The overall objectives of this work are the recognition of the environmental changes (natural and man-induced) which have occurred during the Holocene and the prediction of those that are likely to occur in the future in selected areas of the Portuguese coast, by using a comprehensive study of the sedimentary record. Studies were focused in NW (Minho estuary), in the SW (wet dune slacks) coastal region and in the SW Iberian Continental Shelf. Sediment records of Minho estuary (~20 m long) were studied to establish stratigraphic succession of Holocene sediments. Geochemistry, in particular the elemental distribution in terrigenous (Si, Al, Fe and Ca) and palaeosalinity indicators (Cl and Br) has contributed to recognize the evolution of the northern area of Portugal since 18,000 years ago by identifying fluvial, marine and estuarine sedimentary facies. Sedimentological, geochemical and dating proxies of SW wet dune slacks (Poços do Barbaroxa and Lagoa da Sancha) allowed to establish major steps of coastal evolution, environmental changes and relations with sea-level throughout the Holocene. Results of textural analysis, organic matter and geochemistry (lithogenic and palaeosalinity indicators) have been used in the definition of 4 lithostratigraphic units and 3 sedimentary environments – marine, lagoonal and fluvial, in the last 10,000 years. At the SW Iberian continental shelf downcore profiles on elemental concentrations and sedimentation rates determined by the excess of ²¹⁰Pb pointed out to a register of the beginning of heavy metal pollution in shelf sediments (~200-250 years ago) coincident with the mining exploitation reactivation occurred in the region during the XIX century.

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Geochemical and sedimentological characterisation of salt marsh sediments from Portuguese estuaries (Lima, Tagus and Mira)*R. Cardoso, M.F. Araújo, M.C. Freitas¹, F. Fatela¹*

Salt marshes are transitional zones located along the intertidal estuarine region, characterized by low hydrodynamic conditions and an alluvial substrate which is colonised by halophyte vegetation acting as natural barriers which diminish the impact of floods and prevents coastal erosion. In these environments, the prevailing conditions favour the accumulation of metals and other contaminants in sediments. Salt marsh sediments collected along salt in 7 different settings areas of three Portuguese estuaries (Lima, Tejo and Mira) were characterized by using geochemical and sedimentological approaches, including elemental composition, organic matter, grain size, carbonates and pH determinations. Results demonstrated that samples from high marsh sectors are usually metal enriched, due to the bioaccumulation effect of vegetation. Heavy metals show an enrichment trend in fine fraction, and might also be related to organic matter. Seasonally there are differences in metal concentrations in sediments, as a result of the interaction between climate conditions, salt marsh productivity and metal accumulation by plants. Although some of the enrichment factors calculated have a natural origin such as the presence of specific geologic formations, others are the result of human impact on these environments. There are variations in sediment chemical compositions according to their sampling location in each estuary and significant differences are also found between the three studied estuaries.

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The marine reservoir effect off the western margin of the Iberian Peninsula*A.M. Monge Soares, J.M. Matos Martins, J.A. Alveirinho Dias¹*

Following previous research (see 2005 and 2006 ITN Reports), the sampling program increased during 2007 in order to get reliable ΔR values for the time interval 5000 BP – 3000 BP. It must be noted that this time interval corresponds to Late Neolithic, Chalcolithic and Bronze Age, cultural prehistoric periods that are object of an intense archaeological research by Portuguese archaeologists and, consequently, reliable and precise chronologies are needed. Also, during this time interval, i.e. after the Holocene Optimum, some climatic change is known that certainly will be reflected in the behaviour of the west Iberian coastal upwelling or in the marine reservoir effect values. Besides this research or in complement of it, a ΔR value was determined, for the first time, for the Mesolithic estuarine environment related to the famous and important shell middens of Muge. This ΔR value is different from the correspondent value determined for the open sea environment off the Portuguese western coast and allows the precise calibration of conventional radiocarbon dates from human skeletons discovered in these shell middens, since the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of bone collagen of the skeletons show a mixture of marine and terrestrial diets of the Mesolithic individuals.

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Using radiocarbon dating to test contemporaneity of aeolianite formation

A.M. Monge Soares, J.M. Matos Martins, A. Ramos Pereira¹

Several consolidated sand-dunes (aeolianites) of Late Pleistocene age are known along the south-western Portuguese coast, namely in the coastal region of Lisbon Peninsula. Praia Azul, S. Julião, Samarra, Magoito, Aguda, Praia das Maças and Oitavos are some of these aeolian sand deposits. For two of them, Magoito and Oitavos, reliable dates for their formation were determined. Magoito was formed during the Pre-Boreal, whilst the Oitavos aeolianite was generated during the last interstadial of OIS 3 (ca. 32000 BP). If it is postulated that the carbonate-rich sand that is deflated from the dune field to form the new aeolianite had an apparent radiocarbon age that is characteristic of that dune field at the time when the deflation occurred, then the radiocarbon dates obtained from samples collected at the aeolianite will indicate its relative chronology in relation with the aeolianites from the same region which ages are known. Samples from Magoito and Oitavos aeolianites, and also from S. Julião and Aguda aeolianites were collected in order to prove the postulate referred to above is correct and to determine their relative chronologies. Aguda and Magoito have the same apparent age (ca. 20000 BP), suggesting that Aguda is also of Holocene age. All the samples collected at different places at S. Julião have the same apparent age (ca. 40000 BP). Consequently, this aeolianite is probably of the same age of that of Oitavos.

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Hydrology in urban areas

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

In order to assess surface water / groundwater interaction in Porto urban area, several sampling campaigns were performed along the underground galleries excavated to conduct spring waters. Isotopic signatures from Paranhos spring collection chambers indicate that: i) samples collected along gutters present a homogeneous composition, ii) an isotopic depletion of about 1‰ in ¹⁸O and 7.5‰ in ²H was found, ascribed to groundwater samples collected from the granitic fractures. Coupled isotopic and geochemical signatures indicates that i) groundwaters collected along the gutters are meteoric waters infiltrated along the residual granitic soil; ii) groundwater samples from the granitic fractures could be ascribed to random precipitation events, resulting into a directly infiltration along the fissured granitic rocks. Besides this, geochemical and isotope techniques have greatly contributed to the assessment of the possible damage caused by the military training activities at Santa Margarida Military Camp, where environmental problems have been identified: in the Ervideira area, surface waters (from the stream) and shallow groundwaters (from the spring) present evidences of anthropic contamination. The results so far obtained indicate that the signatures of anthropic contamination found in the Military Camp are mainly the result of diffuse pollution ascribed to: some particular urban waste disposal, pasture ground, a small duck's lagoon, poultry farming and cattle breeding.



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Arid /semi arid zones hydrology

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

An evaluation of the groundwater systems at Santiago island (Cabo Verde) was carried out through the application of environmental isotopes and geochemical data in order identify: origin and mechanisms of groundwater recharge; relation between the hydrochemical evolution of the groundwater systems with the geological matrix (minerals dissolution) or mixture with seawater and aerosol marine influence; identification of seawater intrusion mechanisms and, determination of the apparent groundwater "age". The isotopic composition of the groundwater samples collect at Santiago Island range from -4.72 to -2.61‰ in $\delta^{18}\text{O}$ and from -44.6 to -15.8‰ in $\delta^2\text{H}$, with a mean isotope content of $3.80 \pm 0.53\text{‰}$ in $\delta^{18}\text{O}$ and $-26.6 \pm 5.8\text{‰}$ in $\delta^2\text{H}$ vs. V-SMOW. Two groups of groundwater samples are identified based on the $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Besides, at Esssaouira Basin (Morocco) a multidisciplinary approach has been applied to evaluate the hydrogeological potential of arid zones and environmental / climatic change. Considering the importance of the Esssaouira aquifer in the groundwater supply of the region, the study was conducted in order to comprehend this aquifer groundwater evolution.

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Groundwater resources assessment by anthropogenic and natural contamination sources

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

According to field practice the major cause of pollution in the rural area of Beja comes from fertilizers. The application of stable nitrogen isotopes ($^{15}\text{N}/^{14}\text{N}$ ratios) offers a direct way to identify the pollutant sources in groundwater systems. In the studied area two major sources of nitrate were identified, fertilizer and manure which present different isotopic $\delta^{15}\text{N}$ signatures. The relative contribution of these two sources to groundwater or surface water was estimated by mass balance. The analysis of nitrate $\delta^{18}\text{O}$ together with $\delta^{15}\text{N}$ improves the ability to trace nitrate sources and cycling. The isotope results are not conclusive about the possibility that major source of nitrate-N in groundwater comes from agriculture as expected. Also some studies performed at Aveiro region were carried out in order to use some isotope techniques to evaluate the aquifer vulnerability to nitrate contamination. Groundwater samples were collected from wells and springs for isotopic analysis ($\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ from NO_3 and $\delta^2\text{H}$ and $\delta^{18}\text{O}$ from H_2O). Nitrogen isotopes were used to identify nitrogen sources and assess agriculture, cattle-breeding, urban and industrial contribution to nitrogen cycle in Aveiro ecosystem, based on the fact that the main sources of nitrate in the area have isotopic distinct $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ signatures.

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High mountain areas in catchment water resources

P.M. Carreira, D. Nunes, J.M. Marques¹, J. Espinha Marques², H. Chaminé³

Sampling campaigns were performed at Serra da Estrela Natural Park to understand the i) recharge and discharge processes and ii) role of snowmelt as a source of groundwater resources. Preliminary geophysical studies (a 600m dipole-dipole profile with a dipole distance of 10m) were carried out in order to investigate one of the main potential recharge areas. The seasonal variation of the precipitation stable isotopic composition is reflected in the comparatively low δ -values in the snowfall, which will be reflected in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ contents of meltwater. This shift provides a very useful tracer signal for hydrogeological studies in mountainous areas. The recharge of the thermal waters was studied based on the spatial and temporal variability of the isotopic composition of water ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and ^3H). According to the isotopic gradient in the study area ($-0.10\text{‰}/100\text{m}$ of altitude) and considering the mean isotopic composition of the thermal waters ($\delta^{18}\text{O}_{\text{mean}} = -7.8\text{‰}$ vs. V-SMOW), the upper valley of Zêzere river, should be faced as a potential catchment area of this thermal water system, where the main recharge seems to occur laterally. The Bragança-Vilariça-Manteigas fault zone should play an important role in conducting the laterally infiltrated meteoric waters towards the discharge area at the Caldas de Manteigas Spa.

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Gas geochemistry in CO₂-rich thermomineral waters a contribution to the geothermal potential evaluation and the seismo-volcanic hazard assessment

P.M. Carreira, D. Nunes, J.M. Marques¹, M.R. Carvalho², G. Capasso³, F. Grassa³, J.C. Nunes⁴, P. Madureira⁵



In Portuguese mainland the most important $\text{HCO}_3\text{-Na-CO}_2$ -rich thermomineral waters issue in the Northern part of the country, within the Galicia-Trás-os-Montes region, linked to one of major NNE-trending faults, the so-called Penacova-Régua-Verin megalineament. From the interpretation of chemical and isotopic data, it is evident that the CO_2 -rich mineral waters are part of an open system to the influx of CO_2 gas from a source other than redox reactions. Isotopic data suggests that mantle-derived CO_2 is actively reacting with the groundwater. Stable carbon isotopic data indicate that the external CO_2 is of inorganic origin. The values obtained for the $\delta^{13}\text{C}$ of the CO_2 gas indicate a mantellic origin, supported by the $^3\text{He}/^4\text{He}$ ratio measured in the gas phase. Also, research at Azores archipelago studies are starting 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.

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Archaeometallurgy – Provenance, technology and use of metallic artefacts

M.F. Araújo, P. Valério, E. Figueiredo, A.M.M. Soares, R. Silva¹, J.C. Senna-Martinez², L.C. Alves³

This research combines analytical and archaeological investigations regarding metallurgical activities during the Copper, Bronze and Iron Ages. Metallic artefacts and metallurgical remains (e.g. ores, crucibles and slags) are being characterized by EDXRF, micro-XRF, micro-PIXE, optical metallography and SEM-EDS. The obtained results are integrated with the archaeological evidence in order to resolve specific archaeological issues. In the current year, the research regarding the Southwest Region included the study of gold buttons from Castro dos Ratinhos (Early Iron Age), which present a homogeneous alloy composition and exhibit silver and copper contents within the characteristic EIA values ($10\% < \text{Ag} < 20\%$ and $\text{Cu} > 1\%$). The welding process used is still under study – no solder was identified, which might indicate solid state diffusion welding, a process still not identified in such an early period of the Iberian Peninsula. Copper ores with tin impurities and a mould for flat axes with Cu, Sn and Pb enriched in the carving, all from Casarão da Mesquita 3, attest the practice of the bronze metallurgy during Late Bronze Age at this site. Regarding the Central Portuguese Region, metallurgical productions from Fraga dos Corvos and Canedotes (Late Bronze Age) were found to be made of bronze alloys ($8\% < \text{Sn} < 14\%$) with low lead contents ($< 2\%$). The microstructures of the studied artefacts exhibit sulphide inclusions and establish the use of thermo-mechanical operations that finished either with annealing or mechanical deformation processes.



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Characterization of an ancient Cu-based Chinese coin collection

M. João Furtado, M.F. Araújo, R. Silva¹

Almost four hundred Chinese copper cash (round coins with a square centred hole) part of the collection of the Macao Scientific and Cultural Centre’s Museum (Lisbon, Portugal) are being studied in order to characterize their alloys and main superficial corrosion products. Although the opening question was whether the coins were official or counterfeit, because of their unknown source, soon other issues arose. So far, the coins were analysed by Energy Dispersive X-Ray Fluorescence, a non-invasive analytical technique, which permitted to obtain some interesting results: the presence of very heterogeneous alloys - bronzes up to the 14th century and mostly brasses after that – almost all of them with high lead percentages, possibly because lead was available and cheaper than copper or tin/zinc. Iron and nickel, are present in considerable percentages, and this could be an indication that the alloys may be ancient. Also, it was found that in coins with substantial superficial corrosion products there was commonly an elemental variation between the obverse and reverse. The correlation between obtained analytical information and similar existing or on-going studies, both analytical and historical ones, will increase the knowledge of the Chinese monetary system. Furthermore, the study will also focus on the metallurgy development in China and as such, contribute to the understanding of Chinese technologic and economic History.

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Radiocarbon dating applied to archaeological contexts – building up the South-western Bronze Age Chronology

A.M. Monge Soares, J.M. Matos Martins

Since the beginning of the radiocarbon laboratory, twenty years ago, one of its important tasks has been to build up reliable and precise prehistoric chronologies in closed cooperation with archaeologists. Nevertheless, some cultural periods still fall short of absolute dates that allow a reliable chronology for their phases and sub phases. It is the case for the Bronze Age of the South-western Iberian Peninsula. Recent mitigation works, as a result of Environmental Impact Assessments related to the Alqueva Dam Project, have been carried out by archaeological companies that led to the discover of several Bronze Age settlements and burials. These archaeological contexts, at first sight, seem to be largely diachronic belonging to different cultural phases from Early to Late Bronze Age. Organic samples, i.e. charcoal and bones, have been recovered after archaeological excavations that will allow a good precision and reliability for the chronologies that are actually in process of building up. It must be stressed that this is possible because the excellent cooperation that exists between the radiocarbon laboratory and the archaeological companies and archaeologists that dug or are digging those prehistoric and protohistoric settlements.

Inorganic and Organometallic Chemistry

Noémia Marques and Joaquim Marçalo

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

Relevant facilities maintained by the Group are a laboratory for handling macroscopic quantities of the more radioactive actinides, a laboratory for catalytic studies, prepared for work with CO, a laboratory for calorimetric studies and thermal analysis, and two select mass spectrometers, a Fourier transform ion cyclotron resonance (FTICR) instrument, equipped with electron ionisation (EI) and laser desorption/ionisation (LDI) sources and a quadrupole ion trap (QIT) instrument, equipped with electrospray ionisation (ESI) and atmospheric pressure chemical ionisation (APCI) sources. The QIT mass spectrometer was acquired with the support of the "National Program for Scientific Hardware Renewal" of FCT and is part of the National Mass Spectrometry Network.

FTICR/MS studies were pursued and the first gas-phase synthesis and characterization of mono and polymetallic uranium oxide anions was achieved via LDI of ammonium uranate. The structures of these new uranates were probed by collision induced dissociation (CID) experiments and by reactivity studies with methanol. QIT/MS studies using ESI were initiated and several ionic species generated from thorium, uranyl and lanthanide nitrates in water/methanol solutions were characterized in the gas-phase by CID and condensation reactions with the solvent molecules.

A collaboration study with FCUL and ITQB, using the FTICR/MS facility, doubtless concluded that non protic ionic liquids in the gas-phase behave as neutral ion pairs in opposition to the behaviour of protic ionic liquids. This fact supports the possibility to fractionally distil ionic liquids and will lead to new studies on alkali-metal ionic liquids that reveal a completely unexpected behaviour in a new project supported by FCT.

Studies on the reactivity of yttrium, samarium and uranium complexes with the mono-functionalized tacn ligand [O(3,5-tBu₂Ph)}-tacn(¹Pr₂)] continued. Alkyl and silyl derivatives of yttrium complexes supported by the bis(phenolate)diamine ligand (^tBu₂O₂NN'([Me₂N(CH₂)₂N{CH₂-(2-OC₆H₂-Bu¹₂-3,5)₂}]]) showed to be very active catalysts for the polymerization of ε-caprolactone. Multicoordinate ligands for actinide/lanthanide separations were explored and were the subject of a MSc thesis presented at IST in October 2007.

Pursuing previous work, studies of CO₂ as C1 feedstock were performed, namely through the selective oxidation of methane (OCM reaction) on UFe₂, UFe₂Sn and UFe₅Zn₇.

The collaboration with the Radiation Technologies: Processes and Products Group (Physics Sector) in the study of the gamma radiation effect on several waste water sources was pursued. The collaboration with OMNIDEA, Lda., a start-up company dedicated to R&D of aerospace technology and energy systems continued and a ITN-OMNIDEA cooperation protocol was established.

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

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

Research Team

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Gas-Phase Ion Chemistry of Actinides and Lanthanides

J. Marçalo, A. Pires de Matos, J. P. Leal, M. Santos, J. K. Gibson¹, R. G. Haire¹

Objectives

The gas-phase chemistry of atomic and molecular actinide and lanthanide ions is studied in order to obtain mechanistic, kinetic and thermodynamic information that can be correlated with the electronic structures of the ions and compared with data from condensed phases. The experimental work is based on the use of advanced mass-spectrometry techniques, namely, Laser Desorption/Ionization Fourier Transform Ion Cyclotron Resonance MS (LDI-FTICR/MS) and Electrospray Ionization Quadrupole Ion Trap MS (ESI-QIT/MS). For the actinides, the specific aims are to produce novel species with new ligations and properties, to probe the participation of the 5f electrons in chemical bonding in the first half of the series, and to estimate thermodynamic data for species that may be of interest for condensed-phase processes. Parallel theoretical studies of selected actinide molecular ions are also carried out via collaborations to substantiate the interpretation of the experimental observations.



FTICR mass spectrometer

Results

The FTICR/MS studies of the chemistry and thermochemistry of atomic and molecular actinide ions done in recent years in our laboratory were summarized [1]. A highlight of the work, the first combined experimental and theoretical demonstration of the active role of 5f electrons in organoactinide chemistry, was described in detail [2].

On the experimental side, FTICR/MS studies were pursued and the first gas-phase synthesis and characterization of mono and polymetallic uranium oxide anions was achieved via LDI of ammonium uranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$ [3]. The new species, which can also be considered members of the uranate family, had the general formulas $\text{U}_x\text{O}_{3x}^-$, where $x = 1-6$, $\text{U}_x\text{O}_{3x+1}^-$, where $x = 1$, and $\text{U}_x\text{O}_{3x-1}^-$, where $x = 3-8$. The structures of these new uranates were probed by collision induced dissociation experiments and by reactivity studies with methanol. The mechanisms of the sequential reactions with methanol were studied in detail using $\text{C}^2\text{H}_3\text{OH}$ and $\text{CH}_3^{18}\text{OH}$. Most notably, in the case of UO_3^- , formation of an elusive hydride species with formula $\text{UO}_2(\text{OH})\text{H}^-$ was observed;

theoretical studies performed by M. D. C. Michellini and N. Russo at the University of Calabria confirmed the hydride structure. In the reactions of the anionic clusters, addition of up to three methoxide ligands per U atom was observed; this gas-phase reactivity of polymetallic uranates mimics the condensation of methanol on uranium oxide surfaces (J. A. Lloyd, W. L. Manner, M. T. Paffett, *Surf. Sci.* 423 (1999) 265-275).



QIT mass spectrometer

A new QIT mass spectrometer was installed in the Actinide Chemistry laboratory. It was acquired with the support of the “National Program for Scientific Hardware Renewal” of FCT and is part of the National Mass Spectrometry Network. This instrument is equipped with atmospheric pressure ion sources, ESI and APCI, which allow the study of ions in solution. Several experiments with thorium, uranyl and lanthanide nitrates in water/methanol solutions were performed, which included the gas-phase characterization of several ionic species by collision induced dissociation experiments and condensation reactions with the solvent molecules.

Published work

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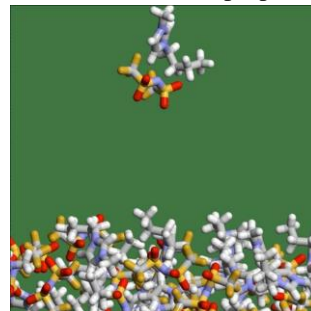
Molecular Energetics of Organic, Inorganic and Organometallic Compounds

J.P. Leal, T. Almeida Gasche, C. Hipólito, M. Faddoul, R. Simões, M.T. Fernandez¹, P. Madeira¹, M. Minas da Piedade¹, J.A. Martinho Simões¹, R. Borges Santos¹

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

During 2007, all enthalpies of formation published for CH and CHO compounds were critically revised and used to improve an extended Laidler method of additive contributions. An *on-line* database with all these values is in progress. New routes for fluoroapatite synthesis were explored and their thermal and structural properties studied. The determination of the enthalpies of formation of several polyalkoxides, $M_x[O(CH_2)_nO]_y$ ($n=2-8$, $x=1$, $y=1$ or $x=2$, $y=3$) with alkaline-earth and lanthanides began, being one of the calcium compound already synthesized. Also, new studies on the gas-phase acidity of substituted phenols were undertaken using FTICR/MS.

A collaboration study with FCUL and ITQB, using the FTICR/MS facility, doubtless concluded that non protic ionic liquids in the gas-phase behave as neutral ion pairs in opposition to the behaviour of protic ionic liquids. This fact supports the possibility to fractionally distil ionic liquids and will lead to new studies on alkali-metal ionic liquids that reveal a completely unexpected behaviour in a new project supported by FCT.



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f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands

M. A. Antunes, B. Vieira, J. Cui, J. M. Carretas, N. Marques, A. M. Martins¹

The search for renewable, biodegradable polymers has increased in recent years. In this context, we have been investigating the catalytic activity of lanthanide complexes supported by the bis(phenolate)diamine ligand ($^{tBu_2}O_2NN'$ ($[Me_2N(CH_2)_2N\{CH_2-(2-OC_6H_2-Bu^1-3,5)_2\}]\})$) in the polymerization of cyclic esters. The complex $[YCl(O_2^{tBu_2}NN')(DME)]$, and the silyl $[Y(^{tBu_2}O_2NN')(N(SiMe_3)_2)]$ and alkyl $[Y(^{tBu_2}O_2NN')(C_6H_4CH_2NMe_2)]$ derivatives have been synthesized. Both derivatives showed to be active catalysts for the polymerization of ϵ -caprolactone giving 100% conversion. In contrast the samarium analogues were not active. This result was understandable when we found that the attempted preparation of the corresponding silyl and alkyl derivatives of $[Sm(^{tBu_2}O_2NN')Cl]_x$ resulted in formation of the bimetallic compounds $[Sm(^{tBu_2}O_2NN')_2]M$ ($M = Li, K$), that are completely inactive in the polymerization of ϵ -caprolactone.

Studies on oxidative chemistry of the f-elements with nitrogen donor ligands continued. (A. Domingos, I. Lopes, J. C. Waerenborgh, N. Marques, G. Y. Lin, X. W. Zhang, J. Takats, R. McDonald, A.C. Hillier, A. Sella, M.R.J. Elsegood, V.W. Day, *Inorg. Chem.* **2007**, *46*, 9415-9424; M. A. Antunes, PhD thesis, FCUL, Feb. 2007). Multicoordinate ligands for actinide/lanthanide separations were explored (B. J. C. Vieira, MSc thesis, IST, Oct. 2007).

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f-Block Element Intermetallic Compounds as Catalysts

J. Branco, A. P. Gonçalves¹

Intermetallic compounds of lanthanide or actinide metals combined with d metals have been found to be active in a variety of reactions. The main objective of this project is (i) to make a systematic study of the f block elements behavior as catalysts or catalytic precursors and (ii) to develop new methods for the preparation of 4f and 5f nanostructured materials for catalytic purposes.

Pursuing previous work, we have studied the oxidative coupling of methane (OCM reaction) on UFe_2 , UFe_2Sn and UFe_5Zn_7 using CO_2 and CH_4 as C1 feedstocks. Preliminary results at 850 °C indicate that, at isoactivity, the selectivity to C2 ($C_2H_4+C_2H_6$) and the selectivity to C_2H_4 is higher on the ternary compounds, e.g. selectivity C2 / C_2H_4 , 36 / 33 % on UFe_2 and C2 / C_2H_4 , 58 / 58 % on UFe_5Zn_7 .

¹ Solid State Group, Chemistry Sector., ITN.

Glass Science with Applications in Radioactive Waste Vitrification, Archaeometry and Art Studies

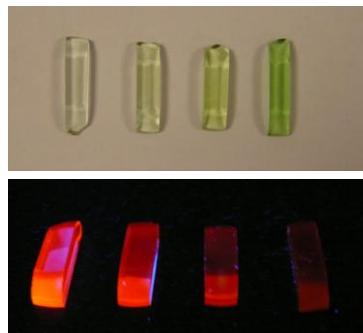
A. Pires de Matos, J. Marçalo, F. Lopes, A. Ruivo¹, V. S. Muralha¹

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

In 2007 the archaeometric studies of portuguese glasses using several techniques continued. The study of Coia glasses and the comparison with glasses from Marinha Grande was the main objective; XRF, atomic absorption spectrometry and ICP/MS (collaboration with IPIMAR) were used for their characterization. A micro-destructive method was also developed, sampling minute amounts of glass and analysing their composition by neutron activation analysis. The first experiments dealt with the determination of sodium (collaboration with the Nuclear Reactor Department, ITN).

Within the project “Provenance Studies of Portuguese Glasses”, uranium glass objects were characterized by XRF. Dose rates were measured in contact and at several distances in a set of 20th century glass objects containing uranium (collaboration with the DPSRN, ITN).

Another research area is related with the development of glasses for artistic applications. Studies on luminescent glasses with rare earths have continued, as well as the quenching of luminescence by d-transition elements. Gold ruby glass was synthesized using gamma radiation for reduction of gold ions and to improve nucleation of the gold nano-particles (collaboration with the Department of Physics, ITN).



¹ VICARTE, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa.

Gamma Irradiated Chitosan/pHEMA Membranes for Drug Release Systems

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

To obtain biocompatible and sterilized matrices for controlled drug release to be used in direct contact with skin, membranes with different contents in chitosan and hydroxyethyl methacrylate (HEMA) have been prepared by γ irradiation from a ⁶⁰Co source. Those membranes naturally exhibit antimicrobial properties with good mechanical behavior. The loading with amoxicillin led to active membranes that show an insignificant level of hemolysis and present a fast rate of amoxicillin release. Studies on the influence of membrane thickness show that an optimal thickness for each membrane composition can be obtained. At these conditions a maximum loading and release of amoxicillin was achieved.



¹ Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra.

Inorganic and Radiopharmaceutical Chemistry

Isabel Rego Santos

Apart from the continuing improvement in equipment and technology, the success of **Nuclear Medicine** is strongly dependent on the availability of powerful probes for molecular imaging and/or targeted therapy. The Radiopharmaceutical Chemistry group does **basic/applied-oriented research and technology transfer** to find radioactive probes for **molecular imaging and/or targeted radiotherapy**. This is a multidisciplinary task based on innovative organic and coordination chemistry, bioconjugation, radiochemistry, radiopharmacy and cellular biology knowledge afforded by modern genomics/proteomic research. We have implemented and developed expertise on these fields, as well as facilities to carry on such activities. This year, our facilities have been expanded with a new laboratory and with the implementation of the **Western Blot** technique.

Our main achievements on **Radiopharmaceutical Sciences** are described in this report. However, we would like to emphasize the following points:

Research

1- The complex **ISATechII** has been **selected by a Pharmaceutical Company** to enter into **clinical evaluation, as a myocardial imaging probe**. We consider this a tremendous achievement for **ITN and for the Portuguese Science and Technology**.

2- Radioactive **metal complexes**, bearing fluorescent DNA intercalators, **target the nucleus** of tumour cells, confirming the utility of **multimodal probes** for nuclear/optical imaging and radionuclide therapy.

3- The **first organometallic complexes** inhibiting nitric oxide synthase (*i*NOS) were isolated, characterized and evaluated.

4- A favourable biological profile (**bone uptake and pharmacokinetics**) has been found for a ^{99m}Tc -**bisphosphonate**, making this complex very promising as a vector to deliver cytotoxic agents to the bone, while minimizing the toxic effects on normal tissues.

Education and Training

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

2- Post-graduation: organization, teaching and coordination of the **Master Course Biomedical Inorganic Chemistry: Diagnostic and Therapeutical Applications** (3th Edition) (DR n^o 123, 26/05/04, II série). This Master course has been adjusted and approved to run under the **Bologna Agreement**. During 2007, we have also **participated** in PhD Teaching Programs organized by other Universities and Associated Laboratories.

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

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

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

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

Publications: Peer-review International Journals - 16; Patents - 2; Chapters in Books - 4; Proceedings/Reports- 7; Thesis: PhD - 1, MSc - 5.

Research Team

Researchers

I. SANTOS, Princ., Agregação, Group Leader
A. PAULO, Princ.
J.D.G. CORREIA, Princ.
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L.GANO, Aux.
F. MARQUES, Aux.
P. RAPOSINHO, Aux.
C.FERNANDES, Assistant

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E. CORREIA, technical assistant

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A. DATTA, Pos-Doc., FCT grant
R. VITOR, PhD student, FCT grant
S. LACERDA, PhD student, FCT grant
C. XAVIER, PhD student, FCT grant
E. PALMA, PhD student, FCT grant
T. ESTEVES, PhD student, FCT grant
C. NETO, PhD student, FCT grant
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S. CUNHA, MSc student
F. LUCENA, MSc student
F. SILVA, MSc student
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M. MORAIS, MSc student
G.CLEMENTE, MSc student
C. MOURA, MSc student
M. VIDEIRA, BIC grantee, POCl
B. MARTINS, undergraduate student
A. SANTOS, undergraduate student

Myocardial Imaging Agent: From Basic/Applied–Oriented Research to Technology Transfer

L. Maria, C. Fernandes, R. Garcia, L. Gano, A. Paulo, I. Santos

Objectives

Nuclear Cardiology is an important noninvasive tool for the clinical evaluation of patients with known or suspected Coronary Artery Disease (CAD), one of the leading causes of death in western countries. The main goal of this project is to find good performing myocardial imaging probes for Nuclear Cardiology.

Results

Among heart diseases, CAD is a leading cause of premature and permanent disability. Detection of perfusion abnormalities when the CAD patients are still asymptomatic would be of considerable benefit to avoid myocardial infarction and to apply therapeutic regimes, before irreversible myocardial damage occurs. This early diagnosis can be achieved with Nuclear Cardiology if a good performing nuclear myocardial probe is available, *i.e.* a probe with a high first-pass extraction, a high heart uptake, a stable retention, and high heart/liver and heart/lung ratios. ^{99m}Tc -MIBI, despite its widespread clinical application, does not meet the requirements of an ideal myocardial probe due to its relatively low first-pass excretion and high liver uptake. Thus, there is a significant interest on finding myocardial probes to overcome such disadvantages.

Our group has introduced novel cationic ^{99m}Tc complexes for myocardial imaging (Figure 1).

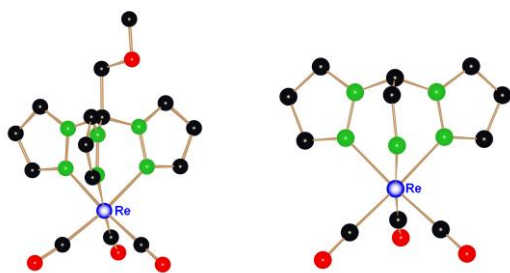


Fig. 1. Lead structures of myocardial imaging agents

Animal studies showed that the pharmacokinetics of the complexes can be modulated by introducing different functional groups in different positions of the tridentate chelators. Among several complexes, **ISATechI** and **ISATechII** were selected as the most promising for further studies (Figure 2). Results from Single Photon Emission Computed Tomography (SPECT) imaging studies in Sprague-Dawley rats have definitively shown that **ISATechII** was an excellent complex, presenting a significant and fast heart uptake, a stable retention and an extremely fast liver clearance. Clear images of the heart could be obtained with **ISATechII**, within a short time post-injection (Figure 3).

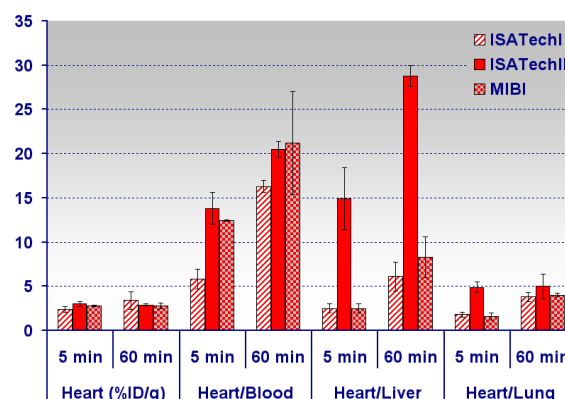


Fig. 2. Relevant target/non target ratios

Due to the excellent pre-clinical results, the complex **ISATechII** has been selected for clinical trials. GMP preparation of **ISATechII** and toxicity studies are underway.

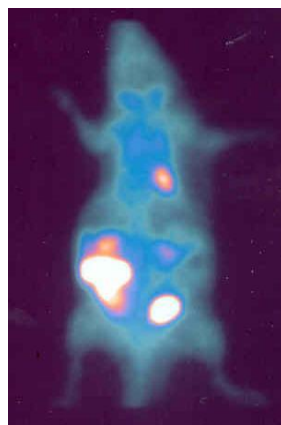


Fig. 3. Rat image 5 minutes post-injection

Published work:

I. Santos, A. Paulo, Tricarbonyl Complexes with Tridentate Chelators for Myocardium Imaging, *PCT/EP2007/010216*.

L. Maria, S. Cunha, M. Videira, L. Gano, A. Paulo, I. C. Santos, I. Santos, Rhenium and Technetium Tricarbonyl Complexes Anchored by Pyrazole-based Tripods: Novel Lead Structures for the Design of Myocardial Imaging Agents, *Dalton Trans.* (2007) 3010-3019. Selected as a **HOT ARTICLE**,

www.rsc.org/Publishing/Journals/dt/HotArticles.asp

Top Ten most popular *Dalton Transactions* article (July)

May Copsey, A clearer view of heart disease: Versatile pyrazole ligands offer a promising future for heart imaging radiotracers, *Chem. Science* (2007) 4.

www.rsc.org/Publishing/ChemScience/Volume/2007/08/Index.asp

Mixed-Ligand Re/^{99m}Tc Complexes for the Labelling of Biomolecules with Clinical Relevance

M. Videira, A. Paulo, I. Santos

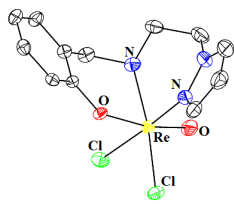


Fig. 1

The finding of novel metal fragments suitable for the radiolabelling of biologically relevant molecules remains a topic of utmost importance in modern radiopharmaceutical chemistry. To achieve such goal we have focused on mixed-ligand oxorhenium (V) complexes containing the NNO/OO donor atom set (Figure 2) which were prepared by reacting the corresponding oxorhenium dichloride (Figure 1) with adequate bidentate co-ligands. All the novel Re(V) oxocomplexes were fully characterized by the common analytical techniques, namely by multinuclear NMR and X-ray crystallography. The possibility of preparing other mixed-ligand complexes anchored by related ligands of different denticity is under evaluation, aiming to select the most promising compounds to pursue with the studies at the no-carrier added level (^{99m}Tc).

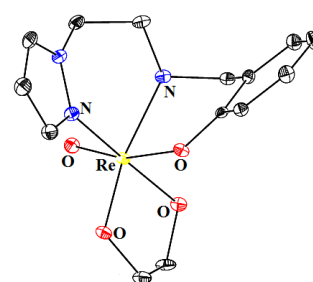


Fig.2

Gallium (III) Metallopharmaceuticals for Chemotherapy and/or Molecular Imaging

F. Silva, R. Garcia, F. Marques, A. Paulo, I. Santos

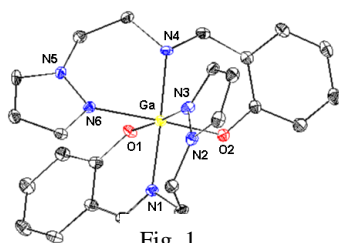


Fig. 1

A DOTA-like macrocyclic ligand was coupled to quinazoline derivatives (Figure 2) and used to prepare ⁶⁷Ga complexes which are being evaluated as biomarkers for *in vivo* molecular imaging of epidermal growth factor receptors (EGFR) overexpressed in cancer cells.

Based on tridentate pyrazolyl-containing chelators and on a DOTA-like macrocyclic ligand we have synthesized novel Ga(III) complexes having in mind their use as cytotoxic metallopharmaceuticals and/or as radioactive probes (⁶⁷Ga/⁶⁸Ga) for *in vivo* nuclear imaging. The pyrazolyl-containing chelators allowed the stabilization of non-radioactive homoleptic complexes (Figure 1) which in some cases displayed cytotoxic activity against murine or human tumour cells, appearing therefore as useful tools for the design of antitumor drugs.

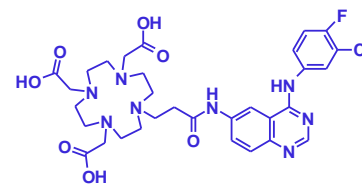
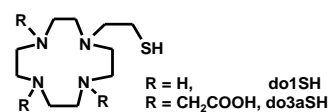


Fig.2

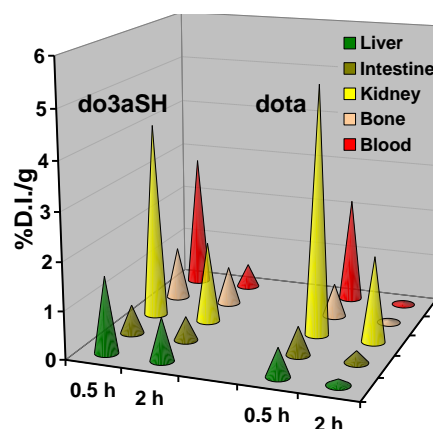
Macrocyclic Ligands with Sulphur Donor Atoms for Labelling Biomolecules with Radiometals

 S. Lacerda, M.P.C. Campello, F. Marques, L. Gano, I. Santos, S. Juran,¹ M. Walther,¹ H.-J. Pietzsch¹


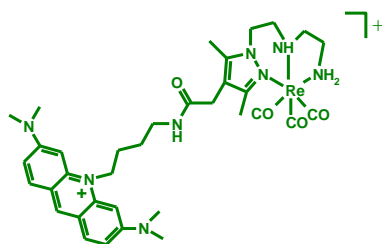
having pendant thiol arms (do1SH/do3aSH) for metal coordination and coupling to biomolecules. The novel ligand do3aSH was successfully used to synthesize complexes with radiolanthanides (¹⁵³Sm and ¹⁶⁶Ho) and copper (^{64/67}Cu). All of these radiocomplexes have been obtained in high radiochemical yield and present good *in vitro* stability. Biodistribution studies in mice have shown that ¹⁵³Sm-do3aSH displays a favourable biological profile, following a similar trend to the well-established ¹⁵³Sm-dota complex. These findings prompted us to explore the coupling of biomolecules through the thiol group, which is currently underway.

Macrocyclic bifunctional chelators are widely used for labelling biomolecules with radiometals aiming their use for *in vivo* diagnosis and antitumor therapy.

As part of our ongoing efforts on this field, we have explored dota-like macrocyclic ligands

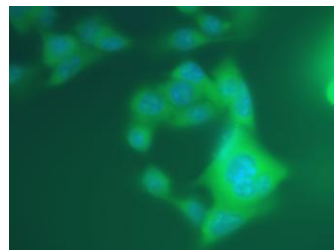

¹ Institut für Radiopharmazie, Forschungszentrum Dresden-Rossendorf, Germany

Multifunctional Organometallic Complexes for Nuclear Targeting

 R. F. Vitor, T. Esteves, C. Xavier, F. Marques, A. Paulo, I. Santos, G. G. Martins¹


Recently, we have shown that $\text{Re(I)}^{99\text{mTc(I)}$ tricarbonyl complexes anchored by pyrazolyl-diamine ligands containing an anthracen-9-yl group at the 4- position of the azole ring are able to target the nucleus of murine B16F1 melanoma cells. These promising results prompted us to evaluate related complexes bearing acridine moieties. By focusing on acridine derivatives, we have taken into account their characteristic fluorescence which provides a sensitive spectroscopic handle to study its interaction with DNA and to

follow *in vitro* the cellular localization of their compounds. Currently, we are evaluating the influence of the different chromophores (anthracenyl vs acridinyl moiety) in the interaction of the compounds with DNA and on their ability to target the nucleus and to induce cell death.


¹ Instituto Gulbenkian da Ciência, Oeiras, Portugal

Peptide Nucleic Acids Labelled with the $\text{fac-}^{99\text{mTc}(\text{CO})_3]^+$ Moiety for Monitoring the Endogenous Gene Expression

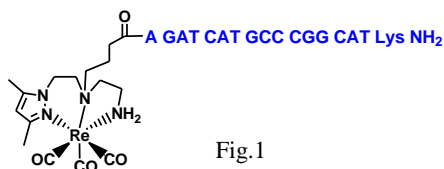
 C. Xavier, C. Giannini¹, S. Maiorana¹, R. Alberto², I. Santos


Fig. 1

The main goal of this research is to find novel $^{99\text{mTc}}$ probes for non-invasive imaging of endogenous gene expression, using the antisense approach. Taking into account the advantages of PNAs (Peptide Nucleic Acids) compared to normal oligonucleotides, we have synthesized a 16-mer PNA antisense sequence (*N*- A GAT CAT GCC CGG CAT-C), complementary to a region of the *N-myc* mRNA

which is amplified in human neuroblastoma. This 16-mer sequence was coupled to a bifunctional pyrazolyl-diamine chelator and the resulting conjugate was used to synthesize a Re(I) tricarbonyl complex (Figure 1). UV melting temperature experiments confirmed that the functionalized Re(I) complex recognizes the complementary DNA sequence (Figure 2). These results encourage further studies at the no-carried added level in order to evaluate the ability of the $^{99\text{mTc}}$ congener to recognize *in vitro* and *in vivo* *N-myc* mRNA.

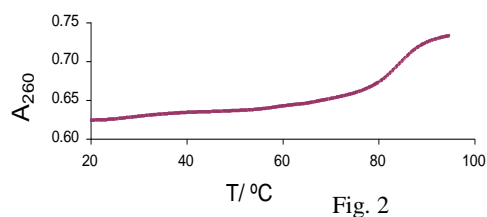


Fig. 2

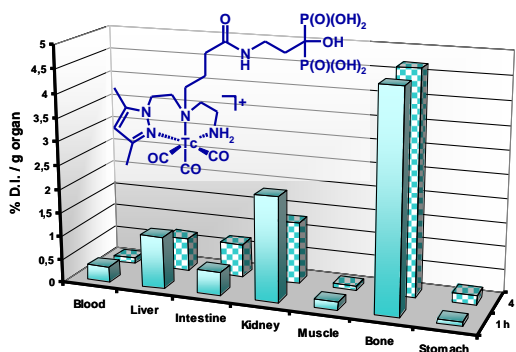
¹ Department of Organic and Industrial Chemistry, University of Milan, Italy;

² Institute of Inorganic Chemistry, University of Zurich, Switzerland

 $^{99\text{mTc}(\text{CO})_3$ -labeled bisphosphonates for bone targeting: radiosynthesis and biological assessment

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

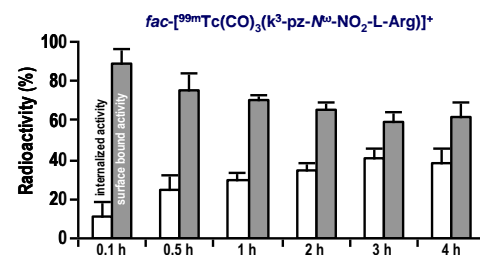
Aiming at the development of new $^{99\text{mTc}(\text{CO})_3$ -based agents with higher affinity for bone, we prepared a new bioconjugate (**pz-pamidronate**) which comprises a pyrazolyl-diamine backbone (**pz**, for metal stabilization) and a pamidronate unit for bone targeting. This bioconjugate allowed the synthesis of $\text{fac-}^{99\text{mTc}(\text{CO})_3(\text{k}^3\text{-pz-pamidronate})]^+$ which has been identified by HPLC comparison with the fully characterized Re(I) surrogate. Biodistribution studies in mice showed that this radiocomplex presented a fast rate of blood clearance and a high rate of total radioactivity excretion, occurring primarily through the renal-urinary pathway. The relevant bone uptake (4.7 ± 0.9 % ID/g organ, 4 h p.i.) and the high stability observed encourage further studies in order to assess the usefulness of $^{99\text{mTc}(\text{CO})_3(\text{k}^3\text{-pz-pamidronate})]^+$ as bone-imaging agent and for application in dual therapy.



$^{99m}\text{Tc(I)}$ -complexes containing L-Arg analogues for probing inducible nitric oxide synthase (iNOS) *in vivo*

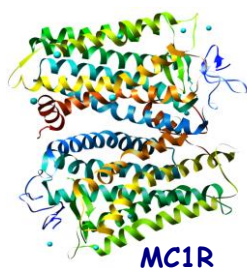
 B. L. Oliveira, J. D. G. Correia, P. D. Raposinho, I. Santos, C. Cordeiro,¹ A. P. Freire¹

Following our studies on the design of radioactive compounds for probing inducible nitric oxide synthase (iNOS) levels *in vivo*, we introduced bioorganometallic complexes of the type *fac*-[M(CO)₃(k³-pzL)] (M = ^{99m}Tc , Re; **pzL** = bifunctional pyrazolyl-containing chelator with a pendant substrate/inhibitor of NOS). Testing of the catalytic activity of iNOS *in vitro* revealed that the Re(I) complexes bearing the *N*⁰-Me-L-Arg (*K*_i = 36 μM) and *N*⁰-NO₂-L-Arg (*K*_i = 84 μM) units presented considerable inhibitory action, being unique examples of organometallic compounds able to inhibit that enzyme. Internalization studies in B16F1 murine melanoma cells showed that the highest internalization level was observed for the $^{99m}\text{Tc(I)}$ complex with the unit *N*⁰-NO₂-L-Arg. In conclusion, $^{99m}\text{Tc}(\text{CO})_3$ -labeled L-Arg analogues may hold potential for monitoring increased levels of iNOS *in vivo*.

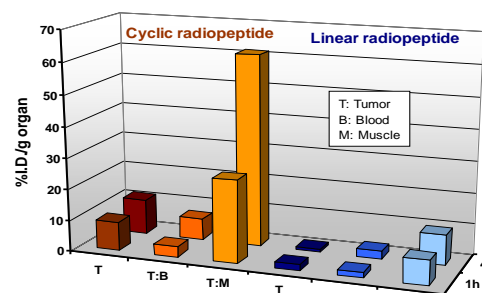


¹ Centro de Química e Bioquímica, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, Portugal.

Melanoma targeting with $^{99m}\text{Tc}(\text{CO})_3$ -labeled α -MSH analogues

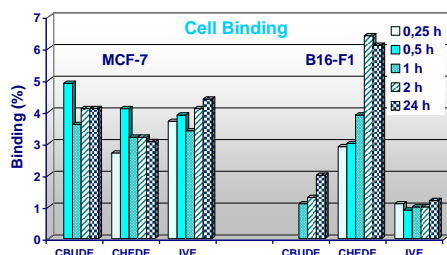
 P. Raposinho, C. Xavier, J. D. G. Correia, I. Santos, S. Falcão¹, P. Gomes¹


Linear and cyclic radiolabeled α -melanocyte-stimulating hormone (α -MSH) analogs were evaluated as radioactive probes to target the melanocortin-1 receptor (MC1R) overexpressed in melanoma. The effect of lactam-based cyclization on the tumor-seeking properties of α -MSH analogues was assessed by comparing the biological properties of the $^{99m}\text{Tc}(\text{CO})_3$ -labeled cyclic peptide conjugate pz- β Ala-Nle-cyclo[Asp-His-DPhe-Arg-Trp-Lys]-NH₂ (pz = pyrazolyl-containing chelator) with those of the corresponding linear analogue. The cyclic radioconjugate presented a remarkable internalization and cellular retention in murine melanoma B16F1 cells. Accordingly, a higher MC1R-mediated tumor uptake and retention was obtained in melanoma-bearing mice for the cyclic radioconjugate (11.31 ± 1.83% ID/g, 4 h) as compared to the linear radiopeptide.



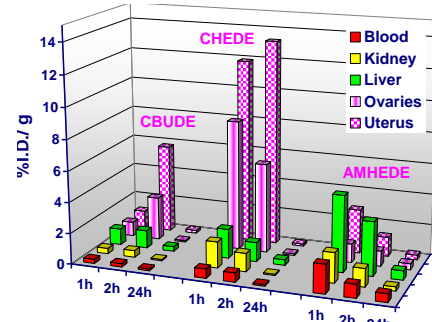
¹ CIQUP, Faculdade de Ciências, Universidade do Porto, Portugal.

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

 C. Neto, M. C. Oliveira, L. Gano, F. M. Marques, I. Santos, T. Yasuda¹, T. Thiemann¹, F. Botelho², C. Oliveira²


Unlike ^{125}I -CHEDE, cellular accumulation of ^{125}I -CBUDE was higher in ER (+) MCF-7 cells than in ER (-) B16F1 cells as observed for 17 α -iodovinyloestradiol (IVE). Consistently, ^{125}I -CBUDE demonstrated a high, selective and receptor-mediated target tissue uptake in immature female rats. These results encourage us to pursue studies with related compounds bearing different functionalized 7-alkyl chains.

As part of our ongoing work on specific ligands for targeted therapy and/or imaging of estrogen receptor positive (ER+) breast tumours a series of radioiodinated 7-alkyl-17 α -iodovinyloestradiols with either a cyano (^{125}I -CHEDE, ^{125}I -CBUDE) or an amide (^{125}I -AMHEDE) terminal group were prepared and their potential as SPECT biomarkers was evaluated.



¹ Interdisciplinary Graduate School of Engineering Science, Kyushu University, Japan.

² CIMAGO, FMUC, Coimbra

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, and maintained by in the group are a high temperature laboratory with crystal growth techniques (Czochralski, Bridgman and float zone), X-ray diffraction (single crystals and powder), EPR and Mössbauer spectroscopy, measurements of magnetisation by 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. These facilities include a new SQUID magnetometer acquired under the recent programme of scientific infrastructures, which became operational this year. The group was responsible for the installation at ITN in 1991 of a helium liquefier, which since then remains the only one operational in Portugal, serving also to many users outside ITN. This year significant services for cryogenic tests of valves were carried out under contract with the industry.

The rare combination of the **preparative chemistry** expertise with the specialised **solid state physics** techniques enables the group to deal with different problems of modern materials science. Thanks to the

valuable techniques developed, the group often act as a key partner of many national and international research projects. His activities have been centered in strategic selected type of materials, namely:

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

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

The group has an established tradition of research on **molecular conductors** since its origin at Sacavém. The two chain compounds, originally reported almost 3 decades ago, remained at the centre of important discoveries as model quasi-1D CDW systems. Recent efforts allowed the development of a new family of metals based on single neutral component which are still rare examples of such type of molecular metals.

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

The research on **intermetallic compounds**, initiated in 1992 with emphasis on the study of phase diagrams of the type (f-element)-(d metal)-(p-element) and on new compounds with strongly correlated electronic behaviour and complex magnetic structures, has been extended to borides and thermoelectric materials. The expertise in high temperature preparation techniques allowed a relevant industrial contract to be carried out.

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

Research Team

Researchers

M. ALMEIDA, Princ., Group Leader
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A. P. GONÇALVES, Princ.
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L. C. J. PEREIRA, Aux.
I. C. SANTOS, Aux.
D. BELO, Pos Doctoral, FCT grant
S. DIAS, Pos Doctoral, FCT grant (since November)
P. GACZYNSKI, Pos Doctoral, FCT grant (until September)
S. RABAÇA, Pos Doctoral, FCT grant
S. SÉRIO, Pos Doctoral, FCT grant
E. TIPSIS, Pos Doctoral, FCT grant
O. SOLOGUB, Pos Doctoral, FCT grant

Students

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M. FIGUEIRA, PhD student, FCT grant
J.P. NUNES, BIC grant (until January)
S. ABREU, BIC grant
A. MACHADO, BIC grant (until July)
C. DUARTE, PEPAP grant
M. MOURA, PEPAP grant, (until September)
B. RIBEIRO, Undergraduate student, (until May)
A. NEVES, Undergraduate student
T. MENDES, Undergraduate student

Technical Personnel

P. LIMA, PEPAP grant.

Collaborators

CASACA, Adjunct Professor, ISEL
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New extended transition metal-bisdichalcogenide complexes for molecular materials; single component molecular metals

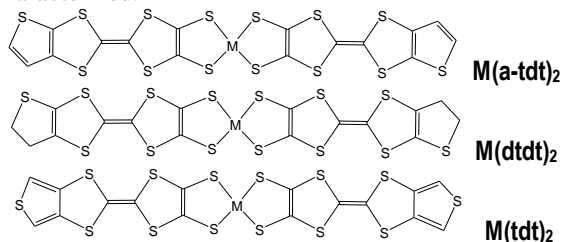
D. Belo, M. Figueira, J. P. Nunes, B. Ribeiro, E. B. Lopes, I. C. Santos, M. Almeida, R. T. Henriques¹, M. T. Duarte¹, D. P. Simão¹

Objectives

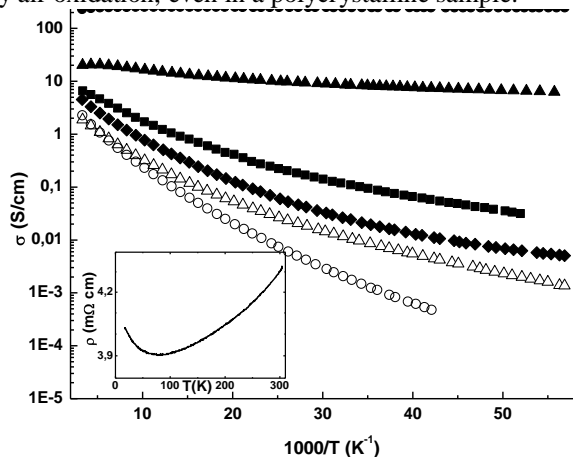
This project aims at to explore new transition metal bisdichalcogenide complexes based on highly extended multisulfurated ligands for the preparation of conducting/magnetic molecular materials. Extended systems are expected to stabilize higher oxidation states and provide larger solid state interactions.

Results

Based on the previous development of the synthesis of a new series of highly extended dithiolene ligands containing fused TTF and thiophenic moieties (α -tdt, dtdt and tdt)¹ a new family of Ni, Au and Cu complexes based on these ligands were obtained and characterized.



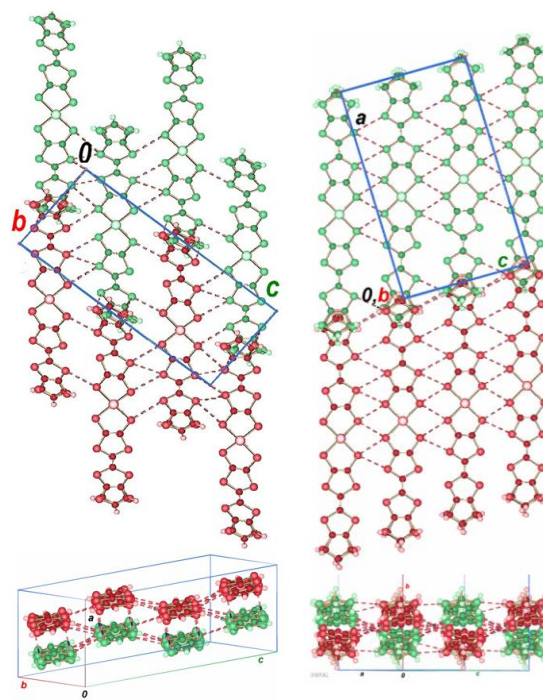
These complexes are obtained initially in Ni^{II}, Au^{III}, Cu^{III} anionic states, in several polymorphic phases, as judged by several Ni and Au complexes crystal structures solved. All these structures are very rich in S^{••}S contacts making extended 2D networks. The anionic complexes present already relatively high conductivity for integral oxidation salts with $\sigma_{\pi} \sim 10^{-3}$ S/cm, and they are readily oxidized to the neutral state upon air exposure or with iodine. The neutral complexes, so far only obtained as a microcrystalline powder, with a degree of crystallinity depending on the oxidation procedure, were found to exhibit a high electrical conductivity that can reach 200 S/cm with a true metallic character in the Ni compounds obtained by air oxidation, even in a polycrystalline sample.



Thus these compounds are new examples of a recent class of metallic materials based on neutral single molecular component that is still rare among molecular metals.

In this new family of single component molecular metals, not less remarkable than the high electrical conductivity, it is the finding that the magnetic susceptibility of these compounds shows large values of effective magnetic moment, indicating that in addition to conduction electrons with a Pauli-type contribution there are localized magnetic moments coexisting in the same solid. Magnetisation data in the Au^{III} compound show that these complexes present a high spin state in agreement with preliminary theoretical calculations confirming a high spin S=1 state as the ground state of these complexes.

The extension of these studies to similar complexes with other metals is currently under way.



Published work (selected)

D. Belo, M.J. Figueira, J.P.M. Nunes, I.C. Santos, M. Almeida, N. Crivillers and C. Rovira, *Inorg. Chimica Acta*, 360, 3909-3914 2007.

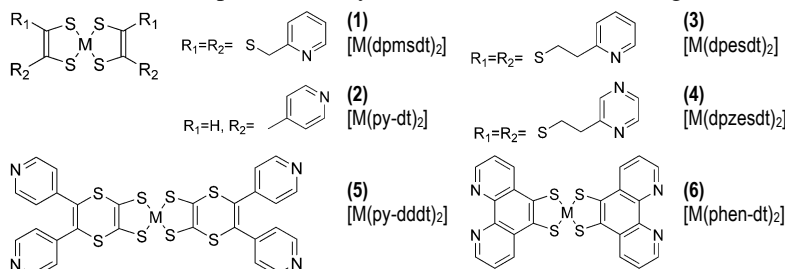
J.P.M. Nunes, M.J. Figueira, D. Belo, I.C. Santos, B. Ribeiro, E. B. Lopes, R. T. Henriques, J. Vidal-Gancedo, J. Veciana, C. Rovira, M. Almeida, *Chemistry a European Journal*, 9841-9849, 2007.

¹-Instituto Superior Técnico

Complexes based on divalent thio-azo ligands for heterobimetallic networks

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

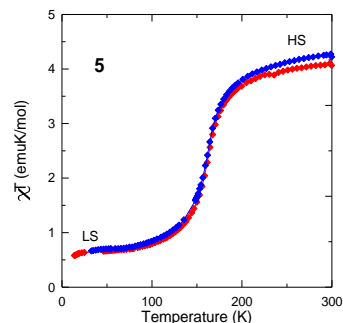
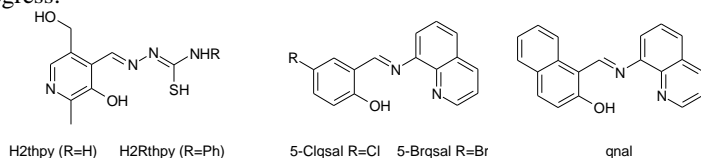
Divalent ligands containing both S and N coordinating atoms have remained essentially unexplored in spite of an enormous potential to be used as key building blocks for preparing heterobimetallic magnetic networks and novel supramolecular coordination architectures. Using the S coordination ability of these thio-azo ligands we have prepared a new class of bisdithiolene complexes which are the first examples of a novel family of complexes. These include bis alkylpyridyl (**1** and **3**), bis alkylpyrazine (**4**) and pyridine (**2** and **5**) substituted dithiolene complexes in which the $[\text{Ni}(\text{dpsdt})_2]$, $\text{TBA}[\text{M}(\text{py-dt})_2]$ and $\text{TBA}[\text{M}(\text{py-dddt})_2]$ ($\text{M}=\text{Au}, \text{Ni}$) are first examples of a tetra-azo substituted bisdithiolene complex. The synthesis of the divalent ligand 1,10-phenantroline-5,6-dithiol was also developed through the corresponding dibenzyl precursor and the first nitrogen coordinated Fe complexes with these ligands, were obtained. The corresponding TTF donors, where the transition metal is replaced by a C=C group, are currently being explored.



Towards Switchable Molecular Conductors

S. Abreu, A. Machado, L.C.J Pereira, I.C. Santos, V. Gama, M. Almeida

The preparation of switchable magnetic conductors is an important challenge in molecular materials science. Following a strategy consisting in the combination of switchable SCO Fe cationic complexes with acceptors such as $[\text{Ni}(\text{dmit})_2]^{x+}$, with the aim of tuning the conducting properties by acting on the bi-stable cation, several Fe^{III} SCO complexes, $[\text{Fe}(\text{L})_2]^+ \text{X}^-$, were prepared and from these the salts $[\text{Fe}(\text{L})_2][\text{Ni}(\text{dmit})_2]$. The obtained materials were characterized by single crystal x-ray diffraction and magnetic measurements. The electrical transport properties were studied for the compounds $[\text{Fe}(\text{HPhthpy})_2][\text{Ni}(\text{dmit})_2]_3$ (**1**) and $[\text{Fe}(\text{Hthpy})_2][\text{Ni}(\text{dmit})_2]_6$ (**2**) that are semiconductors, with $\sigma_{\text{RT}}=0.1$ and 0.01 S/cm respectively. **1** exhibits a gradual spin transition, while **2** is low spin. In case of the $[\text{Fe}(\text{L})_2][\text{Ni}(\text{dmit})_2]$ compounds with $\text{L}=\text{5-Clqsal}$ (**3**), 5-Brqsal (**4**) and qnal (**5**) SCO behaviors were observed. In case of **3** the transition is gradual ($T_{1/2} \sim 150\text{K}$) and incomplete, in **4** two transitions were observed (a gradual at $\sim 150\text{K}$ and an abrupt at 90K) a sharp transition was observed in case of **5** at 160K . The preparation of the conducting SCO materials from the precursors **3**, **4** and **5** is in progress.



Two-Chain Compounds under High Magnetic Field

M. Almeida, M. Figueira, R.T. Henriques, M. Matos¹, J. S. Brooks², D. Graf²,

$(\text{Perylene})_2\text{M}(\text{mnt})_2$ compounds with $\text{M}=\text{Au}, \text{Pt}, \dots$ initially reported by our group more than 20 year ago still offer a unique chance to investigate the coupling between two types of chains (conducting and magnetic) in the same solid and to test the theoretical predictions for the behaviour of quasi 1D CDW systems under large magnetic fields. In these compounds it was recently discovered that under moderate pressures (4–6 kBar) the CDW state is suppressed and a metallic regime is recovered at low temperatures, showing quantum oscillations previously interpreted as due to Stark interference between orbits in closely spaced open Fermi surfaces. A systematic study of the angular dependence of magnetoresistance at low temperature in Au and Pt samples under moderate pressure was pursued at the National High Magnetic Field Laboratory in Tallahassee, Florida, USA. These results allowed a reconstruction of the Fermi surface in qualitative agreement with previous calculations made under the extended Hückel approximation.

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Band Filling and Stacking Modulation Effects in the Conductors $[(n\text{-Bu})_4\text{N}]_2 [\text{M}(\text{dcbdt})_2]_5$, $\text{M}=\text{Cu}$, Ni , Au *E. B. Lopes, I. C. Santos, M. Almeida, E. Canadell¹, D. Graf², J. S. Brooks²*

A comparative study of the isostructural family of molecular conductors based on the partially oxidised complexes $[(n\text{-Bu})_4\text{N}]_2 [\text{M}(\text{dcbdt})_2]_5$ with $\text{M}=\text{Au}$, Ni , Cu (dcbdt = 4,5-dicyanobenzene-1,2-dithiolate) was accomplished. Their crystal structures triclinic, space group P-1 were solved with high accuracy for the Au compound at 120 K and 298 K and for Ni compound at 120 K. The electrical properties (conductivity and thermopower) were compared and related on the basis of extended Hückel calculations to the different electronic band filling imposed by the different metals and their slightly different structure. The lower electrical conductivity, $\sigma_{\text{RT}}=0.15$ S/cm, with a larger activation energy, $E_a=176$ meV, as well as the larger magnitude of thermopower of the Ni compound, were found to be a consequence of both a more pronounced modulation of the stacking and an electronic band filling with a Fermi level at a distortion induced gap. Both Au and Cu compounds present higher conductivity values, $\sigma_{\text{RT}}=10$ S/cm, with very small activation energy (27 and 16 meV respectively) and in the Au compound a clear metallic regime is induced down to 100 K under a pressure of 9 kBar. For the first time in molecular conductors, the band filling effects were clearly put into evidence by a change of metal, preserving the stoichiometry and without being associated with counterion structural variations.

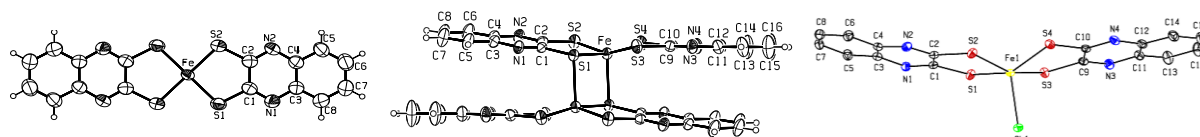
¹- Institut de Ciència de Materials de Barcelona, (CSIC), Spain

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Fe^{III} coordination in bisdithiolene complexes

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The transition metal bisdithiolene complexes are important building blocks in molecular materials. Until recently all known examples of Fe^{III} bisdithiolene complex, a large majority reported by our group, were known to adopt a 4+1 coordination geometry due to the formation of dimers. Following the recent discovery of the first undimerised square planar Fe^{III} bisdithiolene complex, which was based on the quinoxalinedithiolate ligand, $[\text{Fe}(\text{qdt})_2]^-$, a systematic study of salts of this complex with different cations and obtained under different crystallization conditions was undertaken using x-ray diffraction, magnetic susceptibility and Mössbauer spectroscopy measurements to unveil the factors favouring each type of coordination. The results of these study show clear evidence for polymorphism in these salts, the dimerised structure $[\text{Fe}(\text{qdt})_2]_2^{2-}$ with 4+1 coordination occurring as a minority phase easier to crystallise. The square planar coordination geometry occurs as a majority phase as determined by magnetisation and Mössbauer spectroscopy. An additional rare example of Fe^{III} complex with square pyramidal coordination of 4 sulfur atoms and an apical chloride has been also obtained.



Study of Ternary Phase Diagrams based on f and d elements

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The main objective of this research line is to investigate (f -element)-(d -metal)-X ternary systems in order to determine the phase relations, and identify, synthesise and characterise new intermetallic compounds based on f and d elements. This study also provides fundamental information for single crystal growth. During 2007 the study of (f -element)-(d metal)-(p -element) ternary systems was continued. The determination of the U-Fe-B isothermal section at 950°C was finished and it was started the study of the U-Fe-B *solidus* surface. Preliminary results were also obtained for isothermal sections of the R-M-X (R=U, Ce; M=Fe, Au, Pt, Rh; X=Ge, Sb) ternary systems, which allowed the identification of two new ternary compounds, $\text{Ce}(\text{Au,Sb})_2$ and $\text{CeRh}_2\text{Sb}_{2-x}$. These intermetallics were prepared as polycrystalline single-phase samples and their crystal structures were characterised. Finally, two new compounds, $\text{La}_3\text{Ru}_8\text{B}_6$ and $\text{Y}_3\text{Os}_8\text{B}_6$, were synthesized by arc melting and their structural characterization was carried out.

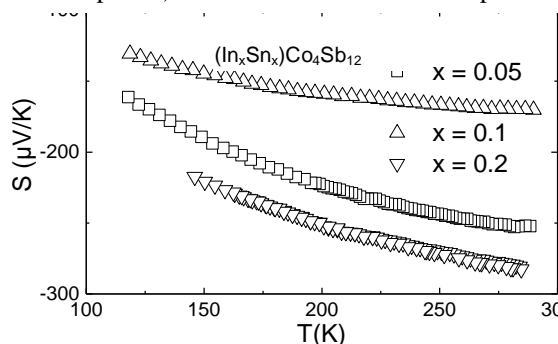
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New materials for thermoelectrical applications

A.P. Gonçalves, E.B. Lopes, M. Moura, B. Ribeiro, E. Alleno¹, C. Godart¹, O. Tougaï², H. Noël²

The main objective of this research line is to find new systems suitable for thermoelectrical applications. The recent development of new concepts, like the Phonon Glass and Electron Crystal, has led to the discovery of new compounds with better thermoelectrical properties, like skutterudites, clathrates, half-Heusler, oxides, etc. During 2007 the electrical transport properties (resistivity and thermopower) of several intermetallic compounds were studied. In particular, the $U_3Fe_2Si_7$, U_2FeSi_3 , $U_{1.2}Fe_4Si_{9.7}$, $U_2Fe_3Si_5$ and UFe_2Si_2 compounds from the U-Fe-Si ternary system were explored, and also the new series of filled skutterudites, $(In_xSn_x)Co_4Sb_{12}$, derived from $CoSb_3$ with double filling of the cage by (In,Sn). All silicides show modest values of the termopower (few $\mu V/K$) in the 20–300 K temperature range. A Seebeck coefficient as high as $-280\mu V/K$ at 300K has been obtained in the $(In_xSn_x)Co_4Sb_{12}$ series, which compares well with the previously reported values of around $\pm 150\mu V/K$ in $(Ce, Yb)_x(Fe, Co, Ni)_4Sb_{12}$.



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Magnetic and strongly correlated electron behaviour in intermetallics

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The detailed understanding of the magnetic and strongly correlated electron behaviour of intermetallics, in particular the role of the actinide or rare-earth, has been the subject of a long-term project in the Solid State group. The ordering temperature of the *f*-element sublattice in AFe_6Sn_6 (*A* = *f* element) was estimated considering their polarization effect on Sn as detected by ¹¹⁹Sn Mössbauer effect. In the frame of the study of heavy fermions, an anisotropic spin-glass behaviour below 2.8K was found for Ce_2NiIn_3 using specific heat, ac and dc magnetic susceptibility measurements. The study of hydrides of compounds with U_2T_2X general formula was pursued in 2007. The hydrogen absorption in these compounds typically increases the ordering temperatures and magnetic moments. For $U_2Ni_2SnD_{1.8}$ the anisotropic lattice expansion leads to U moments reorientation with respect to U_2Ni_2Sn , in which the U-U coordination is poised between two regimes. The new UFe_5Si_3 compound, crystallizing in its own tetragonal type structure, was found to behave as a hard ferromagnet with a high Curie temperature of ~ 310 K. Measurements on magnetically oriented powder suggest that UFe_5Si_3 has an uniaxial anisotropy, with *c* as the easy axis. Its electrical resistivity decreases monotonously below 300 K and, in line with this metallic behaviour, the thermoelectric power remains of the order of several $\mu V/K$, with a maximum value of $12\mu V/K$ at ~ 60 K, which was ascribed to Kondo interactions and/or crystalline electrical field effects.

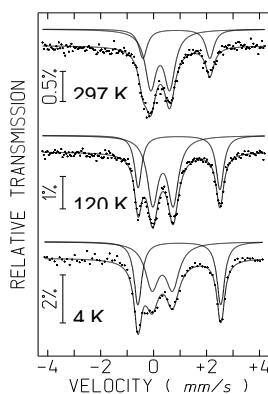
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Mössbauer spectroscopy in Materials Science

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

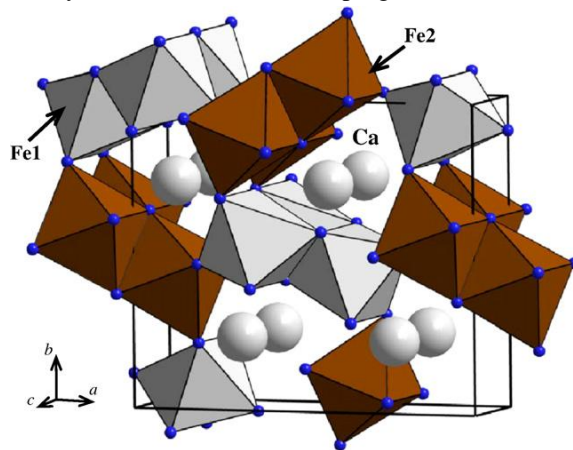
A Mössbauer spectroscopy laboratory has been developed in ITN for about 30 years in order to support local research projects. In addition to the researcher responsible for the facility the team in 2007 was composed of three post-docs. Presently, in the ITN Mössbauer laboratory γ -ray transmission and backscattering as well as conversion electron Mössbauer spectra may be obtained. Transmission spectra may be taken with the sample in the 300–2.2 K temperature range and in external magnetic fields up to 5 T. The expertise developed in ITN has been, in the last years, able to assist other research institutions in Portugal and abroad in the frame of joint research projects as well as supporting those who develop their own Mössbauer facilities. In 2007 studies of the chemistry of ketyl species, glass ceramics with a bioactive matrix, new molecule-based multifunctional materials and intermetallics (using ⁵⁷Co, ¹⁵¹Sm and ^{119m}Sn sources) have been performed in collaboration with Inorganic and Organometallic Chemistry group of ITN, University of Aveiro, University of Valencia, Spain, and Charles University, Prague, Czech Republic.



Materials for solid oxide fuel cells and dense ceramic membranes

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The development of novel materials based on iron-containing oxide phases with perovskite or related structures, with mixed oxygen-ionic and electronic conductivity and high oxygen permeability, is of major importance for energy-related electrochemical technologies, such as electrodes of solid oxide fuel cells. In 2007 our investigation on the improvement of the properties of the SrFeO_{3-d} based perovskites by partial substitution of Sr and Fe by rare-earths and *d*-elements, respectively, was mainly focused on Ce and Nb doping. The hole conductivity was found to be lower for the Ce- and Nb-containing perovskites, primarily as a result of the lower Fe^{4+} concentration. Both dopants decrease oxide-ion conductivity but the effect of Nb-doping is moderate and ion-transference numbers are higher with respect to the Nb-free phase. Brownmillerite-type $\text{Ca}_2\text{FeAlO}_5$ with Fe and Al partially substituted by Mg showed a significant enhancement of the total conductivity, which can be attributed to the presence of Fe^{4+} ions. Looking for a promising combination of properties another calcium-iron oxide compound stable in a wide temperature range, CaFe_2O_4 , was investigated. The partial oxygen conductivity was however found to be low. According to atomistic computer simulations this may be due to significant energetic affinity for defect cluster formation involving oxygen vacancies and Fe^{2+} cations, and unfavourable vacancy location in the oxygen sites forming one-dimensional pathways with minimum migration energy.



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High magnetic field facility

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This unique infrastructure in Portugal permits the study of electrical transport properties of materials under magnetic fields up to 18 T, for temperatures in the range from 0.3 to 300 K, using both AC and DC techniques. The magnetic fields are generated by a superconducting coil inside an OXFORD cryosystem and the system control and data acquisition is fully automated using a LabVIEW software developed in house. This facility allowed pursuing two main areas of research: manganite systems and exotic intermetallics. Manganite systems are an exciting field of research due to the colossal magnetoresistance they exhibit under applied magnetic fields, with potential applications in spintronics, from hard disc memories to magnetic sensors. In this context the characterisation of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3/\text{CaO}$ multilayer systems was initiated by DC magnetoresistance measurements, in order to follow the properties' response to a change in the different layers' thickness. The ferromagnetic intermetallic family UTSb_2 , T=Au, Ag was studied by DC electrical resistivity measurements and magnetoresistance and UAuSb_2 was confirmed to be a semimetallic Kondo system. The ternary boride $\text{Y}_3\text{Os}_8\text{B}_6$ was characterised as a superconductor. High quality CuS synthetic single crystals were characterised by means of longitudinal and transverse magnetoresistance in fields up to 18 T. A careful characterisation of the low temperature superconducting transition and of the high field magnetoresistance, was achieved.

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Development of Differential Thermal Analysis equipments

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This project aims at the development of high temperature instruments namely Differential Scanning Calorimeter (DSC) prototypes of new equipments to be commercialized. Under the AdI/IDEA program and a partnership with TERMOLAB industry, a Differential Thermal Analysis (DTA) and DSC system prototypes were developed and installed at ITN. The main feature of these systems is their flexibility: the first one can reach temperatures above 2000°C and can also be used as a high temperature furnace for heat treatments under vacuum or inert atmospheres; the DSC unit is the first cell being developed as part of a multipurpose system for routine measurements up to 1100°C and under controlled atmosphere; other measuring cells will be developed in the near future.

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