

Chemistry Sector



Chemistry

Directive Board: Isabel Santos (President), M. Isabel Prudêncio and M. Fátima Araújo

The Chemistry Department conducts basic and application-oriented research in key areas of science related with nuclear sciences and other fields. The Department has its strength on the capability of synthesis and characterization of inactive and radioactive compounds and/or complexes of *d*- and *f*-transition elements and in developing and applying nuclear and related analytical methods. These expertises have allowed to proceed research work in well defined areas such as, environmental, cultural heritage, health and material science.

During 2002 a reorganization of the Chemistry has been accomplished and the resulting five multidisciplinary research groups own know-how and infrastructures, in some cases, unique in the Country or even in the Iberian Peninsula. The groups and their main topics are:

- Cultural Heritage and Sciences: Archaeometry, geochemistry of the earth surface and geological environmental studies. These studies involve movable and immovable cultural assets, to establish the location of ancient production centers of pottery, and to identify the causes and mechanisms of degradation of stones in historical buildings.

- Environmental Analytical Chemistry: Study of the Biogeochemical Cycles of Chemical Elements and Light Isotopes in the Environment. The major domains of research has been on sedimentary geochemistry and isotope hydrology. In the first case the studies concern the main Iberian river basins and in the second they aim to obtain a better insight of the dynamic evolution of groundwater systems to Human influences and to climatic evolution.

-Inorganic and Organometallic Chemistry: Synthesis, characterisation and stoichiometric and catalytic reactivity studies of *4f*- and *5f*- coordination and intermetallic complexes. To apply this knowledge to environmental studies, particularly to radioactive waste and migration of actinides is one of the goals and research in waste vitrification, actinide speciation studies and Ln/An separation is being envisaged.

- Inorganic and Radiopharmaceutical Chemistry: Synthesis, characterization and biological evaluation of inactive and radioactive metal *d*- and *f*- and halogen-based specific compounds for application in nuclear medicine. Diagnostic and therapy of cancer as well as Central Nervous System diseases are the two main topics in progress.

- Solid State: Synthesis, characterization and measurement of the magnetic and electrical properties of molecule based materials, U and Ln intermetallic compounds and oxides. To find new materials with unconventional electrical and magnetic properties is one of the main goals.

For developing these activities, the Chemistry operates, maintains and uses a large number of specific and modern techniques as well as specific facilities, in some cases unique in the Country and in the Iberian Peninsula, namely: Neutron Activation Analysis (NAA), Radiocarbon Dating (^{14}C), Luminiscence Dating (TL-OSL), Energy-Dispersive X-Ray Fluorescence Spectrometry (EDXRF), Tritium Dating (^3H) and Mass Spectrometry for Light Isotopes in one case equipped with an elemental analyser, Mössbauer Spectroscopy, X-Ray diffraction, NMR spectroscopy, FTICR/MS, gas chromatography, calorimetry, equipment for magnetisation and electrical transport measurements in a broad range of temperatures and magnetic fields, animal facilities, laboratories for manipulation of radioactive compounds, including the most toxic actinides, clean room for preparation of compounds in aseptic conditions and an high temperature laboratory.

The basic and application-oriented research of the Chemistry has been used for training a significant number of undergraduate, MSc, PhD and Postdoctoral students, and professionals in the nuclear medicine field. Our expertise, know-how and facilities have also been provided to other Institutions and Universities.

The funding has been based mainly on research projects supported by the National Science Foundation and European Commission as well as on Protocols, Services and Contracts. The implementation of new facilities, such as luminescence and radiopharmaceutical laboratories, as well as conditions for manipulation of more toxic actinides in the FTICR/MS and modernization of some of the analytical equipment for characterization and monitoring of radioactive compounds has been supported by ITN.

In order to reinforce their analytical and scientific level the Chemistry presented several proposals within the “Programa Nacional de Re-Equipamento Científico”. Chemistry is co-ordinating the proposal of HR-ICP-MS and X-ray diffraction and is participating as partner in the MS/Network and 500 MHz NMR projects.

Structure of the Sector and Technical staff

Research groups in the Chemistry Sector

- CULTURAL HERITAGE AND SCIENCES
- ENVIRONMENTAL ANALYTICAL CHEMISTRY
- INORGANIC AND ORGANOMETALLIC CHEMISTRY
- INORGANIC AND RADIOPHARMACEUTICAL CHEMISTRY
- SOLID STATE

Administrative and Technical staff

- I.F. FRAZÃO
- E.C. FLORES
- M.F. MARQUES
- P.M. REIS
- M. F. CABRITA
- M.H. SANTOS (retired 31-01-02)
- J. PIRES (retired 30-10-02)
- M.M. COSTA (retired 18-10-02)
- F. ALMEIDA (retired 14-11-02)
- M.B. RUFINO (retired 4-12-02)

Cultural Heritage and Sciences



Cultural Heritage and Sciences

M. Isabel Prudêncio

The research activity of the Cultural Heritage and Sciences (CHS) group is mainly focussed on archaeometry, geochemistry of the earth surface and geological environmental studies. The research is largely based on the use of nuclear methods of analysis.

The analytical methods associated to the CHS group are unique in Portugal, namely the instrumental neutron activation analysis (INAA) - comparative method, radiocarbon dating (^{14}C) and luminescence dating (TL-OSL). These methods allow the chemical characterisation of geomaterials and the establishment of chronologies on both geological and archaeological features.

Detailed studies of geochemistry (especially of trace elements) and mineralogy of geological materials (clays and rocks) are done applied to cultural assets (ceramics and monument stones, for instance), as well as environmental projects through the geochemical natural background knowledge, in order to evaluate anthropogenic influences.

The financed research projects are in collaboration with other national and international laboratories, universities, and other public institutions. Also contracts/services are made with other private or public institutions (ERA, EDIA, Valorsul, Robbialac, City Halls, etc).

The ITN research activities of the CHS group can be divided in the following domains:

-Movable Cultural Assets (ancient ceramics production, technology and provenance):

- The Upper Mondego Basin
- ITN- IPA Protocol
- Raw materials exploitation strategies: The Alqueva and Lisbon cases

- Immovable Cultural Assets (historical buildings and monuments);

- Absolute Dating – Radiocarbon Unit;

- Absolute Dating – Luminescence laboratory;

- ^{57}Fe Mössbauer spectroscopy in Geology and Archaeology;

- Geological Environments;

- Database – Ceramic and Geological Materials Record.

The multidisciplinary character of these research domains is reflected by the diversity of know-how of the team - chemists, geologists, physics, geographers and archaeologists.

- *Movable Cultural Assets* - the archaeometric research in ITN aims to obtain a better knowledge of the production technologies of ceramics through time. The establishment of provenance is also a major objective, contributing to the location of ancient production centers of pottery.

- *Immovable Cultural Assets* - identification of the causes and mechanisms of degradation of stones contributing to the protection of historical buildings and monuments.

- *Absolute Dating – Radiocarbon Unit* -development and application of ^{14}C dating method units in archaeological / museological and geological / hydrogeological materials.

- *Absolute Dating – Luminescence Laboratory* - The set up of the luminescence dating laboratory was completed. Protocols were established for different luminescence dating applications: Thermoluminescence (TL), Blue-Optically-Stimulated-Luminescence (B-OSL), Infrared-Stimulated-Luminescence (IRSL), on different types of materials, such as heated flint/quartzite, coarse grain quartz sediment, polymineral fine grain sediment and pottery/bricks.

- ^{57}Fe Mössbauer Spectroscopy in Geology and Archaeology - this method (available at the Solid State group of ITN) has been applied to ancient ceramics, monument stones and geological environmental samples.

- *Geological Environments* - detailed geochemical / mineralogical studies of different geological environments of the earth surface, essential to evaluate potential anthropogenic inputs, are also performed.

- *Database – Ceramic and Geological Materials Record* – inventory which will be available worldwide in the internet of all characteristics of samples and corresponding analytical results.

The consolidation of the scientific research and its application to the Portuguese cultural heritage and geological environment is a long-term goal of the CHS group, becoming a unique research group in Portugal, based on nuclear techniques of analysis.

The main results of the research projects developed for the previous presented six domains during 2002 are summarised in the following pages.

Cultural Heritage and Sciences

Research Team

Researchers

- M.I. PRUDÊNCIO, Principal Researcher, Group Leader
- M.A. GOUVEIA, Principal Researcher
- A. MONGE SOARES, Auxiliary Researcher
- D. RICHTER, Invited Auxiliary Researcher
- M.I.DIAS, Invited Auxiliary Researcher
- M. NASRAOUI, Post-Doctoral
- K. PRZEGIETKA, Post-Doctoral

- G. CARDOSO, undergraduate student, ITN grant

Technical Personnel

- L. FERNANDES, laboratory technician
- A. AMARO, laboratory technician

Students

- A. JORGE, MSc Student
- R. MARQUES, ITN grant
- D. FRANCO, undergraduate student, ITN grant

Funding (€)

Research Projects:	74 991
Services:	41 559
Total:	116 551

Publications

Books:	2
Journals:	9 and 7 in press
Proceedings:	2
Conf. Communications:	9
Other publications:	1
Theses: MSc	1

Movable Cultural Assets

Ancient Ceramics production, Technology and Provenance

The Upper Mondego Basin

M.I. Dias, M.I. Prudêncio, M.A. Gouveia, A. Jorge¹, A.C. Valera²

Objectives

In the CHS group the research domain concerning movable cultural assets, is mainly voted to archaeometric studies of ceramics, always with the posture of an interdisciplinary approach.

This line of investigation is always in direct contact with archaeologists, trying to contribute to solving problems, such as: How were these ceramic artefacts have been done? With what kind of materials were they produced? Where did they come from? Of course this kind of approach besides the use of analytical capacities it also involve field-work, looking for clay deposits, trying to figured out potential raw materials.

In general our contribution consists on a detailed geochemical and mineralogical study of pottery and potential related raw materials aiming to establish trade patterns, manufacturing techniques employed and production organisation, sometimes crossing large chronological periods in order to establish continuity or discontinuity in ceramics production for a certain archaeological site.

Results

Fornos de Algodres Project

This project makes part of a PhD Thesis in course (2), including all the archaeometric approach. We have now available a very good chemical and mineralogical characterisation of ceramics from three archaeological sites (C.Santiago, Malhada, F. Pena) which represents the pre-history of that region respectively from the first half of the third millennium B.C., the middle of the third millennium and the last quarter of that millennium B.C.. So we are able to establish for F. Algodres pre-historical settlement network a detailed description of production technology and provenance of ceramics, as well as specify local clay deposits as raw materials for most of the pottery, even in some specific cases different origins for raw materials and/or ceramics is suggested.

Archaeometry of Pre-historical sites from the upper Mondego basin: the Penedo da Penha and Buraco da Moura cases

A collaboration project with the University of Sheffield - Department of Archaeology and Prehistory is in course, and during this year a dissertation of a Masters Thesis (MsC) was done in Archaeomaterials (1). Two Neolithic sites were studied from the upper

Mondego basin. This project is in direct correlation with the Fornos de Algodres one, being the sites (P. Penha, B. Moura S. Romão) excavated by the same archaeologist, having the potential of giving for Beira Alta region an important overview of ceramic technology, production and provenance from Neolithic, through Chalcolithic to the early Bronze Age. The archaeometric investigation was done by means of both petrographic examination (Figures 1) and chemical analysis, providing evidence for the understanding of the Early Neolithic settlement in the Upper Mondego Region by establishing: firstly, the nature of the occupation of the sites as habitat; second, a cultural / technological continuum between potentially interrupted moments of inhabitation of the sites; finally, close inter-site relations between them. The technological characterisation of pottery from PPE1 and BMSR sites also appears to reinforce the image of cultural homogeneity or refute previous approaches to the inter-regional suggested by stylistic variation of pottery assemblages.

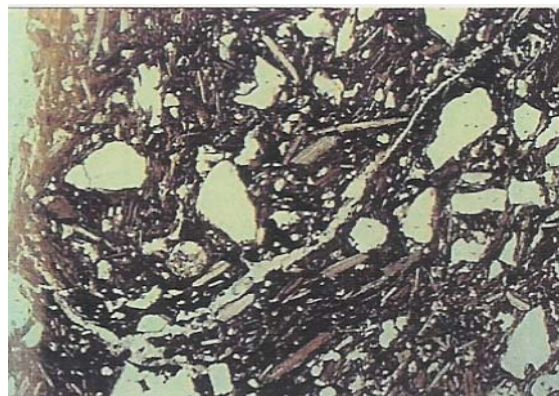


Figure 1 – **Forming Techniques:** Coiling is indicated by very clear building joints, orientated diagonally to the vessel wall. **Firing Conditions:** The presence of a sharp margin along the outer surface suggests rapid cooling after firing in reducing atmosphere.

Published, accepted or in press work

1. M.I. Dias, M.I. Prudêncio, M.A. Sequeira Braga, M.A. Gouveia, C.A. Alves, A.C. Valera, Provenance and Technology of Pre-Historic Pottery from Fornos de Algodres (Portugal): the Fraga da Pena archaeological site. *British Archaeological Reports*, International Series 1011 (2002), P.253-263.

¹ University of Sheffield – Department of Archaeology and Prehistory, England

² GAFAL archaeologist (C.M. F. Algodres), Portugal

Movable Cultural Assets

Ancient Ceramics production, Technology and Provenance

ITN – IPA PROTOCOL

M.I. Dias, M.I. Prudêncio, M.A. Gouveia, J. Bugalhão¹, A.C. Valera², M. Lago²

Objectives

The ITN-IPA protocol represent a huge step in order to increment archaeometry in Portugal, specially concerning the characterisation of archaeomaterials.

Results

The running projects in 2002 (ITN-IPA protocol) are:

Pottery production in occidental neighbourhood of Islamic Lisbon

The project concerning Islamic pottery studies from Lisbon is an important one, as it follows, in a chronological way, our previous project for roman ceramics from Lisbon. So, we will have data to figure out the pottery production tradition in our capital through several centuries. It was settled the utilization of the Lisbon kilns to the firing of ceramics found in Castelo de S. Jorge and Sé de Lisboa, mainly with two different types of raw materials. Being aware of the importance of Lisbon projects the CHS group decided to begin a new one about raw materials strategies in that region.

Funeral environments in the Perdigões settlement: ceramics from the late Neolithic - SW Chalcolithic

The Perdigões site is one of the largest known portuguese Chalcolithic settlement, occupied during the late 4th - 3rd millenium B.C in the Reguengos de Monsaraz region, in South of Portugal. Generally the group of pottery artefacts includes all the typical morphologies of the Late Neolithic and Chalcolithic of the South West of the Iberian Peninsula (Figure 1) and there are some differences between the funerary and the domestic recipients. So, it turns out to be important to realize if there are specific differences between the raw materials and the production technologies used on the making of those two functional types of recipients. An archaeometric study was performed comprising the chemical analysis of one hundred and seventeen ceramic samples. The chemical analysis was done by means of instrumental neutron activation analysis (INAA). The elements determined are used as variables in a multivariate statistical approach (Cluster analysis, R-mode Factor analysis, Discriminant analysis, Canonical analysis, etc.) in order to obtain chemical signatures of each group. The establishment of geochemical fingerprints, was achieved allowing to specify possible artefact production specificities in funerary ritual pottery, when compared with domestic function ceramic.

Preliminary results point to the recourse of spread raw materials in the funerary ceramics case, when compared with domestic ones, which have a more homogeneous chemical composition (figure 2). The As, Zn, Ta and Light Rare Earth Elements contents have a higher range in the funerary pottery. A few of these ceramics point to a complete different source, especially in the Rare Earth Elements.



Figure 1 – Pottery artefacts of Perdigões archaeological site (chemical analysis of those and others was performed).

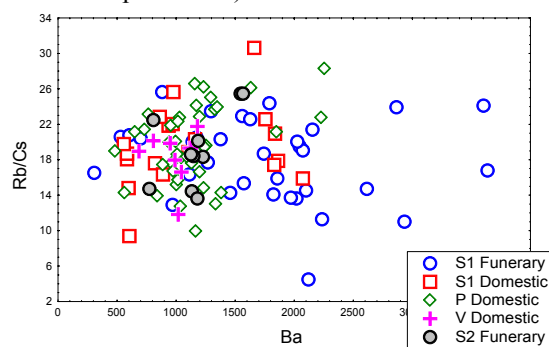


Figure 2 – Rb/Cs vs Ba pottery composition

Published, accepted or in press work

1. M.I. Dias, M.I. Prudêncio, A.C. Valera, M. Lago & M.A. Gouveia, Composition, technology and functional features of Chalcolithic pottery from Perdigões, Reguengos de Monsaraz (Portugal). *Geoarchaeological and Bioarchaeological Studies*, 2002 (in press)

¹ IPA

² ERA Arqueologia S.A.

Movable Cultural Assets

Ancient Ceramics production, Technology and Provenance

Raw Materials exploitation strategies: Alqueva and Lisbon cases

M.I. Dias, M.I. Prudêncio, M.A. Gouveia, A.C. Valera¹, J. Albergaria¹, S. Gomes¹, S. Brazuna¹,
J. Bugalhão², A. Gomes³, A. Gaspar³

Objectives

The running projects concerning archaeometric studies of ceramics from archaeological sites of Alqueva barrage impact, and from Lisbon archaeological sites involve projects of several chronologies. In both cases the most important problem to be solved is the pottery provenance, which can be achieved with the establishment of raw materials exploitation strategies, comprising one of the CHS research lines.

Results

Three research projects concerning Alqueva impact are running with archaeologists from the ERA-Arqueologia:

Archaeometric study of ceramics from the proto-historic occupation from the left side of the Guadiana basin (Moura) – Block 9

Archaeometric study of ceramics from recent pre-history of the left side of the Guadiana basin (M. Tosco, M. Valadares, Mercador) – Block 5

Archaeometric study of ceramics from the roman occupation of the right side of the Guadiana basin (Xerez de Baixo) – Block 10

This research includes the chemical characterisation of ceramics from those three archaeological sites, as well as potential raw materials with sampling in local/regional clay deposits.

Published, accepted or in press work

1. J.M.P. Cabral, S.M. Fonseca, M.A. Gouveia, Caracterização química das produções de ânforas do Vale do Tejo: III- Quinta do Rouxinol (continuação), *Revista Portuguesa de Arqueologia* 5, nº2 (2002) 325–338.
2. J. Raposo, C. Fabião, A. Guerra, J. Bugalhão, A.L. Duarte, A. Sabrosa, M.I. Dias, M.I. Prudêncio &

Fieldwork has already been done with clays sample collection, as well as ceramics sampling. Chemical analysis is running. Results obtained so far, point to the use of local materials for most of the ceramics, even for some a foreign origin is purposed.

This research is included in the cultural heritage minimizing impacts of the building of the Guadiana barrage.

Ceramic provenance of Lisbon archaeological ceramics : Raw Materials exploitation

In accordance with the archaeometric projects of ceramics from Lisbon archaeological sites (roman and Islamic) a new need was created, implying the seek of potential clay pits of Lisbon potters, specially considering the toponymy of centre Lisbon, which tells us a lot of, from where those materials could have come.

So, an intense sample collection has been done in Lisbon centre (sometimes collecting the most clayey banks find out in archaeological excavations or in street works or building excavations) so in the near future it can be compared with ceramics from roman and medieval Lisbon kilns.

Till now all the fieldwork has been carried out and samples have been prepared for chemical analysis that is in course.

Preliminary results point the use of the same type of raw materials for sites with different chronologies and the need of more field-work.

M.A. Gouveia, Orest Project: late Roman pottery productions from the Low Tejo. *1st International Conference on Late Roman Coarse Wares, Cooking Wares and Amphorae in the Mediterranean: archaeology and archaeometry*, Barcelona, Espanha, 2002 (in press).

¹ ERA Arqueologia S.A.

² IPA

³ IPPAR

Immovable Cultural Assets - Historical Buildings and Monuments

M.I. Prudêncio, M. Nasraoui, M.A. Gouveia, J.C. Waerenborgh¹, E. Bilal²

Objectives

This research domain aims the identification of the responsible mechanisms of alteration of igneous rocks in historical buildings and monuments, with the identification of the main decay agents, and the evaluation of the prevailing degradation state of the stones. A contribution for a better definition of preservation actions is a major objective of the research results and interpretations. This research has been supported by FCT and ICCTI.

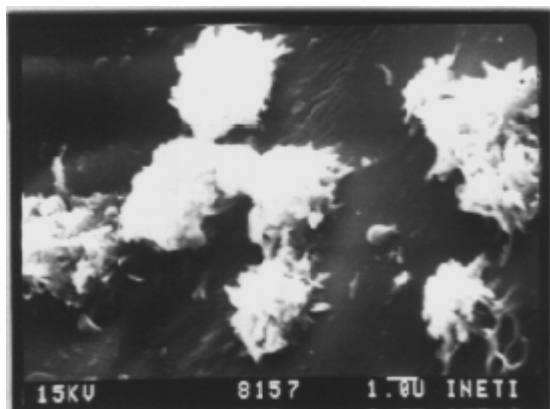


Fig. 1. Secondary rare earth elements phosphates growth in monument stone fissures.

Published, accepted or in press work

1. M. Nasraoui, J.C. Waerenborgh, M.I. Prudêncio & E. Bilal, Typology of the granitic stones of the cathedral of Évora (Portugal): a combined

Three projects include the research work developed in this domain, two financed by FCT and one by the Protocol ICCTI Portugal/France Embassy:

- (1) Alteration Processes and Conservation Methods of the Built Patrimony Made of Granite
- (2) Effects of Different Pollution Sources in the Decay of Igneous Stone Monuments
- (3) Geochemical and mineralogical characterization of the salts and other phases from the Évora cathedral: evaluation of their effects in the degradation with a view to its conservation.

Results

Field and laboratory work has proceeded in the Alentejo region particularly in granite rocks of Évora.

The study strategy of Évora cathedral has been delivered under different steps:

- 1- Mineralogical/Geochemical Approach (Learning from the past);
- 2- Salt phases occurrence (Learning from the present).

contribution of geochemistry and ⁵⁷Fe Mössbauer spectroscopy. *Journal of Cultural Heritage*, 3 (2002).127-132.

¹ Solid State Group of ITN

² École des Mines de Saint Etienne, 158 Cours Fauriel, 42023 Saint Etienne cedex 02, France.

Absolute Dating - Radiocarbon Unit

M.I. Prudêncio, A.M. Soares, R. Marques

Objectives

The good performance of this dating laboratory is a major objective, supporting the scientific community in solving chronological problems. Through the ITN-IPA protocol several projects are running with the archaeological community. This laboratory has also supported the geological community, contributing to date geological events.

Published, accepted or in press work

1. A.M. Soares, A duna de Magoito Revisitada, *Revista Portuguesa de Arqueologia*.

Results

During this year the archaeological and geological communities send us about fifty samples of different natures to be dated and included in corresponding research projects. This laboratory also contributed to the work undertaken in PhD thesis.

2. A.M. Soares, A.C. Sousa, Cronologia absoluta para os concheiros de S. Julião, *Publicação Monográfica "Concheiros de S. Julião"*

Absolute Dating - Luminescence Laboratory

D. Richter, K. Przegietka, M.R. Krbetschek¹

Objectives

The set up of the Luminescence Dating Laboratory was completed. All sources and equipment were calibrated using various techniques and materials. Protocols were established for the 3 main luminescence dating applications of TL, B-OSL, IRSL, on the 4 main materials of heated flint/quartzite, coarse grain quartz sediment, polymineral fine grain sediment and pottery/bricks. The protocols were tested by dating samples that were previously analyzed by other independent laboratories. The overall agreement of results was found to be good to excellent, and the laboratory is thus capable of independently applying the standard methods of luminescence dating, employing the required modern protocols for multiple and single aliquots.

Training of the laboratory technician was started in the technique of TL dating of heated SiO₂-bearing rocks. First results of test measurements were obtained for the Middle Palaeolithic sites of Hummal in Syria, and Oliveira in Portugal. Due to the required large size of samples, the number of samples available for dating is limited. Therefore the following technique for dating small samples was developed.

Results

Several projects are running with the geological and archaeological communities, some of them within the ITN-IPA protocol.

Luminescence dating of small samples of heated silex. New ways in dating archaeological sites by employing the orange-red emission and a SAR protocol.

The main purpose of this project is to optimise dating small samples. Multiple aliquot additive in conjunction with regenerative protocols are commonly employed for the determination of the equivalent dose

(the numerator of the age equation) flint has received since its last heating in prehistoric times. Due to the irregular shape of flint artifacts, the contribution of alpha and beta radiation from the surrounding sediment to the total dose of ionizing radiation cannot be estimated to an appropriate accuracy. It is thus necessary to remove the outer 2mm of each sample.

The dose rate calculation is thus simplified, and has to include only the parameters of external gamma and cosmic dose rates, plus the internal alpha, beta and gamma contribution as the denominator of the age equation. The required sample size is therefore >15-20g, depending on the shape of the flint. This is in contrast to the availability of large numbers of small heated flint samples from archaeological sites. A method is thus desirable to date such small samples.

The use of an orange-red TL-emission was suggested as probably being suitable for dating purposes. Following the results on volcanic material, a Single Aliquot Regeneration (SAR) protocol was tested, which requires much smaller sample amounts. Nevertheless, the outer 2mm still need to be removed, in order to achieve reasonable precision. The TL detection window was restricted to 550 – 640 nm, employing a standard bi-alkaline photomultiplier.

The TL sensitivity of the orange-red emission was found not to change due to heating. This allows the use of a very simple SAR-protocol, consisting of 2 regeneration points, which are set just above and below the intensity of the natural signal. As the material has been zeroed (checked by a plateau-test) no extrapolation to a zero point is necessary. As the two regeneration points are close to the natural signal no assumptions regarding data fitting are needed, as any deviation of the dose curve from a straight line within such in small range is insignificant for the evaluation of the natural dose.

Published, accepted or in press work

- 1- D. Richter, B. Schroeder, W.J. Rink, P.J. Julig, P.J., Long, D.G.F. & Schwarcz, H.P., The Middle to Upper Palaeolithic transition in the Levant and new TL dates for a Late Mousterian assemblage from Jerf al-Ajla Cave near Palmyra, Syria. *Paléorient* 27/ (2002) 29-46.
- 2- A.E. Marks, K. Monigal, D. Richter, W.J. Rink, H.P. Schwarcz, Preliminary results on the excavation of the Lower Palaeolithic site of Brecha das Lascas, Almonda, Portugal, *European Prehistory*.
- 3- W.J. Rink, D. Richter, N. Mercier, H. Valladas, A.E. Marks, H.P. Schwarcz, D. Kaufman, Age of the Middle Palaeolithic Site of Rosh Ein Mor, Central Negev, Israel, *Journal of Archaeological Science*.
- 4- W.J. Rink, L.A. Schepartz, S. Miller-Antonio, W. Huang, Y. Hou, D. Bakken, D. Richter, H.L. Jones, Electron Spin Resonance (ESR) Dating of Tooth Enamel at Panxian Dadong Cave, Guizhou, China, *British Archaeology Reports, International Series*. D. Richter, M.R. Krbetschek, U. Rieser, T. Trautmann, G.A. Wagner, Spectral investigation of the thermoluminescence of heated flint (silex). *Quaternary Science Reviews* 18 (1999), 113-119.
- 5- D. Richter, Thermoluminescence dating of heated flint. Method and Application. *Proceedings of the VIII International Flint Symposium, Bochum*

¹ Quaternary Geochronology Section, TU Bergakademie Freiberg, Freiberg/Sa., Germany

^{57}Fe Mössbauer spectroscopy in Geology and ArchaeologyJ. C. Waerenborgh¹, M. Nasraoui, E. Bilal², A. Mateus³, J. Figueiras³, M. I. Prudêncio**Objectives**

Identification of Fe-containing phases and determination of the oxidation state and distribution of Fe in different crystallographic sites. This investigation is applied to the establishment of metallogenetic models for ore-forming systems and in the study of the mineralchemistry behaviour of Fe in weathering processes, in the alteration mechanisms of rocks used as building materials and in clay firing.

Results

Iron is the most abundant element on the Earth as a whole, making up to 30% of its total mass. It constitutes over 80% of the core and is also the 4th most abundant element of the crust. Natural solid materials such as soils, sediments, rocks, etc., typically contain Fe in a concentration that is sufficiently high to allow the observation of good-quality Mössbauer spectra.

During 2002, besides the applications to Materials Science, described in detail for intermetallics, selective oxygen separation membranes and molecular metals under the corresponding headings of this annual report, Mössbauer spectroscopy has been applied in research areas of the CHS group. ITN has also promoted the application of this technique to support geological research projects from Universities and other research institutions.

Besides the contributions to the investigation of ancient ceramics production technology and historical buildings conservation, Mössbauer spectroscopy was intensively used for the crystalchemical characterization of minerals.

Mössbauer spectra of smectites from weathered basalt profiles in central and southern Portugal suggested the presence of interlayer Fe^{3+} in the smectites resulting from the evolution of olivines in a drier climate. Higher rainfalls seem to imply a more intense leaching of Fe. This element is incorporated only as structural Fe into smectites.

In the frame of the investigation of the geodynamic evolution of the South Variscan Iberian Suture, the nature and mechanism of the alteration of ilmenites from the Beja-Acebuches Ophiolite Complex was studied by ^{57}Fe Mössbauer spectroscopy and X-ray diffraction. Experimental data gave no evidence of crypto-exsolution textures within the ilmenite. Fast cooling from magmatic temperatures and decomposition of ilmenite in supergene conditions was suggested.

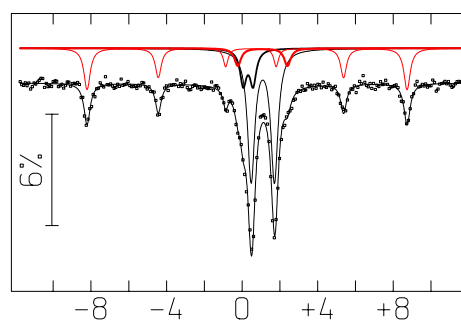


Fig. Mössbauer spectrum showing Fe^{3+} in hematite and oxidized ilmenite.

Published work (or accepted)

1. J.C. Waerenborgh, J. Figueiras, A. Mateus, M. Gonçalves, ^{57}Fe Mössbauer spectroscopy study of the correlation between the Fe^{3+} content and the magnetic properties of natural Cr spinels, *Eur. J. Min.* **14** (2002) 437-446.
2. J. Figueiras, A. Mateus, M. Gonçalves, J.C. Waerenborgh, P. Fonseca, Geodynamical evolution of the South Variscan Iberian Suture as recorded by mineral transformations, *Geod. Acta* **15** (2002) 45-61.
3. J.C. Waerenborgh, J. Figueiras, A. Mateus, M. Gonçalves, Nature and mechanism of ilmenite alteration: a Mössbauer and X-ray diffraction study of oxidized ilmenite from the Beja-Acebuches Ophiolite Complex (SE Portugal), *Min. Mag.* **66** (2002) 421-430.
4. M. Nasraoui, J.C. Waerenborgh, M.I. Prudêncio, E. Bilal, Typology of the granitic stones of the cathedral of Évora (Portugal): a combined contribution of geochemistry and ^{57}Fe Mössbauer spectroscopy, *J. Cult. Heritage* **3** (2002) 127-132.
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¹ Solid State Group of ITN

² École des Mines de Saint Etienne, 158 Cours Fauriel, 42023 Saint Etienne cedex 02, France.

³ Dept. Geology of Fac. Sciences Univ. Lisbon, P-1749-016 Lisboa, Portugal.

Geological environments

M.I. Prudêncio, M.I. Dias, J.C. Waerenborgh¹, M.A. Gouveia,

Objectives

Geochemistry and mineralogy of the earth surface, as a basic study to be applied in different fields, such as the environment quality control, is an important research domain of the CHS group. The characterization of the natural background is essential for the evaluation of the anthropogenic input in the geological environment. In this way, an important objective of the CHS group is the study of the geochemistry of the earth surface, particularly the behavior of trace and major elements and some major elements in secondary natural systems, and the alterations due to pollution actions.

Results

Among the CHS running projects, concerning the quality control and identification of pollutants of geological environments, the following projects are in course:

Lagoon environment

- A. Non-point Pollution in the Hydrosphere Due to Agricultural Practices: Source Characterization and Pollutants Mobility in the Vadose Zone**
- B. COLASU – Sustainability of Mediterranean coastal lagoon ecosystems under semi-arid climate**

Lagoons with different origin are studied: the Sete Cidades lagoon corresponding to a volcano crater in Terceira Island Azores (FCT project) and two coastal lagoons in the north of Africa -Nador in Morocco (Fig. 1) and El Meleh in Tunisia (EC project). Detailed studies of chemical and mineralogical speciation are undertaken.

Published, accepted or in press work

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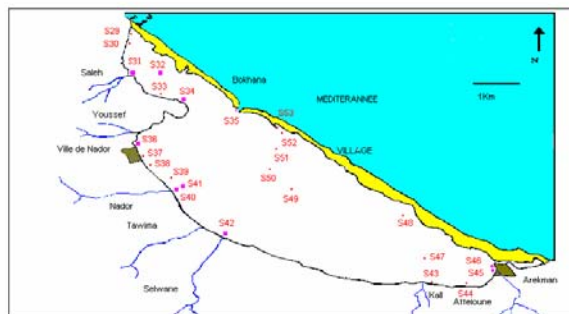


Fig. 1. Nador lagoon (Morocco) with sampling location.

Estuarine environment

A. – Continuous monitoring of trace elements in the vicinity of the Municipal Solid Waste Processing Plant (CTRSU).

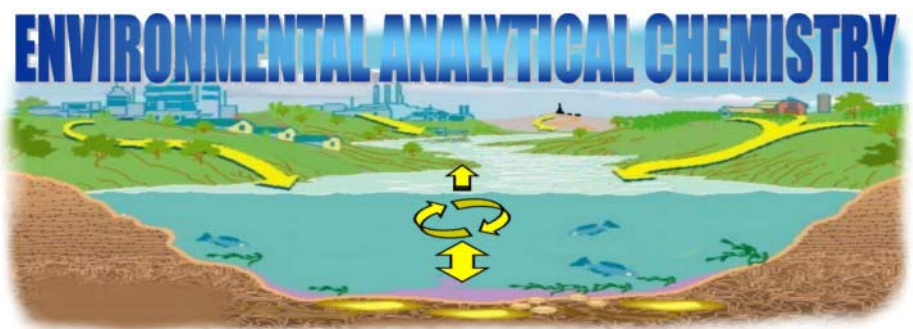
In order to follow the environmental evolution around the Municipal Solid Waste Processing Plant (CTRSU), a continuous monitoring program is running since 1998, financed by Valorsul, in the Tagus estuary, being CHS group responsible for the Trace Elements study. Samples of soils, vegetation, water and sediments are undertaken, as well as, chimney filters of the incinerator, so a more accurate evaluation of the pollutants contribution of this central may be established. Valorsul invited us to public presentations where our results are discussed not only within the scientific community, but also with the general public namely the local population and the local authorities. For the year 2002 the ITN staff proposed a new sampling protocol, increasing the number of sample sites and type of samples, which was recognized very advantageous, particularly for the right margin of the Tagus river, in order to obtain a better understanding of the overall influence of the CTRSU.

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- 2.M. I. Dias, M. Suárez Barrios, S. Prates, J.M. Martín Pozas Characterization and acid activation of Portuguese special clays, in *Applied study of cultural heritage and clays*, D.C. Bain and J.L. Pérez-Rodríguez (eds) (in press).

¹ Solid State Group of ITN

Environmental Analytical Chemistry



Environmental Analytical Chemistry

Maria de Fátima Araújo

The research within the **Environmental Analytical Chemistry** Group has been mainly dedicated to the study of the Biogeochemical Cycles of Chemical Elements and Light Isotopes in the Environment. This multidisciplinary Group is constituted by chemists, geologists and biologists and for the last three years has reinforced the analytical capabilities and enlarged the expertise towards a strengthening on the Environmental and Analytical fields. The most important equipments available for this purpose are the Energy-Dispersive X-Ray Fluorescence Spectrometer, the Tritium Dating Unit and Mass Spectrometers for Light Isotopes (one of them has been equipped with an Elemental Analyser during the current year). The combination of powerful multielemental, isotopic and dating techniques with the growing expertise (analytical and isotopic chemistry, environmental geochemistry, hydrology and dating) within the team has made possible a substantial increment in our research. This has been developed under projects which are externally financed, run in collaboration with other research teams and other National and International Institutions.

The major domain of research developed during the current year has been *Environmental Geochemistry*, focused in the *Sedimentary Geochemistry and Isotope Hydrology* fields:

1. *Sedimentary Geochemistry* – Evaluation of the consequences caused by the changes that occurred during the last decades in the main Iberian river basins. Studies on multielemental and isotopic composition, as well as geochronology and dating combined with meteorological, climatic, oceanographic, sedimentological and historical aspects are being applied to understand the evolution of those basins and to assess the continental influence in the coastal marine environment. The set of obtained data will allow suggestions concerning legislation involving river basins, including their estuaries and adjacent shelves and coastlines.
2. *Isotope Hydrology* – studies aiming to contribute to a better understanding of the dynamic evolution response of groundwater systems to Human influences and to the climatic evolution. These resources have become progressively more endangered by accelerated modification of the natural conditions. A national network for isotopes in precipitation provides important information for hydrological investigations, relevant for the management, protection and development of water resources.

The non-destructive characteristic of the EDXRF method has been driving for many years some of our

research to the study of archaeological metallic artefacts with museological and archaeological interest aiming to identify their Provenance, Technology and Use. In recent years, *Archaeometallurgy* has had a growing relevant interest in our research activities. The absence of research teams in this area within the country and the significance of the obtained results are justifying the expansion of our research on this subject.

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

During 2001, a meaningful improvement of our collaborations was accomplished by the running of the multidisciplinary project Consequences of River Discharge Modifications on Coastal Zone and Continental Shelf (CRIDA), funded by the Programa de Apoio à Reforma dos Laboratórios do Estado – PLE/8/00. As a result of the reinforcement of our collaborations, nine projects have been submitted for funding.

Another important achievement was the coupling of the mass spectrometer SIRA 10 with an Elemental Analyser dedicated to the ^{13}C , ^{15}N and ^{18}O isotopic determinations in solid and liquid samples, funded by the projects and services rendered by the group. This new equipment is of utmost importance in *Environmental Geochemistry* (sources of pollutants, e.g. fertilisers, pesticides, industrial), palaeoceanographic and palaeobiological changes.

Concerning the reinforcement of the analytical capabilities we have been making proposals in order to install Mass-Spectrometer based elemental and isotopic analyser, in particular an HR-ICP-MS (High Resolution, Inductively Coupled Plasma-Mass Spectrometry). The International Advisory Board that followed the ITN activities for the last years has repeatedly supported this proposal. During the call of the “Fundação da Ciência e Tecnologia” within the “Programa Nacional de Re-Equipamento Científico”, we have led a National proposal, aiming at the implementation of a “Centre of Elemental and Isotopic Analysis”, located at the ITN, which includes this equipment.

An important goal within the group is the training of young research students and the enlargement and reinforcement of collaboration with other research groups and Institutions. However, it is worth noting that in spite of our efforts in enlarging the group with graduated and post-doctoral students, the permanent staff is fairly small and in order to strengthen our research it is becoming urgent the contract of at least one more researcher.

Environmental Analytical Chemistry

Research Team

Researchers

- M.F. ARAÚJO, Auxiliary researcher, Group Leader
- P.M. CARREIRA, Auxiliary researcher
- D. BURDLOFF, Post-Doctoral, FCT grant since March 2002
- F. VITALI, Post-Doctoral, FCT grant until October 2002
- L.R. JAYASEKERA¹, Professor, IAEA fellowship since November 2002

Students

- P.G. FERNANDES, PhD student, FCT grant
- C. CORREDEIRA, MSc student², FCT grant
- M. ANDRADE, MSc student, FCT grant
- M. LAMBÉRIA, MSc student
- T. BARBOSA, graduate student, ITN grant until October 2002
- S.A. GOMES, graduate student, FCT grant until March 2002

Technical Personnel

- P. VALÉRIO, graduate technician
- D. NUNES, graduate technician
- M. CORREIA, laboratory technician

¹ On leave from Kelaniya University, Sri Lanka.

² MSc degree obtained in 13 November 2002.

Funding (€)

Research Projects: 125 760

Total: 125 760

Publications

Journals:	8	and 10 in press
Proceedings:	6	
Conf. Communications:	6	
Other publications:	1	
Theses: MSc	1	

Sediment Geochemistry of the Northern Iberian Coastal Area

M.F.Araújo, C. Corredeira, J.-M. Jouanneau¹, P. Valério, A. Gouveia², M. Lambéria

Objectives

This research aims at the study of interactions between estuarine, *Rias* and continental shelf sedimentary facies at the north of Iberia. A primary objective is the identification of the environmental impacts suffered in this area, distinguishing between natural and man-induced disturbances. Chemical, sedimentological and geochronological studies were carried on the northwestern Iberian coastal zone. This region is drained by major river basins among which, Minho and Douro rivers are of a greater importance due to the dimension of their basins and to the amount of the transported sediment load. In spite of the dams built during the last decades, they still represent the main continental sources of sediments at the coastal region. At the Galician region the presence of the *Rias* drastically changes the coastal morphology. Studying the biogeochemical processes and dispersal pathways of the river-borne materials, *Rias* and shelf sediments assesses the continental influence on the shelf.



Fig. 1 – Crestuma dam in Douro river.

Results

The geochemical studies of the collected samples indicate that sediments deposited at the Northern Iberian Shelf have mainly two different sources: lithogenic and biogenic. Within the estuaries and *Rias* (Vigo and Pontevedra) anthropogenic influences have been detected. Particularly, *Rias* regions seem to have been exposed to some recent local anthropogenic (Zn and As) contamination due to Human activities. In fact contamination was mainly detected at the surficial layers of the studied cores. Besides, results demonstrated that Galician *Rias* do not behave as sediment source to the continental shelf, since there are no signs of lithogenic and/or anthropogenic elemental exportations to the adjacent Continental Shelf. As a consequence it seems that no materials are being exported to the coastal marine environment. The gradient on the zirconium distribution off the Vigo *Ria* indicates that the unique possible exchange of sediments would be from the marine environment towards the Coast. Southwards, at the NW Portuguese Continental shelf, the Douro River seems to have made a substantial sediment contribution to the muddy deposit located in the middle of the adjacent shelf, although not by a direct process. The trace metal distribution in the sediments provides evidence for the release of these sediments into the marine environment. In fact, none of the anthropogenic heavy metals enrichment detected within the Douro estuary was detected on the shelf.

Published, accepted or in press work

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5. C. Corredeira, Caracterização Química de Sedimentos Finos da Plataforma Continental Minho/Galiza, *MSc Thesis in Ecology, Management and Modeling of Marine Resources*, Instituto Superior Técnico (2002).

¹ DGO-UMR 5805 CNRS, Université Bordeaux I, Bordeaux, France.

² PCC Group.

Consequences of River Discharge Modifications on Coastal Zone and Continental Shelf

M.F.Araújo, F. Vitali, P.M. Carreira, C. Corredeira, D. Burdloff,
P. Valério, A. Gouveia¹, J.-M. Jouanneau²

Objectives

Run-off and sediment load carried by large river basins of the West Iberian margin to estuaries and to the continental shelf has been drastically modified in the course of this century because of a range of anthropic activities. As a result, the frequency and magnitude of the floods have progressively decreased, depriving rivers of their capacity to clean their hydrographic basins of accumulated sediment. This work aims at the evaluation of the consequences caused by the changes that occurred during the last decades in the Tejo and Guadiana river basins. Studies include meteorological, climatic, oceanographic, geochemical (elemental and isotopic), mineralogical, sedimentological and historical aspects.



Fig. 1 - Guadiana Basin.

Results

Investigations are being carried out on chemical, isotopic and mineralogical composition of the fine sediment supply along the southwestern Iberian continental shelf. Surficial sediments were collected along three transects defined off Guadiana, Tinto-Odiel and Guadalquivir estuaries. Cores (with depths down to 4 meters) were also sampled along the southern shelf to evaluate the temporal variations and associated phenomena with sediment deposition.

The geochemical characterisation of surficial sediments comprising 22 trace elements (REE included) quantified along the three transects allowed

establishing individual distribution patterns characteristic of each transect that identify the individual influence of the rivers.

For transect off Guadiana estuary, in which Pb, As, Zn, Cu and Co anomalies were found, concentration of these elements becomes slightly higher with the distance from the coast. A similar tendency is shown by the organic matter concentration indicating its important role in the fixation of those heavy metals. The accumulations of Pb, Zn and Cu were found to be related to industrial activities. For transect off Guadalquivir estuary the concentrations of all the analysed trace elements show the highest values both in the mid and outer shelf, to some extent due to grain size control. The relatively higher Sr and Ba concentrations are directly correlated with the relatively higher carbonate content existent in the sediments. In general, REE contents in the shelf surficial sediments decrease with the distance to the coastline, probably due to the change of a dominant detrital sedimentation near the coast to a chemical sedimentation far from the coast. The strong Ce negative anomaly is indicative of a more hydrogenised environment in the sediment/water interface.

Recently, we have started investigating the change in the source of organic matter possibly induced by the river discharge modifications on coastal zone and continental shelf, by using $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotope tracers. These environmental isotopes are used in marine environments for the assessment of paleoceanographic and paleobiogeochemical changes. They are important on the identification of terrestrial and marine organic sources, since they display contrasted isotopic signatures. Measurements are currently being carried out along sections of collected sediment cores to estimate the temporal variations on the origin of the sediment load supplied to estuaries and shelf.

Published, accepted or in press work

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2. A. Machado, F. Rocha, M.F. Araújo, F. Vitali, J.A. Dias, C. Gomes, Application of Chemical and Mineralogical Parameters for the Characterisation of Surficial Sediments of the Continental Shelf Off Guadiana Estuary, *Proceedings of the XI Seminário Ibérico de Química Marinha* (2002) 57.
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¹ PCC Group.

² DGO-UMR 5805 CNRS, Université Bordeaux I, Bordeaux, France.

Groundwater Resources as Indicators and Archives of Palaeoclimatic Changes

P.M. Carreira, D. Nunes, M.P.L. Andrade, P.A. Fernandes, J.M. Marques¹, F.A. Monteiro Santos², M.O. Silva³ and M.A. Marques da Silva⁴

Objectives

In the last decades, the groundwater resources have become progressively more endangered, both in quality and quantity, by accelerated modification of their natural conditions due to industrial development associated with the growing of the demographic density and intense agriculture.

Isotopic and geochemical data are being used to evaluate the origin of groundwater systems, characterise the deep aquifers in relation to the shallow groundwater and define the properties of the groundwater with respect to environmental issues.

Isotopic, geochemical and geophysical methodologies are being applied into the development of conceptual geohydrological circulation models, which in a near future could be used in the appraisal of the deep groundwater resources and in the identification of palaeoclimatic changes.

Results

Taking into account the delimitation of recharge protection zones, our main goals are: identification of groundwater mixtures between different types of aquifer systems (cold dilute groundwater and mineralised deep groundwater); determination of residence time. Work is being developed under research projects in Caldas do Moledo geothermal mineral water, Monção, Cadelas Gerês Spas in the groundwater systems of Vilarelho da Raia / Chaves

group and Vidago / Pedras Salgadas group at Caldas do Moledo. The isotopic signatures of the geothermal fluids reveal to be depleted in ¹⁸O and ²H, relative to local shallow groundwater, and point to a recharge area located at high elevations (900-1000 m a.s.l.). Also, as shown by means of chemical and isotopic data, some of the geothermal spring waters of Caldas do Moledo area result from mixing between shallow groundwater and geothermal waters. During the long residence time (apparent ¹⁴C groundwater age 15.66 ± 2.86 ka BP) the infiltrated waters are mineralised by water-granite interaction, as indicated by the HCO₃-Na chemistry of the geothermal waters, in a low-temperature environment.

Special emphasis was also put on the use of coupled ³H, ^δ¹³C and ¹⁴C data of CO₂-rich mineral waters (N Portugal Vilarelho da Raia / Chaves group and Vidago / Pedras Salgadas group). ^δ¹³C values measured in the TDIC range between -6.00 ‰ and -1.00 ‰ vs VPDB. These values indicate that the concentration of carbon dioxide is being modified by large quantities of mantle CO₂ (free of radiocarbon), since the recharge waters (cold dilute spring waters) present a mean ^δ¹³C value around -23 ‰ vs VPDB. On the other hand, the systematic ³H content found in these thermomineral systems should be faced as a signature of a short underground circulation path, which is incompatible with the low ¹⁴C content (between 4 and 10 pmc).

Published, accepted or in press work

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¹ Laboratório de Mineralogia e Petrologia (LAMPIS), I.S.T., Av. Rovisco Pais 1, 1049-001, Lisboa, Portugal.

² Instituto de Ciência da Terra e do Espaço. Rua da Escola Politécnica 58, 1269-102 Lisboa, Portugal.

³ U. de Lisboa, Centro de Geologia, Faculdade Ciências, Campo Grande C3, 5º Piso, 1749-016 Lisboa, Portugal.

⁴ Universidade de Aveiro, Departamento de Geociências, Campus de Santiago, 3810-193 Aveiro, Portugal.

National Network for Isotopes in Precipitation

P.M. Carreira, L. Gourcy¹, M.F.Araújo, D. Nunes, P. Valério, T. Barbosa and M. Correia

Objectives

Portugal through ITN / Environmental Analytical Chemistry research group has been participating in the IAEA/WMO (International Atomic Energy Agency / World Meteorological Organisation) in the Global Network for Isotopes in Precipitation (GNIP) since 1988. The work developed aims to provide basic isotope data for hydrological investigations, by determining the temporal and spatial variations of environmental isotopes (oxygen-18, deuterium and tritium). The data can be used as tracers of the isotopic composition of past and present precipitation, which are of great importance for climate and water studies. These informations are also very relevant for water resources inventory, planning and development.

Results

The spatial and temporal isotope distribution in precipitation can be related to a number of environmental parameters, which characterise the source region but also and the sampling site. Seasonality, amount of precipitation, altitude dependence, continentality, the role of local temperature, together with the source specific fractionation between ¹⁸O and ²H, all contribute to the isotope content of precipitation. This information is being applied in hydrogeological research studies.

Using the existent database from Portuguese stations, the EAC Group obtained several conclusions:

1. Relation between the isotopic composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) with the amount of precipitation:
 $\delta^{18}\text{O} = (-0.01 + 0.003) \text{ Pp} + (-4.46 + 1.36)$
 $\delta^2\text{H} = (-0.08 + 0.02) \text{ Pp} + (-27.28 + 9.34)$
2. Relation between the isotopic composition of precipitation and temperature:
 $\delta^{18}\text{O} = (0.21 + 0.02) \text{ T} + (-8.59 + 1.07)$
 $\delta^2\text{H} = (-1.23 + 0.16) \text{ T} + (-51.56 + 7.91)$

Published, accepted or in press work

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3. The isotopic gradient with the altitude of the meteorological stations obtain is the following:

$$\Delta\delta^{18}\text{O} = -0.2 \text{ ‰} / 100 \text{ m and } \Delta\delta^2\text{H} = -1 \text{ ‰} / 100 \text{ m}$$

Besides, a mixture of different air masses can be identified in Faro station (South coast of Portugal), traduced by a shift in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values from the observed pattern.

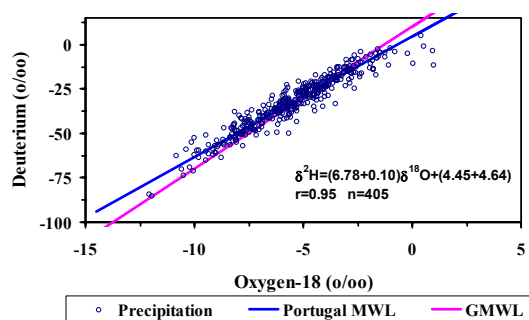


Fig. 1 – $\delta^2\text{H}$ and $\delta^{18}\text{O}$ relationships for monthly data of Portugal Network for Isotopes in Precipitation.

ITN participation under the IAEA Coordinated Research Programme “*Isotopic composition of precipitation in the Mediterranean Basin in relation to air circulation patterns and climate*”, includes the determination of the isotopic composition in precipitation in daily and monthly events. This study also involves the investigation of the isotopic variation and evolution of atmospheric water vapour in the Lisbon area (ITN campus).

Isotopic results are compiled and gathered in the IAEA Data Base and disseminated via IAEA publications to be used in international hydrogeological and climatologic studies (www.iaea.org/programs/ri/gnip/gnipmain.htm).

Mediterranean Basin in Relation to Air Circulation Patterns and Climate, Final Report (2002).

2. T. Barbosa, Manual do Laboratório de Datação por Trítio, ITN Internal Report (2002) 19p.
3. www.iaea.org/programs/ri/gnip/gnipmain.htm

¹ IAEA – Isotope Hydrology Section.

Archaeometallurgy; Provenance, Technology and Use of Archaeological Metallic Artefacts

M.F. Araújo, P. Valério, A.A. de Melo¹, L. de Barros², A.C. Sousa³ and J.S. Martinez⁴

Objectives

This area intent to study the chemical composition of material remains from past societies, namely metallic artefacts, in order to understand their origin, production and use by ancient man. The obtained knowledge improves the comprehension of the human behaviour during the pre-history of Portugal, including different chronological periods, such as, the Calcolithic, Bronze, Iron and Roman Age Culture groups.

Results

Some artefacts and collections have been studied during the current year in collaboration with some archaeologists. Projects were run within the IPA/ITN protocol for the following archaeological sites:

- *Quinta do Almaraz (Almada)*
- *Penedo do Lexim (Mafra)*
- *Quinta do Fojo (Canas de Senhorim)*
- *Senhora da Guia (Baiões)*

In order to improve the work developed during last year in Quinta do Almaraz, additional metallic artefacts and foundry fragments were studied. Latest results clearly indicate the existence of the extraction of silver by cupellation, a technology introduced by the Phoenician in this region during the Iron Age³.

The study on Penedo do Lexim was enhanced with the investigation of some more artefacts. Their chemical composition proved the existence of different Prehistorical occupations of the site: Calcolithic (copper with arsenical impurities), Late Calcolithic or Early Bronze Age (Arsenical copper), Bronze (copper and tin alloy) and Late Bronze Age (bronzes with considerable amounts of lead).

Another research includes a comparative analytical study carried out at the ID-22 of the ESRF in Grenoble (in collaboration with Dr. Teresa Pinheiro, Physics Department) and at ITN of a Roman metallic artefact - *Centaurus* from Canas de Senhorim (Fig. 1). The chemical composition determined by both techniques permitted to assess the extent of the surface enrichment. The *Centaurus* original alloy is a bronze with a rather high Pb content². The corroded surface layer appears to be enriched in Sn, Pb and Sb. The addition of Pb to the molten alloy increases its fluidity and therefore high contents of this element are common in bronze decorative artefacts. The obtained composition is comparable with published values for Roman bronze statues from Eastern Europe.



Fig. 1 – Roman *Centaurus* from Canas de Senhorim.

The set of metallic artefacts from Senhora da Guia (Baiões) is the most important collection from the Late Bronze Age in Portugal. This work is still on its early stage with the study of the elemental composition of more than 70 artefacts, including moulds, slags and foundry fragments.

Published, accepted or in press work

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3. M.F. Araújo, L. Barros, A.C. Teixeira, A. Melo, Energy Dispersive X-Ray Fluorescence Spectrometry – Study of Pre-Historical Artefacts from Quinta do Almaraz (Cacilhas, Portugal), *Book of Abstracts of the 5th International Topical Meeting on Industrial Radiation and Radioisotope Measurement Applications* (2002) 123.

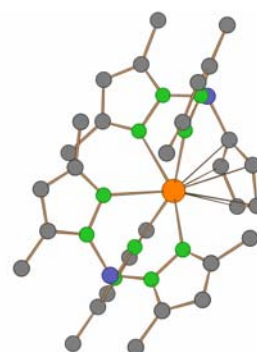
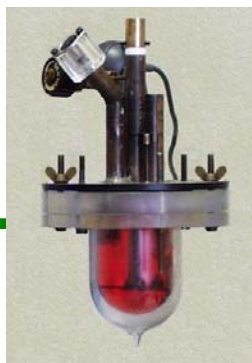
¹ Museu Nacional de Arqueologia, Praça do Império, 1400-206 Lisboa.

² Museu Municipal de Almada, Olho de Boi, 2800 Almada.

³ Câmara Municipal de Mafra, Praça do Município, 2644-001 Mafra.

⁴ Faculdade de Letras da Universidade de Lisboa, Alameda da Universidade, 1600-214 Lisboa.

Inorganic and Organometallic Chemistry



Inorganic and Organometallic Chemistry

António Pires de Matos

The activities of the group comprise the synthesis, characterisation and chemical reactivity studies of inorganic, organometallic and intermetallic compounds of actinides and lanthanides in order to understand the influence of the electronic configuration and of the size of these elements in the chemical behaviour of their compounds. Chemical reactivity is assessed by stoichiometric reactions and by homogeneous and heterogeneous catalytic studies. Gas-phase ion chemistry studies with the same elements and the study of the energetics of *f*-element compounds are also made with the same objective.

As this is the only Group in ITN which can handle macroscopic quantities of the most toxic actinides, having a dedicated laboratory for this purpose, we are starting to apply our knowledge to environmental studies, particularly research concerning radioactive waste and migration of actinides. Research in waste vitrification, actinide speciation studies and lanthanide/actinide separation are being envisaged.

We have been investigating the complexation of trivalent uranium and lanthanide ions by multidentate nitrogen ligands, a class of ligands that can be relevant for An(III)/Ln(III) separation, due to the better affinity of the soft nitrogen ligands for 5*f* vs 4*f* trivalent ions.

As the chemistry of the elements of the *f* block is very rich, we are trying to explore the very interesting catalytic properties of some uranium, thorium and lanthanide compounds, both in homogeneous and heterogeneous phases, for applications in Ziegler-Natta catalysis and oxidative coupling of methane.

An important part of the output of the Group is the training of young research students. Collaborations with other research groups of ITN and of the universities continue to be intensified. We should also refer a recent collaboration with the industry in a waste treatment research project and with the Faculty of Arts in the University of Lisbon to develop new materials for art.

The work made during 2002, described in the following pages, is summarized as follows:

A series of *f* block metal complexes with the hexadentate ligand [(SiMe₂NPh)₃-tacn]³⁻ have been prepared and structurally characterized. A related ligand resistant to hydrolysis is being prepared in order to be applied to extraction studies.

Gas-phase ion chemistry studies of transuranium actinides by FTICR/MS have been continued, with a focus on oxidation reactions. We performed a thermodynamic characterization of the americium

oxides AmO and AmO₂, for which no data was previously known.

Calorimetric studies on U(III) and U(IV) organometallic compounds were performed. Preliminary results on U(IV) compounds seem to show that the different reactivity of UCl₂R(Tp^{Me2}) (R=CH₂SiMe₃ and CH(SiMe₃)₂) compounds cannot be attributed to a difference in the U-C bond strength.

A new ansa-metallocene type ligand, the dianionic hydrobis(3-methylpyrazolyl)(tetramethylcyclopentadienyl)borate, [B(3-Mepz)₃(C₅Me₄)], has been synthesized and its interaction with *f*-elements is being pursued.

The heterobimetallic oxides Ln₂CuO₄.3CuO (Ln=La, Pr, Nd, Eu, Gd), Ln₂Cu₂O₅.2CuO (Ln=Dy, Tm, Yb) and MO₂.2CuO (M=Ce, Th) were synthesized to be used as catalysts in the oxidative coupling of methane to C₂ hydrocarbons. A prototype for studies by temperature programmed reduction (TPR) of the heterobimetallic oxides was built and tested.

Pursuing previous work on the synthesis of lanthanide alkoxides, the compounds [Eu(OC₆H₃Bu^t₂-2,6)₂(THF)₃].0.75C₇H₈ and [Yb(OC₆H₃Bu^t₂-2,6)₂(NCMe)₄] were synthesized. Samarium, europium and ytterbium divalent complexes (Yb(OC₆H₃Bu^t₂-2,6-CH₃-4)₂(THF)₃, Eu(OC₆H₃Bu^t₂-2,6-CH₃-4)₂(THF)₃, Sm(OC₆H₃Bu^t₂-2,6-CH₃-4)₂(THF)₃) and trivalent complexes (Yb(OC₆H₃Bu^t₂-2,6-CH₃-4)₃(THF)₃, Sm(OC₆H₃Bu^t₂-2,6-CH₃-4)₃) were synthesized and immobilized on silica surfaces.

The ²⁹Si MAS NMR spectra for the activated support before and after impregnation with the divalent and trivalent ytterbium compounds have been made.

A small chemical reactor was designed to study plastic gasification using molten copper as catalyst. The plastics already tested (polyethyleneterephthalate, polypropylene and polyethylene) showed that the process is adequate, being CO₂, H₂ and CO the major products.

The work made was financially supported by 5 projects of FCT, one project supported by an industrial association, SPV, one NATO post-doctoral grant, one ICCTI/DAAD grant and one PhD grant. 10 new projects were submitted to FCT.

Inorganic and Organometallic Chemistry

Research Team

Researchers

- A. PIRES de MATOS, Coord. Researcher, Group Leader
- Â. DOMINGOS, Principal Researcher
- N. MARQUES, Principal Researcher
- J. MARÇALO, Auxiliary Researcher
- J. BRANCO, Auxiliary Researcher
- J.P. LEAL, Auxiliary Researcher
- T.A. GASCHE, Auxiliary Researcher
- J.M. CARRETAS, Auxiliary Researcher

- B. RAMOS, BIC grantee, POCTI
- C. DIAS, BIC grantee, POCTI
- M. SANTOS, BIC grantee, POCTI
- V. GAFFNEY, grantee, SPV
- A.S. DIAS, grantee, POCTI

Technicians

- A. CARVALHO, laboratory assistant
- A.J. SOARES, analyst

Students

- D. ROITERSHTEIN, Post-Doc, NATO grant
- M.A. ANTUNES, PhD student, FCT grant

Funding (€)

Research Projects:	63 146
ITN:	3 962**
Other Sources:	4 729
Total:	71 837

Publications

Journals:	7 + 1 in press *
Proceedings:	1
Conf. Communications:	11
Other Publications:	1
Theses: PhD	1

* One member of the Group, Ângela Domingos, contributed as crystallographer to another 5 published papers and 2 in press from the Inorganic and Radiopharmaceutical Chemistry Group of the Chemistry Department of ITN.

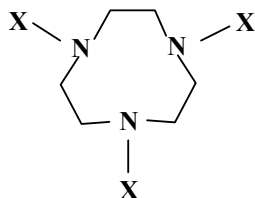
** 3487 spent on a laboratory ventilation system.

Uranium and Lanthanide (III) Triazacyclononane Derivatives

B. Ramos, Â. Domingos, N. Marques

Objectives

The aim of this study is to investigate the complexation of trivalent uranium and lanthanide ions by multidentate nitrogen ligands, a class of ligands that can be relevant for An(III)/Ln(III) separation. It has been noted that soft nitrogen or sulfur ligands should be used within separation processes, taking advantage of the better affinity of the soft nitrogen ligands for 5f vs 4f trivalent ions. Also, 4f and 5f trivalent ions are strongly solvated in aqueous solutions and to compete with the water molecules for bonding these ions, these soft nitrogen or sulfur ligands should be preferably multidentate. These features can be fulfilled by TACN- X_3 ($X = \text{HCl}$, SiMe_2NPh , $\text{SiMe}_2\text{N}^t\text{Bu}$) ligands.



Results

Reaction of yttrium and lanthanide trichlorides ($\text{Ln} = \text{La}, \text{Eu}, \text{Yb}$) with one equivalent of the trisodium salt of 1,4,7-tris(dimethylsilylphenyl)aniline-1,4,7-triazacyclononane ($\text{Na}_3[(\text{SiMe}_2\text{NPh})_3\text{-tacn}](\text{THF})_2$) gives good yields of the compounds $[\text{M}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}]$ ($\text{M} = \text{Y}$ (**1**), Eu (**3**), Yb (**4**)), and $[\text{La}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}(\text{THF})]$ (**2**). Reduction of **3** with Na/Hg followed by recrystallization in the presence of diglyme yielded crystals of $[\text{Eu}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}][\text{Na}(\text{diglyme})_2]$ (**5**). Synthesis of the uranium (III) complex $[\text{U}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}]$ (**6**) is achieved by reaction of one equivalent of $\text{Na}_3[(\text{SiMe}_2\text{NPh})_3\text{-tacn}](\text{THF})_2$ with uranium trisiodide.

The U(IV) complexes, $[\text{U}\{(\text{SiMe}_2\text{NPh})_3\text{-tacn}\}X]$ ($X = \text{Cl}$ (**7**); I (**8**)), were prepared via oxidation of **6** with benzyl chloride or I_2 , but salt metathesis from UCl_4 provided a higher yield route for **7**. The solid state structures of **1-7**, were determined by single crystal X-ray diffraction. The metal centre in the neutral complexes **1**, **3**, **4**, and **6** and in the ionic **5** is six-coordinate by the three nitrogen atoms of the amide groups and the three nitrogen atoms of the triazacyclononane ring with trigonal prismatic

geometry. In **2** the six nitrogen atoms of the ligand are in a trigonal prismatic configuration with the oxygen atom of the THF capping one of the triangular faces of the trigonal prism (Fig. 1).

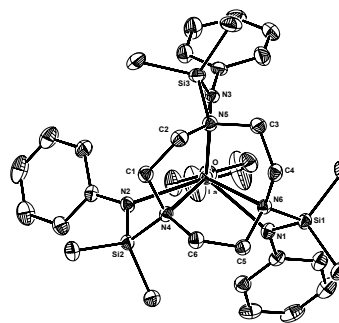


Figure 1-ORTEP drawing of **2**.

In **7** the coordination geometry around the uranium atom is best described as bicapped trigonal bipyramidal (Fig. 2).

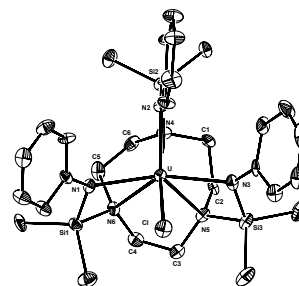


Figure 2-ORTEP drawing of **7**.

A new ligand resistant to hydrolysis has been synthesized, $\text{TACN}-(\text{CH}_2\text{NPh})_3$. Studies of the extraction of the different ions with this ligand are in progress.

Part of this work was presented as a communication[1] and a manuscript entitled Complexes of Group-3 Metals with the Hexadentate 1,4,7-Tris(dimethylsilylphenyl-aniline)-1,4,7-Triazacyclononane was submitted to *Inorg. Chem.*

Published, accepted or in press work

1. B. Monteiro, D. Roitershtein, H. Ferreira, Â. Domingos, A. M. Martins, N. Marques, Complexos de Metais do Grupo-3 com o Ligando 1,4,7-

Tris(dimetilsililfenilnililina)-1,4,7-Triazaciclononano, *XVIII Encontro Soc. Portuguesa de Química*, Aveiro (2002) 131.

Gas-Phase Ion Chemistry of Lanthanides and Actinides

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

Objectives

As a contribution to a better knowledge of the chemistry of the lanthanide (Ln) and actinide (An) series elements, we have been studying the gas-phase reactivity with organic and inorganic molecules of ions deriving from the metals, metal oxides, metal oxide clusters, intermetallic and organometallic compounds of these elements. The experimental work is based on the use of Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS), a technique that is specially suited for the study of the chemistry of ion/molecule systems in the gas phase. Special attention is given to the kinetics, mechanisms and energetics of the reactions, that we try to correlate with the electronic structure of the ions and to compare with analogous processes occurring in solution and on solid/gas interfaces. In the case of the actinides, we intend to gain a better insight into the potential 5f electron contribution to reactivity in the first half of the An series, and to estimate energetic data for An species that may be of interest for condensed-phase processes.

Results

We have recently reported on the first gas-phase ion chemistry studies of the transuranium actinides Np and Pu by FTICR-MS, in which contributions were made to the characterization of the oxidation reaction kinetics and thermodynamics of Np and Pu ions [1-2]. Charge-transfer “bracketing” experiments to determine the ionization energy of PuO₂ were performed, from which a value of 7.03 ± 0.12 eV was obtained. This IE(PuO₂) is 2-3 eV lower than the literature values, but according to our observations

for the oxidation thermodynamics. Keeping a focus on the oxidation of transuranium ions, we have extended our previous study by performing for the first time experiments with americium using FTICR-MS. Reactions of Am⁺ and AmO⁺ with the oxidants N₂O, C₂H₄O (ethylene oxide), H₂O, O₂, CO₂, and NO have been studied. Am⁺ formed AmO⁺ with all the reagents except NO, while AmO⁺ only reacted with C₂H₄O to form AmO₂⁺ and other products. These results allowed to estimate the previously unknown Am⁺-O and OAm⁺-O bond dissociation energies. The ionization energies of AmO and AmO₂ could also be determined by two different types of experiments: charge-transfer “bracketing” with AmO₂⁺, yielding IE(AmO₂) = 7.23 ± 0.15 eV, and AmO⁺ reactivity with dienes, following a model developed by Helmut Schwarz and co-workers, leading to IE(AmO) = 5.9 ± 0.2 eV. With this last method, we were also able to resolve between two disparate literature values for the ionization energy of PuO.

We also performed experiments aimed at a comparative study of the gas-phase reactivity of An ions with organic molecules along the first half of the An series. Previous studies of Th and U metal and metal oxide cations with C₆H₅Cl [3] were complemented with experiments involving Np, Pu and Am. Both the metal and the metal oxide ions of the transuranium An revealed smaller reactivities towards C₆H₅Cl as compared to thorium and uranium. Another organic substrate studied was indene (C₉H₈), with which all the An metal and metal oxide cations were rather reactive, leading in most cases to the formation of An bis(indenyl) species.

Published, accepted or in press work

1. M. Santos, J. Marçalo, A. Pires de Matos, J.K. Gibson, R.G. Haire, Gas Phase Oxidation Reactions of Neptunium and Plutonium Ions Investigated via Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, *J. Phys. Chem. A* 106 (2002) 7190.
2. M. Santos, J. Marçalo, A. Pires de Matos, R.G. Haire, J.K. Gibson, Estudo em Fase Gasosa de Iões de Neptúnio e Plutónio e seus Óxidos por FTICR-MS”, *XVIII Encontro Nacional da Sociedade Portuguesa de Química*, Aveiro, March 2002.
3. J. Marçalo, M. Santos, A. Pires de Matos, Estudo por FTICR-MS das Reacções em Fase Gasosa de Iões de Tório e Urânio com Clorobenzeno, *XVIII Encontro Nacional da Sociedade Portuguesa de Química*, Aveiro, March 2002.

¹ Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Energetics of f- Element Compounds

J.P. Leal, N. Marques, M.A. Antunes

Objectives

The main objective of the project is to foster the knowledge on energetics of f-element compounds (both on solid state and in solution). To achieve this goal both lanthanide and actinide organometallic and intermetallic compounds were studied. Also, alkaline and alkaline-earth compounds (alkoxides, phenoxides, thiolates and cyclopentadienyls) will be addressed in order to provide adequate models that allow a deeper understanding and improve our capability of prediction of properties.

Results

During 2002 the work followed different paths to achieve the stated objectives.

The synthesis of U(III) and U(IV) organometallic compounds and their reactivity were undertaken. These compounds were also studied on conditions similar to the ones in the calorimetric cell in order to know if the proposed reactions are suitable for calorimetric studies. For uranium (IV) compounds, as expected, the alcoholysis reaction shows to be an adequate one. For the compounds with trivalent uranium, the more promising reaction is the one with $\text{HB}(3,5\text{Me}_2\text{-pz})_3$ or the corresponding potassium salt. All the other reactions studied lead to oxidation/decomposition of the compounds or are too slow to be measured in the available apparatus. The preliminary results on U(IV) compounds seem to show that the different reactivity of $\text{UCl}_2\text{R}(\text{Tp}^{\text{Me}_2})$ ($\text{R}=\text{CH}_2\text{SiMe}_3$ and $\text{CH}(\text{SiMe}_3)_2$) compounds cannot be attributed to a difference in the U-C bond strength.

To develop a large enough database of alkaline and alkaline-earth metal compounds that permit to predict, with a high precision, enthalpies of formation for new lanthanide alkoxides, some additional enthalpies of formation of lithium, sodium, potassium, rubidium and caesium alkoxides and phenoxides were studied [1]. With these new values, an improved model of the previously developed one (J.P. Leal, J.A. Martinho Simões, J. Organomet. Chem. 460 (1993) 131) was proposed to estimate the enthalpies of formation of alkoxide species *via* their lattice enthalpies (Figure).

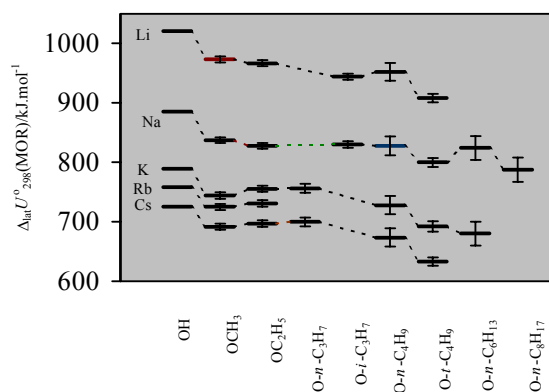


Figure - Lattice energies of alkaline metal alkoxides and phenoxides.

A solid state thermal bath conduction calorimeter (conceived and designed in our group) was built. This calorimeter will allow simultaneous thermal and gas chromatography analysis over the same sample.

Published, accepted or in press work

1. P. Nunes, J.P. Leal, V. Cachata, H. Raminhos, M. E. Minas da Piedade, Bonding Energetics in Alkaline Metal Alkoxides and Phenoxides,

accepted for publication in *Chemistry – A European Journal*.

Oxidative Coupling of Methane Using f Block Element Compounds as Catalytic Precursors

C.J. Dias, J. Branco, T.A. Gasche, A.P. Gonçalves¹,
A. Pires de Matos

Objectives

The main objective of this work is to study the oxidative coupling (OCM) to C₂ hydrocarbons (ethane and ethylene), with high ethylene selectivity, using binary intermetallic compounds LnCu₂ (Ln = La, Ce, Pr, Nd, Eu, Ho, Tm, Yb) and AnCu₂ (An = Th, U) as catalytic precursors.

Results

The heterobimetallic oxides Ln₂CuO₄·3CuO (Ln=La, Pr, Nd, Eu, Gd), Ln₂Cu₂O₅·2CuO (Ln=Dy, Tm, Yb) and MO₂·2CuO (M=Ce, Th) were prepared by controlled oxidation of the LnCu₂ and ThCu₂ intermetallic compounds. Their characterisation has been done by powder X-ray (Figure 1), temperature programmed reduction (TPR) (Figure 2) and SEM.

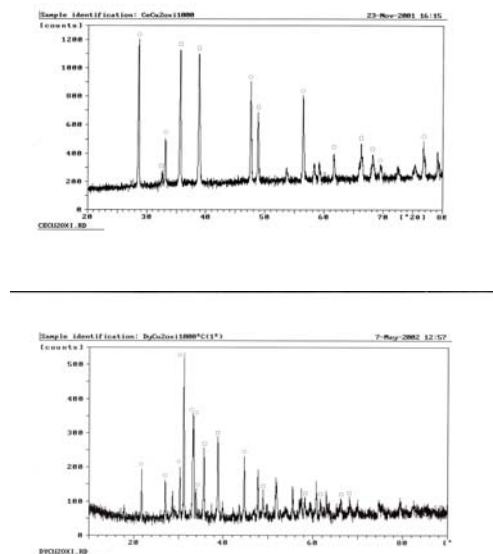


Figure 1. XRD powder spectra of CeO₂·2CuO and Dy₂Cu₂O₅·2CuO. Legend: O, CuO and □ CeO₂ or Dy₂Cu₂O₅.

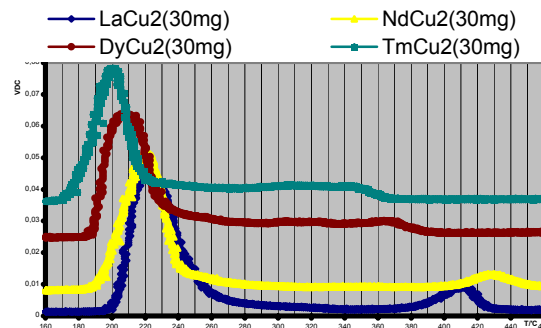


Figure 2. Temperature programmed reduction profiles of Ln₂CuO₄·3CuO (Ln=La, Nd) and Ln₂Cu₂O₅·2CuO (Ln=Dy, Tm).

A prototype for studies by temperature programmed reduction (TPR) of the heterobimetallic oxides was built (Figure 3) and tested.



Figure 3. TPR prototype.

Our purpose is to prepare new types of supported catalysts using rare earths intermetallic compounds as catalytic precursors. We intend also to correlate their activity with the 4f and 5f block element properties.

Two manuscripts are in preparation, one on reduction studies of heterobimetallic copper-lanthanide oxide catalysts, and the other on the oxidative dehydrogenation/dehydration of isopropanol with the same type of catalysts.

Published, accepted or in press work

1. C.J. Dias, T.A. Gasche, J. Branco, Aplicação do Método Frontal (TCD) na Caracterização de Óxidos Heterobimetálicos Obtidos a Partir de

Compostos Intermetálicos do Tipo LnCu₂ (Ln=La, Ce, Pr, Nd, Gd, Tm), XVIII Encontro Nacional SPQ, Aveiro, 2002.

¹ Solid State Group, Chemistry Department, ITN.

Synthesis of Heteroscorpionate Ligands. Lanthanide Compounds with Applications in Ziegler-Natta Catalysis and C-H Activation.

D. Roitershtein, B. Monteiro, Â. Domingos, N. Marques

Objectives

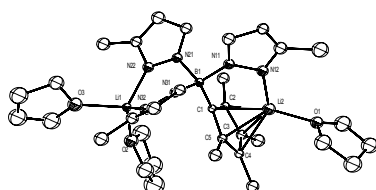
The aim of this project is to study the reactivity of lanthanide compounds stabilized by modified (pyrazolyl)borate ligands. We intend to increase the electron donor power of the ligands Tp by replacing one of the pyrazolyl rings by an appropriate substituent that can be further deprotonated to yield a dianionic ligand [1-3].

The project is based on our finding that thermolysis of $\text{Sm}(\eta^3\text{-Tp}^{\text{Me}_2})(\eta^2\text{-Tp}^{\text{Me}_2})(\eta^5\text{-Cp})$ led to formation of $\text{Sm}(\eta^3\text{-Tp}^{\text{Me}_2})[\text{HB}(3\text{-5Me}_2\text{pz})_2(\text{C}_5\text{H}_4)]$, a compound in which the Sm is coordinated to a Tp ligand and to a novel, dianionic ligand, $\text{HB}(3\text{-5Me}_2\text{pz})_2(\text{C}_5\text{H}_4)$, due to C-H activation mediated by the metal centre. We intend now to synthesize this ligand by a synthetic route that can be a real source of the ligand and to use it as a replacement cyclopentadienyl species in lanthanide chemistry. Another goal of the project is to model the electronic properties of the lanthanide centre by using neutral donor ligands N-N (N-N=phenantroline and bipyridyl).

Results

The first goal of the project has been achieved. The synthesis of the new dianionic hydrobis(3-methylpyrazolyl)(tetramethylcyclopentadienyl)borate ligand, $[\text{B}(3\text{-Mepz})_3(\text{C}_5\text{Me}_4)]$, has been carried by a multistep procedure. The ORTEP drawing of the ligand, $\text{Li}_2(\text{THF})_3[\text{B}(3\text{-Mepz})_3(\text{C}_5\text{Me}_4)]$, is shown in Fig 1.

Figure 1



The interaction of the new ansa ligand with lanthanides and uranium trisiodide is being studied.

We have also been studying the reduction of neutral nitrogen donor ligands when coordinated to a lanthanide centre. The systems under study are $\text{M}(\text{Tp}^{\text{Me}_2})\text{Cl}_2(\text{N-N})$ ($\text{M}=\text{Y}, \text{La}$; N-N=phenantroline and

bipyridyl).

The ORTEP diagram of one of these compounds, $\text{La}(\text{Tp}^{\text{Me}_2})\text{Cl}_2(\text{phenantroline})$, is shown in Fig.2.

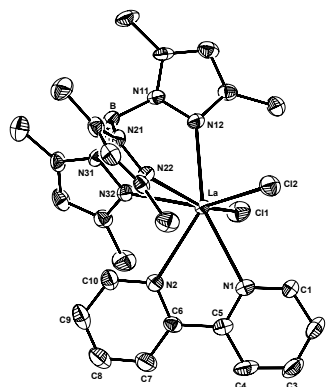


Figure 2

The compounds can be reduced with excess of Na/Hg to yield radical monoanionic species in the case of the lanthanum compounds (Fig. 3) or species in which the nitrogen donor ligands are in its dianionic form in the case of the yttrium compounds. The ORTEP diagram of $\text{La}(\text{Tp}^{\text{Me}_2})_2(\text{bipyridyl})$ is shown as a representative in Fig. 3.

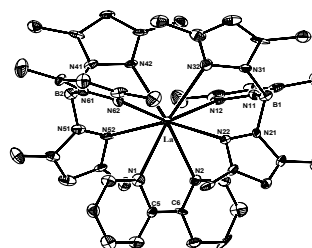


Figure 3

Hence, we have found a new synthetic route for getting reduced phenantroline and bipyridyl complexes.

Published, accepted or in press work

1. N. Marques, A. Sella, J. Takats, Chemistry of the Lanthanides Using Pyrazolylborate Ligands, *Chem. Rev.* 102 (2002) 2137.
2. Â. Domingos, M.R.J. Elsegood, A.C. Hillier, .Lin, S.Y. Liu, I. Lopes, G.H. Maunder, N. Marques, R. McDonald, A. Sella, J.W. Steed, J. Takats, Facile

pyrazolylborate ligand degradation at lanthanide centres: X-ray crystal structures of pyrazolylborinate-bridged bimetallics, *Inorg. Chem.* 41 (2002) 6761.

3. I. Lopes, R. Dias, Â. Domingos, N. Marques, Organo-*f*-Element Chemistry with Multidentate Nitrogen Ligands, *J. Alloys Comp.* 344/1-2 (2002) 60.

Glass Science with Applications in Radioactive Waste Vitrification and Art Studies

A. Pires de Matos, J. Marçalo, M. Santos, F. Araújo¹, P. Valério¹

Objectives

One objective of this project is to develop in ITN know how in glass science to contribute to the research on waste vitrification processes. The final goal is to study glass samples containing radioactive elements (actinides and fission products) and to obtain structural information as well as to investigate the chemical behaviour in leaching processes.

Concerning the structural information, the main technique we are using is laser desorption Fourier transform ion cyclotron resonance mass spectrometry (LD-FTICR/MS) trying to correlate the gas phase clusters formed with the basic structure of the glass [1]. For the speciation studies necessary to investigate the glass leaching we intend, among other techniques, to follow our previous work on uranyl speciation using electrospray ionization mass spectrometry. ("Uranium Speciation Studies in Aqueous Solutions by FTICR Mass Spectrometry", A. Pires de Matos, J. Marçalo, M.A. Freitas, A.G. Marshall, G.R. Choppin, *15th International Mass Spectrometry Conference*, Barcelona, Spain, August, 2000).

As we are developing, expertise on synthesis and characterization of glasses, two other applications

were envisaged in collaboration with University research Groups. One concerns the development of new glasses for art applications and involves researchers from the Faculty of Fine Arts of the University of Lisbon and a researcher from the University of S. Paulo, Brazil.

The other concerns the characterization of glass objects of the Museum of Marinha Grande, and the study of a set of samples from a recent archaeological excavation, also in Marinha Grande.

Results

LD-FTICR/MS studies of several silica based glasses were continued in order to obtain structural information and to analyse some of the metal oxides present.

Rubi glasses containing Se, S and Cd were studied using X-ray fluorescence and LD-FTICR/MS. SeSCd⁺ and SeSCd⁻ could be identified. Surprisingly no simple cadmium selenide or sulphide ions were found.

New fluorescent sodosilicate glasses were synthesized with europium, samarium, terbium and uranium. This work was made in collaboration with Prof. Paulo Celso Isolani from the University of S. Paulo, Brazil.

Published, accepted or in press work

1. M. Santos, J. Marçalo, A. Pires de Matos, Characterization of Glasses by FTICR Mass

Spectrometry, *Phys. Chem. Glasses* 43C (2002) 421-423.

¹ Environmental Analytical Chemistry Group, Chemistry Department, ITN.

Waste Treatment

A. Pires de Matos, J. Norte¹, J. Marçalo, J. Branco, J.P. Leal, N. Pinhão², K. Kutasi³, V. Gaffney³

Objectives

This project is in partnership with the industry and the main objective is to investigate chemical recycling of plastic materials. This project is supported by the industrial associations Sociedade Ponto Verde S.A. and Plastval S.A.

The know-how acquired will eventually be applied also to the treatment of low level radioactive waste.

Results

A small chemical reactor was designed to study plastic gaseification using molten copper as catalyst. The plastics already tested (polyethyleneterephthalate, polypropylene and polyethylene) showed that the process is adequate being CO₂, H₂ and CO the major products.

The reaction with polypropylene and polyethylene gave only negligible amounts of benzenic species.

With polyethyleneterephthalate, with aromatic rings in the polymer structure, it was observed that the decomposition of the benzenic rings was quite efficient.



Picture of the reactor.

A laboratory dielectric barrier discharge system for gas cleaning, a mass spectrometric gas analysis system for atmospheric pressure sampling and a gas mixture system for controlled admixture of volatile organic compounds have been used to study the decomposition of residual organic compounds in the effluent gases.

Published, accepted or in press work

1. J. Branco, J.V. Gaffney, K. Kutasi, J. Norte, J.P. Leal, J. Marçalo, A. Pires de Matos, N.R. Pinhão, M. Santos, "Tratamento e Valorização de Resíduos Plásticos para

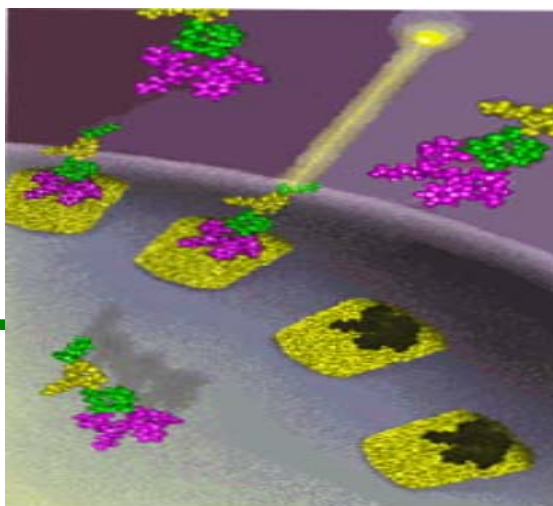
Reciclagem Química", Proceedings - "Jornadas de Investigação e Desenvolvimento da Sociedade Ponto Verde/Universidade de Aveiro, Aveiro, (Ed. CD ROM, 5 pages) April 23, 2002.

¹ Companhia Industrial de Reciclagem.

² Physics Department, ITN.

³ Grantees (Sociedade Ponto Verde)

Inorganic and Radiopharmaceutical Chemistry

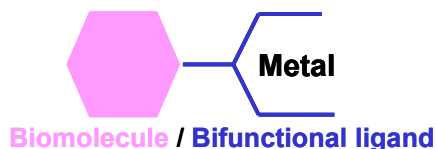


Inorganic and Radiopharmaceutical Chemistry

Isabel Rego Santos

Since its formation in 2000, the Inorganic and Radiopharmaceutical Chemistry Group has focused its basic and application-oriented research on **metal-*(d- and f-)* and halogen-based specific radiotracers**, as molecular probes to make the human body biochemically transparent with regard to individual molecular reactions. These activities have taken into account the Nuclear Medicine needs, background and facilities of the group and available conditions at the Portuguese Research Reactor (RPI).

The group is *multidisciplinary* combining a wide range of expertise namely, organic, inorganic and organometallic chemistry, radiochemistry and radiopharmacology. Such a combination, unique in the country, involves the manipulation of inactive and radioactive compounds, as well as the use of animal models and cells, using special and specific facilities. Concerning *d*-transition metals, we are predominantly engaged in the coordination chemistry and radiopharmacology of Tc and Re. These two elements are of outstanding interest in the development of novel radiopharmaceuticals for routine diagnostics and/or therapy in Nuclear Medicine or oncology. Concerning *f*-transition elements we are interested on ^{153}Sm , ^{166}Ho and ^{177}Lu , which can be prepared at the RPI and are of widespread interest in oncology. The application of these transition metals requires a sophisticated coordination chemistry in order to design complexes that are specifically recognized by target molecules in the human body. Therefore, our research involves the design of bifunctional ligands to stabilize the above referred metals, in different oxidation states, and to link them to different biomolecules.



However, the linkage of the metal to the biomolecule has a great and not always predictable impact on its *in vivo* behaviour, which makes the design of these compounds challenging: the specificity has to be maintained, the penetration through membranes has to be done, particularly through the blood-brain barrier (BBB), the clearance from nontarget sites and the pharmacokinetics in the region of interest has to permit imaging and target assessment.

Metal-*d* and *f*- Based Radiotracers: During 2002, we explored the pharmacological behaviour of new building blocks introduced, previously, by our group. For Re and Tc, we found that some of them are adequate to CNS (heterofunctionalized phosphines

and mercaptoimidazolylborates building blocks) and others (pyrazolyl building blocks) are suitable for labelling biologically active peptides. Functionalization with biomolecules started. Interesting and promising results, in terms of binding affinities, crossing of BBB, labelling of CNS receptor ligands and peptides, have been achieved. Searching for novel tumor seeking agents, we pursue our chemistry, radiochemistry and biological evaluation of macrocycle Ln complexes and we initiate the design of more selective therapeutic drugs, this means directed to DNA.

Halogen- Based Radiotracers: During 2002 the group has been involved on the synthesis and characterization of two different classes of compounds potentially useful as radioligands for estrogen receptors: estrone and triphenylethylene derivatives. Some hard synthetic work has been overcome and radiolabelling studies are underway.

Our basic and application-oriented research allowed us to provide **training and expertise** on chemistry, radiochemistry and radiopharmacy.

During 2002, several undergraduate, BIC, PhD and Post-Doctoral researchers, funded by **FCT grants**, **have been trained in our laboratories**. A one week intensive course on Radiopharmacy, for clinicians and pharmacists, has been organized. Radiopharmacy was also taught, in a regular way, in the Technical Nuclear Medicine Course, at the ESTeSL. Twenty students of this course have been trained during two weeks in our laboratories. Lectures have been given at the Faculdade de Farmácia of Lisbon and at the Basic Course on Radiopharmaceuticals, organized by HSC in Carcavelos. At the International level the group participated in the European Radiopharmacy Course, (INSTN), and in the European Community Shared COST RTD ACTION, Virtual Radiopharmacy (VIRAD). Our expertise has also been provided to some Nuclear Medicine Centers and to the Portuguese Medicines Evaluation Agency. As experts, we have also been invited by the AIEA for participating on a Consultant Meeting on *Recent Advances in ^{99m}Tc Labelling of Small Molecules*.

Some of the above referred activities have been developed in collaboration with National and International Universities, Research Institutes and Companies, through National Projects funded by FCT, through bilateral cooperation (ICCTI/DAAD) and European projects (Shared COST RTD ACTION, ACTION B12 and D18).

Inorganic and Radiopharmaceutical Chemistry

Research Team

Researchers^(*)

- I. SANTOS, Principal Researcher, Professor
“agregado” in Chemistry, Group Leader
- A. PAULO, Auxiliary Researcher
- J.D.G. CORREIA Invited Auxiliary Researcher
- M.P.C. CAMPELLO, Auxiliary Researcher
- M.C. MELO e SILVA, Auxiliary Researcher
- C. FERNANDES, Research Assistant
- L. GANO, Auxiliary Researcher
- F. MARQUES, Auxiliary Researcher

Students

- L. MARIA, PhD student, FCT Grant.
- S. ALVES , PhD student, FCT Grant
- R. GARCIA, PhD student, FCT Grant
- R. VITOR, PhD student, FCT Grant
- E. PALMA, BIC POCTI
- S. LACERDA, BIC POCTI
- R. OLIVEIRA, MSc Student, FFP, UP
- I. PEREIRA, Graduate Student, FCUL
- C. XAVIER, Graduate Student, FCUL

Technical Personnel

- A. RODRIGUES
- E. CORREIA

Funding (€)

Research Projects: 115 807
PIDDAC: 78 033
Services: 11 538

Total: 205 378

Publications

Journals: 13 (4 in press)
Proceedings: 6
Conf. Communications: 32
Theses: BSc 2

Tc(I) Mixed-Ligand Complexes for Labeling CNS Receptor Avid Molecules

R. Garcia, A. Paulo, L. Gano, I. Santos

Objectives

Labeling of CNS-receptor ligands with new building blocks, based on poly(mercaptoimidazoly)borate Re and Tc carbonyl complexes, without loss of biological activity.

Results

Biodistribution studies in mice of the new building blocks $[\text{}^{99\text{m}}\text{Tc}\{\kappa^3\text{-R}(\mu\text{-H})\text{B}(\text{tim}^{\text{Me}})_2\}(\text{CO})_3]$ (R= H (**1**), Ph (**2**)) demonstrated their ability to cross the BBB, with a slow washout from the brain (Table 1).

Table 1 - Biodistribution data for complexes **1** and **2** in CD-1 mice (% ID/g; mean \pm SD; n =4; 5 min and 2h p.i.).

Organ	Complex 1		Complex 2	
	5 min	2 h	5 min	2 h
Blood	3.2 \pm 0.6	1.2 \pm 0.2	3.4 \pm 0.4	1.8 \pm 0.4
Liver	16.3 \pm 0.6	28.3 \pm 4.7	17.3 \pm 1.8	19.4 \pm 3.0
Kidney	7.6 \pm 0.5	4.0 \pm 0.6	8.8 \pm 0.7	6.3 \pm 1.2
Brain	2.4\pm0.3	0.42\pm0.04	1.5\pm0.1	0.6\pm0.1

These biological features indicated that **1** and **2** are particularly adequate for the labeling of CNS-receptor avid molecules. Different possibilities can be used, being one of them the cleavage of the B-H...M agostic interaction with functionalised neutral substrates (**2+1 approach**). Within this approach, we prepared mixed-ligand Re(I) complexes with isonitriles bearing a methoxyphenylpiperazine (MPP) fragment (Fig. 1).

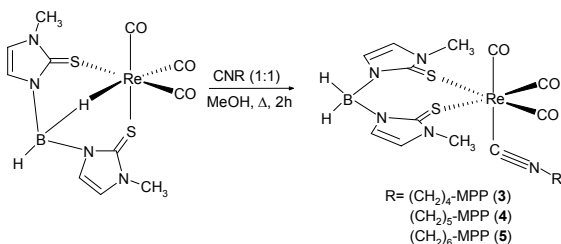


Fig. 1 - Re(I) Mixed-Ligand Complexes

The rhenium complexes, **3-5**, were fully characterised, including by X-ray diffraction analysis in the case of **3** (Fig. 2).

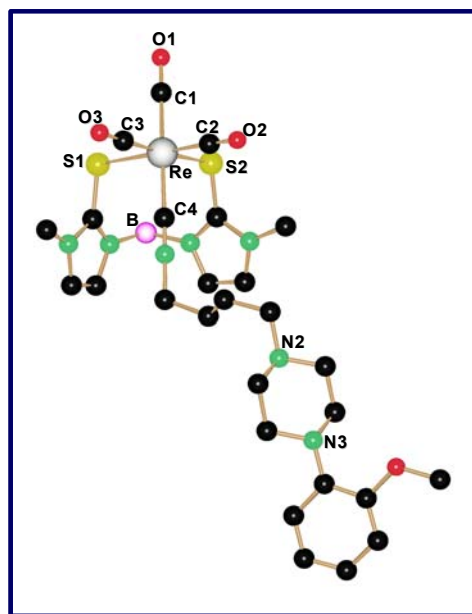


Fig. 2 - Molecular structure of complex **3**

Complexes **3-5** display moderate affinities for the 5-HT_{1A} subtype of serotonin receptors. The receptor affinity increases with the alkylspacer length, as well as the selectivity against the 5-HT_{2A} receptor (compound **5** - IC₅₀ for the 5HT_{1A} receptor: 23.2 \pm 0.2 nM; competitor 5HT_{2A}: 324 \pm 9 nM).

Preliminary studies have shown the possibility of preparing the analogous $^{99\text{m}}\text{Tc}$ mixed-ligand complexes: $[\text{}^{99\text{m}}\text{Tc}\{\kappa^2\text{-H}(\mu\text{-H})\text{B}(\text{tim}^{\text{Me}})_2\}\{\text{CN-R}'\}]$. The *in vivo* evaluation of these target-specific smart compounds is in progress, aiming to assess their ability to cross the BBB.

Published, accepted or in press work

1. R. Garcia, A. Paulo, A. Domingos, I. Santos, Reactivity of $[\text{Re}\{\kappa^3\text{-H}(\mu\text{-H})\text{B}(\text{tim}^{\text{Me}})_2\}(\text{CO})_3]$ towards neutral substrates, *Inorg. Chem.* 41 (2002), 2422.
2. R. Garcia, Y.H. Xing, A. Paulo, A. Domingos, I. Santos "Rhenium(I) tricarbonyl complexes with mercaptoimidazolyborate ligands bearing piperazine fragments" *J. Chem. Soc. Dalton Trans.* (2002) 4236.
3. R. Garcia, A. Paulo, A. Domingos, I. Santos, H. Spies, H.-J. Pietzsch, R. Bergmann, R. Alberto "Mixed rhenium(I) tricarbonyl complexes for the development of radiopharmaceuticals for CNS-receptor imaging" *Technetium and Rhenium in Chemistry and Nuclear Medicine 6*. Edited by M. Nicolini, U. Mazzi, SGEditionali, Padova (2002) 143-146.
4. R. Garcia, Y.H. Xing, L. Gano, A. Paulo, A. Domingos, I. Santos, R. Alberto "Rhenium and technetium complexes with poly(mercaptoimidazoly)borates relevant for the design of radiopharmaceuticals" *First International Symposium on Bioorganometallic Chemistry*, Paris, França, 2002, poster.

Phosphine-Based Chelators for Labelling CNS Receptor-Binding Ligands with $[\text{}^{99\text{m}}\text{Tc}(\text{CO})_3]^+$

J.D.G. Correia, Â. Domingos¹, T. Kniess, E. Palma, I.F.A. Pereira, I. Santos, H. Spies², Syhre²

Objectives

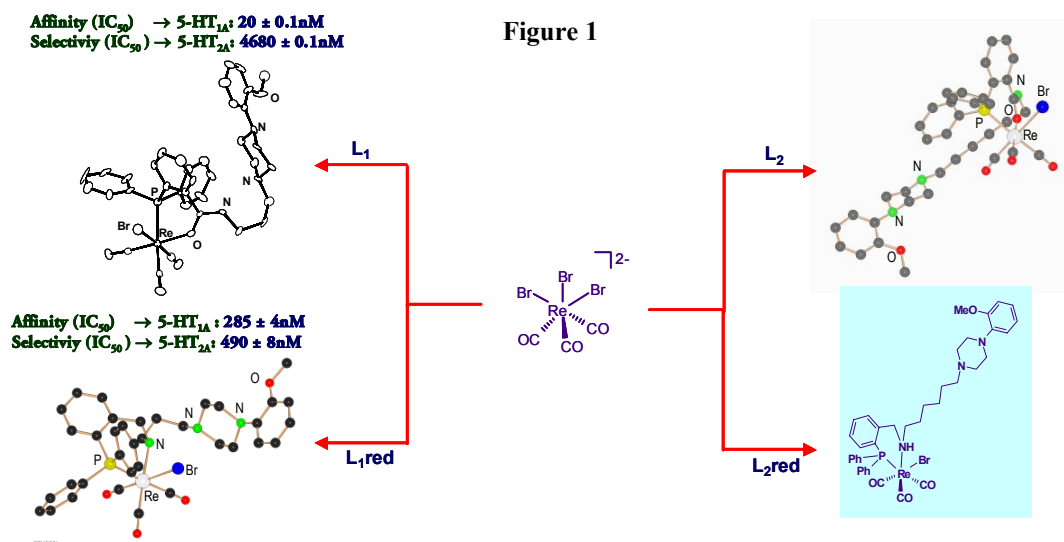
The main goal of this study is the labelling of CNS receptor-binding ligands with the organometallic moiety $\text{fac-}[\text{}^{99\text{m}}\text{Tc}(\text{CO})_3]^+$, using phosphine-based chelators.

Results

The new phosphine-based chelators, **H₂PNO** and **H₃PN₂**, previously introduced by our group, were reduced under controlled conditions with borane dimethylsulfide, yielding the novel heterofunctionalized phosphines 2-(diphenylphosphanyl)-*N*-(2-hydroxyethyl)-benzyl-amine (**H₂PNOred**) and *N*-(2-aminoethyl)-2-(diphenylphosphanyl)-benzylamine (**H₃PN₂red**), respectively. **H₂PNOred** was further derivatized, through the secondary amine, with a

propyl-1-(2-methoxyphenyl)piperazine unit giving the new ligand **H₂PNOred-Pip**.

Reaction of the $\text{fac-}[\text{M}(\text{CO})_3]^+$ moiety (M = Re, Tc) with the ligands **H₂PNOred** and **H₂PNOred-Pip** gave the neutral and the cationic complexes $[\text{M}(\kappa^2\text{-H}_2\text{PNOred})\text{X}(\text{CO})_3]$, $[\text{M}(\kappa^2\text{-H}_2\text{PNOred-Pip})\text{X}(\text{CO})_3]$ (X = Cl, Br) and $[\text{M}(\kappa^3\text{-H}_2\text{PNOred-Pip})(\text{CO})_3]^+$. Other new phosphine-based chelators containing 5-HT_{1A} receptor-binding ligands, **L₁**, **L₁red**, **L₂** and **L₂red**, were also synthesized and their coordination properties towards the $\text{fac-}[\text{M}(\text{CO})_3]^+$ moiety (M = Re, Tc) were studied. Figure 1 shows the novel organometallic Re (I) complexes, as well as their affinities and specificities for the 5HT_{1A} sub-class of serotonergic receptors. The analogous $^{99\text{m}}\text{Tc}$ -complexes were synthesized and fully characterized (90-99% yields).



Published, accepted or in press work

1. I.F.A. Pereira, J.D.G. Correia, T. Kniess, Â. Domingos, I. Santos, Coordenação de um Antagonista dos Receptores Serotonérgicos 5HT_{1A} à Unidade $[\text{Re}(\text{CO})_3]^+$, XVIII Encontro Nacional da SPQ, Aveiro, Portugal (2002) poster.
2. I.F.A. Pereira, T. Kniess, E. Palma, J.D.G. Correia, Â. Domingos, I. Santos, Coordination Chemistry of New Phosphine-containing Ligands Towards the Organometallic Moiety $\text{fac-}[\text{Re}(\text{CO})_3]^+$, *Technetium, Rhenium, and Other Metals in Chemistry and Nuclear Medicine* (2002) 119–121.
3. J.D.G. Correia, Heterofunctionalized Phosphines as Chelating Ligands for the Labelling of a Serotonergic Receptor Ligand with the $\text{fac-}[\text{}^{99\text{m}}\text{Tc}(\text{CO})_3]^+$ Moiety, *Conference on Advances and Perspectives in Radiotracer Development*, Dresden, Germany (2002) Oral.
4. J.D.G. Correia, Phosphine-based Chelators for Labelling a Serotonergic Receptor Ligand with $\text{fac-}[\text{}^{99\text{m}}\text{Tc}(\text{CO})_3]^+$, *Radiotracers for in vivo assessment of biological function*, Cost Action B12 Meeting, Lisbon, Portugal (2002) Oral.
5. I.F.A. Pereira, Specific Radiopharmaceuticals based on Phosphine-Based Chelators, Graduation Thesis, FCL, UL (2002).

¹ Inorganic and Organometallic Chemistry Group, ITN.

² Forschungszentrum Rossendorf, Institute of Bioinorganic and Radiopharmaceutical Chemistry, Germany.

Re and Tc "3+1" Complexes with the [PNS/S] Donor Atom Set

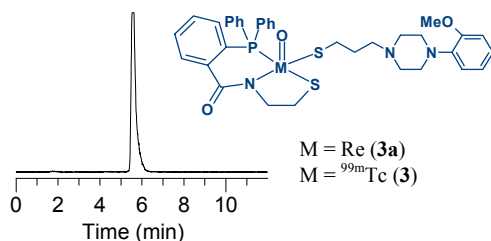
C. Fernandes, J.D.G. Correia, T. Kniess, I. Santos, S. Seifert¹, H. Spies¹

Objectives

The aim of this study is the preparation of mixed-ligand ^{99m}Tc oxo-complexes for *in vivo* visualization of serotonin receptors. We are also interested on the influence of organosilicon groups on the transportation and accumulation in the organism of the mixed complexes.

Results

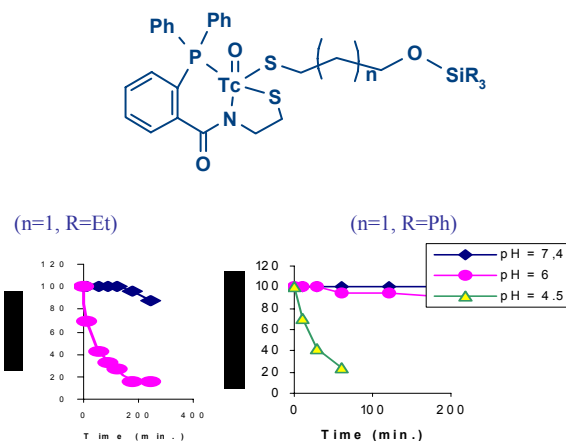
1. Complexes for 5-HT_{1A} Receptors: Using the heterofunctionalized phosphine 2-(diphenylphosphanyl)-N-(2-thioethyl)benzamide (H₂PNS) as tridentate ligand and different arylpiperazines derivatives (L1-L4) as co-ligands we succeeded on the preparation of the mixed-ligand "3+1" oxocomplexes of general formula [M(O)(κ³-PNS)(κ¹-SL)] (M = ^{99m}Tc (**1-4**) (80-95% yield), Re (**1a-4a**)). All the ^{99m}Tc complexes are stable in saline and 0.01M PBS (pH 7.4) at 37°C and no significant exchange with glutathione (1mM and 10mM solutions, 37°C) was observed.



In order to determine the effect of the chemical modifications introduced in the monodentate ligand, and the effect of the chelate unit, binding affinities for the 5-HT_{1A} and 5-HT_{2A} receptors were determined. The complex **3a** has high affinity and selectivity for the 5-HT_{1A} receptor (IC₅₀ for the 5-HT_{1A} 2.35±0.02

nM; competitor 5-HT_{2A} 372±11nM). Biological studies are underway.

2. Organosilicon bearing Re/Tc complexes: Oxo-complexes of general formula [^{99m}Tc(O)(PNS)(S(CH₂)_nOSiR₃)] (**1a-c**) were synthesized by direct reduction of [^{99m}TcO₄]⁻ with stannous chloride in the presence of the tridentate H₂PNS and of the monodentate [HS(CH₂)_nOSiR₃] ligands (n=2, R= Ph; (**1a**); n=3, R= Ph, (**1b**); n=3, R=



Et, (**1c**)). The ^{99m}Tc complexes were obtained with high radiochemical purity (>95%), and their identity was accomplished by comparing their radioactive HPLC profiles with the UV/Vis HPLC profiles of the analogous rhenium complexes (**2a-c**). All the complexes are stable in PBS pH 7.4 as well as in the presence of glutathione, at 37°C. Their resistance to hydrolysis is strongly dependent on the nature of the substituent at the silicon atom, providing a fine tuning of this cleavage *in vivo*.

Published, accepted or in press work

1. C. Fernandes, J.D.G. Correia, I. Santos, H. Spies, S. Seifert, New '3+1' Tc(V) Oxocomplexes Containing a Tridentate H₂PNS Ligand and Different Monodentate Ligands for the 5HT_{1A} Receptor, *Advances and Perspectives in Radiotracer Development, Dresden, Germany, March 7-8 (2002)*.
2. J.D.G. Correia, Labelling of Small Biomolecules with Phosphorus-Containing Ligands Using the "3+1" Approach, *COST Action B12 Meeting, Radiotracers for in vivo assessment of biological function, Dresden, Germany, March 7-8 (2002)*.
3. T. Kniess, C. Fernandes, I. Santos, W. Kraus, H. Spies, Silylated Mixed-Ligand Rhenium Complexes with the [PNS/S] Donor Atom Set, *Inorg. Chim. Acta*, in press.
4. C. Fernandes, T. Kniess, S. Seifert, H. Spies, A. Zablotskaya, I. Santos, Synthesis of Hydroxyl Silylated Rhenium and (^{99m}Tc)Technetium "3+1" oxo-complexes with the H₂PNS Tridentate Ligand, in *Technetium, Rhenium and Other Metals in Chemistry and Nuclear Medicine*, 6, M. Nicolini and U. Mazzi SGEditional (2002) 211-213.
5. H. Spies, C. Fernandes, Organosilicon bearing Re/Tc complexes: Aim and Status, *COST Action B12, Radiotracers for in vivo assessment of biological function, Lisbon, November (2002)*.

¹ Forschungszentrum Rossendorf, Institute of Bioinorganic & Radiopharmaceutical Chemistry, Germany

Labelling of Peptides with *fac*-[M(CO)₃]⁺ (M=Re, Tc) Using Bifunctional Pyrazolyl Containing Ligands

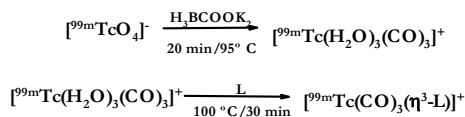
S. Alves, A. Paulo, J.D.G. Correia, L. Gano and I. Santos

Objectives

The main goal of this project is to develop new building blocks, based on pyrazolyl containing ligands, for labelling biologically active peptides with the moiety [^{99m}Tc(CO)₃]⁺.

Results

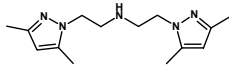
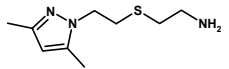
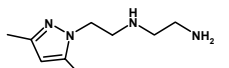
The coordination capabilities of several pyrazolyl containing ligands towards the [Re(CO)₃]⁺ moiety were studied and the most promising complexes were synthesized with ^{99m}Tc (Scheme 1).



Scheme 1: Synthesis of ^{99m}Tc complexes.

All the hydrophilic ^{99m}Tc-complexes were obtained with high radiochemical yield and high specific activity (Table 1).

Table 1: Labelling yields and properties of ^{99m}Tc complexes.

LIGAND [L]	YIELD (%)	[L] (M)	LogP _{o/w}
	> 90	10 ⁻⁴	0.87 ± 0.03
	> 95	10 ⁻⁵	-0.07 ± 0.01
	> 99	10 ⁻⁵	-0.25 ± 0.04

Published, accepted or in press work

1. S. Alves, A. Paulo, J.D.G. Correia, Â. Domingos, I. Santos, Coordination Capabilities of Pyrazolyl Containing Ligands Towards the *fac*-[Re(CO)₃]⁺ Moiety *J. Chem. Soc., Dalton Trans.* (2002) 4714.
2. S. Alves, A. Paulo, J.D.G. Correia, L. Gano, I. Santos, New Building Blocks for Labeling Peptides with the [^{99m}Tc(CO)₃]⁺ Core, *Technetium, Rhenium and Other Metals in Chemistry and Nuclear Medicine 6*. Edited by M. Nicolini, U. Mazzi, SGEEditoriali, Padova (2002) 139-142.
3. S. Alves, Â. Domingos, A. Paulo, J.D.G. Correia, Novos Compostos de Re e de ^{99m}Tc para Marcação de Péptidos, XVIII Encontro Nacional, Sociedade Portuguesa de Química, Aveiro, March (2002) Poster.
4. S. Alves, Labeling of Small Peptides with *fac*-[M(CO)₃]⁺ Using Bifunctional Pyrazolyl Containing Ligands, *Cost Action B12 Meeting: Radiotracer for in vivo assessment of biological function*, Lisboa, November (2002) Oral.

All the complexes are stable in the presence of strong tridentate ligands, like cysteine and histidine, after 6 h at 37°C in PBS. *In vivo* studies have also been undertaken showing clearly the suitability of some of these building blocks for labelling peptides (Figure 1)

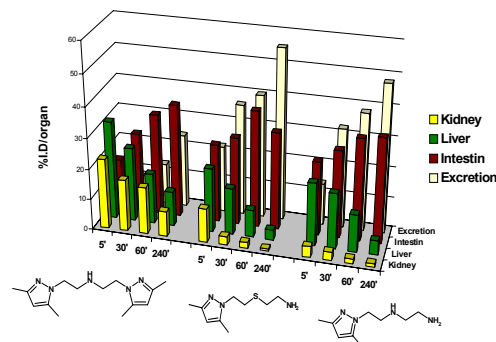


Figure 1. Biodistribution studies.

The labeling of biologically active peptides has been started and will continue during the next year.

Cationic Re and Tc Oxocomplexes with Cyclic and Acyclic Polyamines: Design of Radiopharmaceuticals for Selective Tumour Therapy

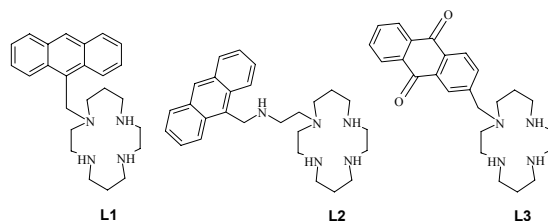
C. Xavier, R. Vitor, A. Paulo, M.P.C. Campello, F. Marques, I. Santos

Objectives

To get chemical and radiochemical data for a novel family of cationic technetium and rhenium complexes stabilised with bifunctional polyamines bearing a DNA intercalator moiety. This information is used to assess the influence of the radionuclide and bifunctional ligand or intercalator in the damage of cellular DNA. This is a crucial factor in the potential usefulness of ^{99m}Tc radiopharmaceuticals for targeted anti-tumour therapy.

Results

Several *cyclam* derivatives containing an appended polyaromatic moiety, with recognised capacity of intercalating into cellular DNA, have been synthesized (Scheme 1).



Scheme 1 - Functionalized *cyclam* ligands.

These functionalised ligands (L1-L3) reacted with *trans*-[$\text{ReOCl}_3(\text{PPh}_3)_2$] leading the *trans*-[$\text{ReO}_2(\text{L})$]⁺ (L = L1 (1), L2 (2), L3 (3)) complexes which were identified by the common spectroscopic techniques (IR, ^1H and ^{13}C NMR, FAB-MS).

The synthesis of the analogous ^{99m}Tc compounds was also studied. Under optimized labelling conditions, cationic ^{99m}Tc complexes were obtained in high radiochemical yield (80-90%). The cationic character of the ^{99m}Tc complexes was confirmed by electrophoresis. Nevertheless, it is necessary to compare the HPLC behaviour of the ^{99m}Tc and Re complexes (1-3), in order to confirm that we are in the presence of the same species.

Contrarily to *cyclam*, the basic coordination chemistry of *cyclen* with rhenium or technetium was completely unexplored. Aiming to evaluate the usefulness of *cyclen* ligands for the design of radiopharmaceuticals, we have studied the coordination behaviour of *cyclen* towards Re(V) metallic centres. By reacting *trans*-[$\text{ReOCl}_3(\text{PPh}_3)_2$] or [NBu_4][ReOCl_4] with *cyclen*, the compound [$\text{ReO}(\text{cyclen-H})\text{Cl}]\text{Cl}$ (4) was obtained. Compound 4 was characterized by the common spectroscopic techniques (IR, ^1H and ^{13}C NMR) and by X-ray diffraction analysis (Figure 1).

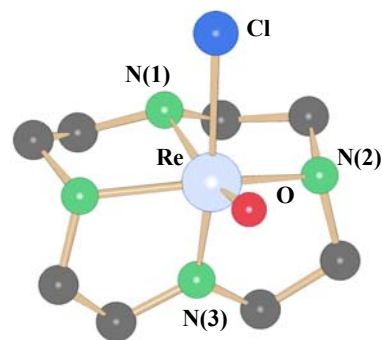


Figure 1 - Molecular Structure of 4.

The X-ray diffraction analysis confirmed the cationic character of complex 4. *Cyclen* acts as a monoanionic ligand, an unprecedented coordination mode in the chemistry of this type of ligands. Compound 4 is remarkably stable under aerobic and aqueous conditions, a crucial requirement for its application in radiopharmaceutical development. We are currently exploring the possibility of preparing the analogous ^{99m}Tc cation, under the standard conditions of radiopharmaceutical preparation. Derivatisation of the *cyclen* framework with a DNA intercalator is also underway.

In the next future, the effect on DNA of the dioxo or monoxo M(V) (M = Re, ^{99m}Tc) complexes containing cyclic polyamines (*cyclam* or *cyclen*) will be studied. These studies will be extended to complexes with linear polyamines.

Published, accepted or in press work

1. C. Xavier "Complexos Macroscópicos de Rénio e Tecnécio com Interesse em Radioterapia Selectiva", *Graduation Thesis*, Faculdade de Ciências, Universidade de Lisboa (2002).
2. C. Xavier, A. Paulo, P. Campello, A. Domingos,, A. Domingos, I. Santos, Complexos Macroscópicos de Rénio com Interesse em Radioterapia Selectiva, *XVIII Encontro Nacional da SPQ*, Aveiro, 2002.

Tetraazamacrocyclic Lanthanide Complexes for Therapy

M.P.C.Campello, F. Marques, L. Gano, P. Antunes¹, Krassimira¹, R. Delgado¹, I. Santos

Objectives

This project intends to explore the chemistry, radiochemistry and biological behaviour of a family of tetraazamacrocyclic lanthanide complexes (Sm, Ho, Lu), potentially interesting for imaging and/or therapy of tumours.

Results

Several tetraazamacrocyclic ligands with or without pyridinic or benzo groups in the backbone and containing methylcarboxylate or methylphosphonate pendant arms have been studied. Protonation constants of the novel macrocyclic ligands as well as their stability constants with Sm^{3+} , Ho^{3+} and Lu^{3+} have been determined by fitting the potentiometric data using the HYPERQUAD program. The replacement of one nitrogen atom on [14]ane- N_4 methylphosphonate ligand by a pyridinic group induces lower basicity and also lower stability for the complexes with Sm^{3+} , Ho^{3+} and Lu^{3+} . The X-ray structure of the novel benzo[14]ane- N_4 ligand is shown in Figure 1.

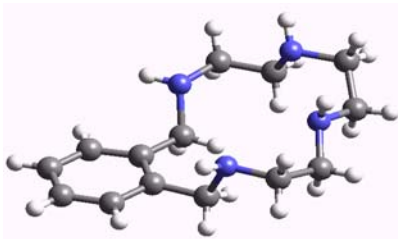


Figure 1 – Molecular structure of benzo[14]ane- N_4 ligand.

The stability constants of this ligand with several metals were calculated and the values found with larger metals are, respectively, comparable and higher than the values found for Cyclen and Cyclam.

Published, accepted or in press work

1. I. Santos, M.P. Campello, P. Antunes, R. Delgado, Lanthanide (^{153}Sm , ^{166}Ho , ^{177}Lu) Complexes With Tetraazamacrocycles *COST Chemistry Action D18, Lanthanide Chemistry for Diagnosis and Therapy, Mid Term Evaluation Workshop, Heidelberg, Germany, 22-25 de Julho* (2002).
2. P. Antunes, M.P.C. Campello, R. Delgado, L. Gano, F. Marques, I. Santos, Lanthanide Macrocyclic Complexes: Radiochemical and Chemical Studies, *XXXVth International Conference on Coordination Chemistry- ICC 35, Heidelberg, Germany, 21-26 de Julho* (2002).
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^{153}Sm , ^{166}Ho and ^{177}Lu nitrates, produced at the RPI, reacted with some of the above referred macrocycles yielding the corresponding radioactive complexes with relatively high yields (70-100%). The radiochemical behaviour and *in vitro* stability of the complexes at different physiological conditions (NaCl 0.9%, phosphate buffer saline, glycine/ HCl solution pH 4.0/37° C) were evaluated by TLC, ITLC and electrophoresis.

All the radioactive complexes studied are strongly stable at least 3 days, except complexes with [14]ane- N_4 methylcarboxylate and with [13]ane- N_4 methylphosphonate which are unstable in PBS and in NaCl 0.9%, respectively.

Some ^{166}Ho complexes were studied *in vivo* and the results in CD-1 mice indicated a rapid tissue clearance with more than 80% of the activity excreted at 2 h p.i. for the methylcarboxylate derivatives, while the complex with the pyridine[14]ane- N_4 methylphosphonate ligand presents a very slow clearance from most of the organs (Figure 2).

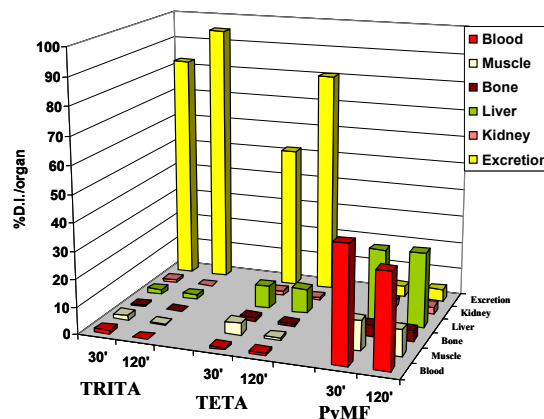


Figure 2. Biodistribution data for ^{166}Ho -complexes in CD-1 mice

¹ Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Oeiras, Portugal

Synthesis, Radiolabelling and Evaluation of Steroidal and non-Steroidal Biomolecules as Radioimaging Agents for Human Breast Cancer

M.C.M.e Silva, L. Gano, F.M. Marques, M.M. Marques¹, G.C. Costa¹,
T. Thiemann², M. Watanabe², J. Wang², T. Matsumoto², Y. Yamamoto², S. Mataka²

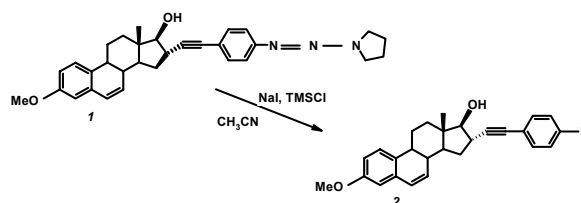
Objectives

The assessment of estrogen receptor (ER) concentration in human breast cancer carcinoma has significant clinical applications for the selection of effective therapy. To find γ -emitting estrogen receptor-binding radioligands for the non-invasive detection of estrogen receptors is the main goal of this work.

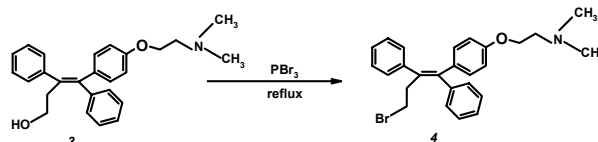
Results

In our search for novel radioligands for estrogen receptors, to be used as diagnostic or therapeutics for estrogen positive human breast cancer, two different classes of compounds are being explored: estrone and triphenylethylene derivatives.

***p*-Iodophenylethynyl substituted estrones (2)** have been synthesised by reacting amino-pyrimidino-annulated estranes (1) with NaI/TMSCl in acetonitrile.



The **halogenated triphenylethylene derivative**, β -bromotamoxifen (4), was obtained by reacting β -hydroxytamoxifen (3) with PBr_3 . Compound 4 is a good precursor for the radiolabelling with ^{125}I .



Both reactions were monitored by reversed-phase high performance chromatography (HPLC) (Figure 1).

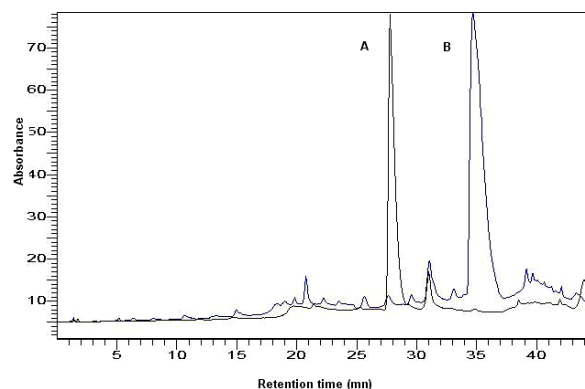


Figure 1. HPLC separation of β -bromotamoxifen (B) from β -hydroxytamoxifen (A).

The synthesis of the radioiodinated complexes is underway and the potential use of these steroidal and non-steroidal compounds as imaging agents for estrogen positive human breast tumors will be evaluated by *in vitro* estrogen receptor binding affinity studies and *in vivo* biodistribution assays in immature female rats.

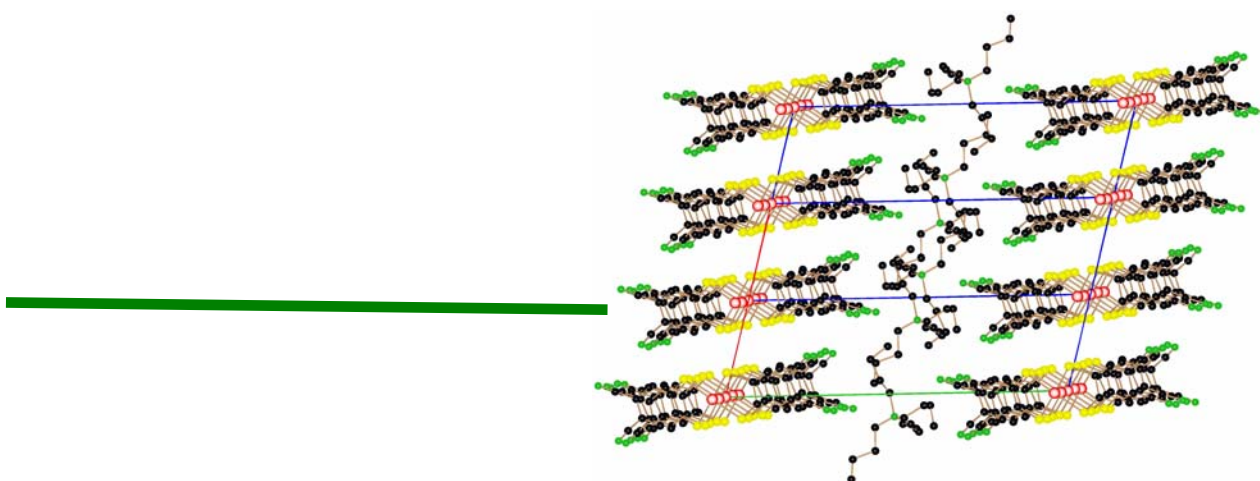
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¹ Centro de Química Estrutural, Complexo I, IST, Lisboa

² Interdisciplinary Graduate School of Engineering Science, Kyushu University, Fukuoka, Japan.

Solid State



Solid State

Manuel Leite de Almeida

The *Solid State Group* in the Chemistry Department has developed during the past years a broad range of expertise in complementary areas of solid state science and focused, under a global approach, on selected new materials with unconventional electrical and magnetic properties. The nature of the group is multidisciplinary combining a wide range of 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, maintained and used by in the group are a high temperature laboratory with crystal growth techniques (Czochralski, Bridgman, float zone, ...), X-ray diffraction both in single crystal and powder, EPR spectroscopy, a Mössbauer spectroscopy laboratory, magnetisation measurements by Faraday and extraction techniques and AC-susceptibility measurements, electrical transport measurements, specific heat, in a broad range of temperature and magnetic fields. The use of all these specialised characterisation techniques, often requiring low temperatures down to 0.3 K and high magnetic fields up to 18 T, lead to the development of a strong expertise in cryogenics. The group was the main promoter of the installation at ITN in 1993 of a helium liquifier, that since then remains the only one operational in Portugal providing helium also to many users outside ITN, under the supervision of the group.

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. Due to strategic reasons the group has centered his activities in selected type of materials:

- Molecule based conducting and magnetic materials.
- Intermetallic compounds with uranium and lanthanides
- Oxides including high temperature superconductors.

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

The **molecular conductors** have since the discover of the first organic metals in 1973 remained one of the most active areas of research of modern materials

science, and the group has a long and established tradition of research in this field. However, in order to take profit from some common molecular precursors and synthetic procedures, the interests of the group have recently been extended to **molecular magnetism**. The group intends to further develop its expertise in molecular design and chemical synthesis to the crystal engineering of new molecular materials with desired electrical and magnetic properties.

The research on **intermetallic compounds** was initiated after 1992 in structures thought to be good candidates for hard magnets and, due to specific characteristics of ITN as a nuclear laboratory, containing mainly U and Fe. The Mössbauer spectroscopy was used as a valuable tool to probe the role of iron atoms in the magnetic properties of these materials in complement to all other techniques. The group intends to extend its activities to compounds with lanthanides, whose role can be also studied by Mössbauer spectroscopy using non-commercial sources to be activated in the RPI. More recently the interests of the group in intermetallics extended to other f-element compounds where more exotic properties derived from strongly correlated electrons are observed.

As a strategic effort to extend the expertise of the group in the study of bulk materials to artificially confined structures, and wishing to take profit from possible synergies with other valuable surface characterisation techniques available at ITN, in 1999 a project aiming at to install facilities for the preparation of **uranium thin films and multilayers** was started. In spite of the very limited support available the first results were already obtained during 2000 and the system is currently under improvement.

The research in the field of **superconductors** was initiated soon after the discover of high T_c materials. Presently the research in this field is focused on the use of the excellent low temperature and high magnetic field facilities existing in the group, to study the vortex motion and pinning mechanisms in thin films and multilayers of top quality made in other laboratories. These techniques have been also used to characterise other oxide materials including multilayers with manganites.

More recently, as a way to further develop the cryogenic expertise in our group, we were lead to a joint project with the New University of Lisbon for development of small **pulsed tube cryocoolers** for specific applications.

Solid State

Research Team

Researchers^(*)

- M. ALMEIDA, Principal Researcher, Group Leader.
- R.T. HENRIQUES, Associated Professor, IST.
- G. BONFAIT, Associated Professor, FCT-UNL.
- V. GAMA, Auxiliary Researcher.
- J.C.WAERENBORGH, Auxiliary Researcher.
- A.P. GONÇALVES, Auxiliary Researcher.
- E.B. LOPES, Auxiliary Researcher.
- L.C.J. PEREIRA, Auxiliary Researcher.
- I.C. SANTOS, Auxiliary Researcher.
- I. CATARINO, Assistant Professor, FCT-UNL.
- D.BELO, Pos Doctoral, FCT grant
- O. SOLOGUB, Pos Doctoral, FCT grant, April-June
- P. SALAMAKHA, Pos Doctoral, FCT grant

Students

- I. CATARINO, Teaching Assistant FCT-UNL, until July.
- H. ALVES, PhD Student, FCT grant
- S. RABAÇA, PhD Student, FCT grant
- S. SÉRIO, PhD Student, FCT grant.
- R. MEIRA, PhD Student, FCT grant.
- J.C. DIAS, BIC PRAXIS XXI (until September) PhD Student (after September) , FCT grant.
- J. MENDONÇA, BIC PRAXIS, until September 2002.
- A. ROSA, MSc Student, FCT-UNL.

Technical Personnel

- So far none

Funding (€)

Research Projects: 188 269
ITN: 3 000

Total: 191 739

Publications

Books: 2
Journals: 16 and 14 in press
Proceedings: 1
Conf. Communications: 30
Theses: PhD 2

Multisulfurated molecule based conductors

H. Alves, D. Belo, J. Mendonça, R.T. Henriques¹, V. Gama, M. Almeida, E.B. Lopes, I.C. Santos, M.T. Duarte¹, D. P. Simão¹

Objectives

Study the physical properties of new conducting charge transfer solids based in multisulfurated organic donors and transition metal dichalcogenates, as a part of the general effort aiming at establishing correlations between structure and physical properties of molecule-based conductors with special emphasis on the role of the intermolecular S...S interactions.

Results

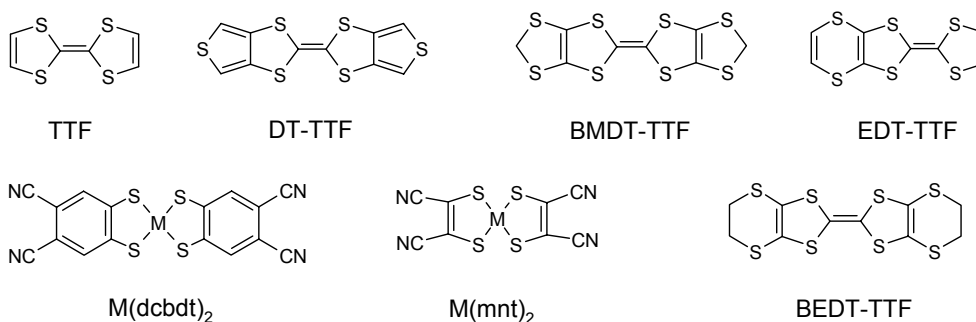
The series of $M(\text{dcbdt})_2$ complexes based on the new ligand *dcbdt* was further extended for different transition metals $M = \text{Zn, Au, Cu, Co, Fe, Ni, Pd, Pt}$ which were prepared in different oxidation states and characterised [1,2]. The occurrence of stable partially oxidised $[M(\text{dcbdt})_2]_s^{2+}$ compounds with semiconducting properties appears as a general feature of these complexes.

Both these complexes and more simple bisdithiolene complexes as $M(\text{mnt})_2$ were combined with multisulfurated donors derived from TTF. In this way several charge transfer salts were obtained and characterised, showing that in some cases there are both conduction electrons and localised magnetic moments in mutual interaction [3].

Several Cu and Au thiadiaxolethiolate complexes were prepared and their structure characterised.

The study of $(\text{TTDM-TTF})_2[\text{Au}(\text{mnt})_2]$ demonstrated to be an extreme 1D system that even under extreme pressures remains in the Mott-Hubard insulator regime, an important contribution to the understanding of the generalised phase diagram of the Bechgaard-Fabre superconducting salts [4].

A BEDT-TTF salt with a polioxovanadate trianion was characterised by electrical transport measurements and it revealed to be the first molecular metal with a polyoxometalate. [5].



Published, accepted or in press work

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4. E. B. Lopes, H. Alves, E. Ribera, M. Mas-Torrent, P. Auban-Senzier, E. Canadell, R. T. Henriques, M. Almeida, E. Molins, J. Veciana, C. Rovira and D. Jérôme, "Electronic localization in an extreme 1-D system: the new charge-transfer salt $(\text{TTDM-TTF})_2[\text{Au}(\text{mnt})_2]$ ", *European Physics Journal B*, (2002) 29, 27-33.
5. E. Coronado, J.R. Galán-Mascarós, C. Giménez-Saiz, C.J. Gómez-García, E. Martínez-Ferrero, M. Almeida, E.B. Lopes, "Metallic conductivity in a polioxovanadate radical salt of BEDT-TTF: Synthesis, structure and physical characterization of $\beta\text{-ET}_3[\text{H}_3\text{V}_{10}\text{O}_{28}]\cdot 4\text{H}_2\text{O}$ ", *Advanced Materials*, submitted.

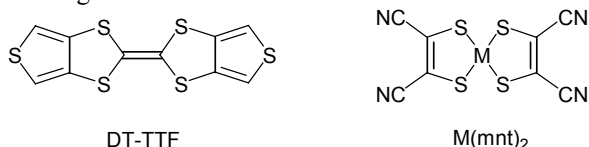
¹ Departamento de Engenharia Química, Instituto Superior Técnico, Universidade Técnica de Lisboa.

Molecular spin ladder compounds

J.C. Dias, H. Alves, D. Belo, R.T. Henriques¹, J. Morgado¹, M. Almeida, E.B. Lopes, I.C. Santos, M.T. Duarte¹

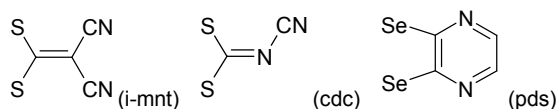
Objectives

Preparation of compounds derived from the first organic spin ladder system $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ in order to obtain new ladder compounds and correlate the magnetic behaviour with structural variations.



Results

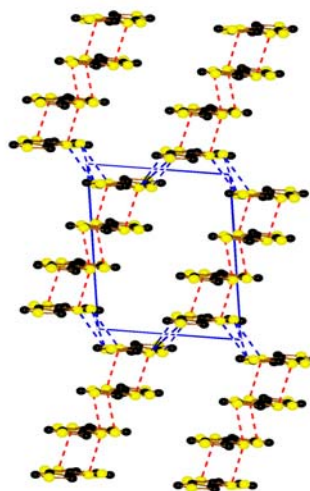
Different diamagnetic complexes similar to $\text{Au}(\text{mnt})_2$, such as $\text{Au}(\text{i-mnt})_2$, $\text{Au}(\text{cdc})_2$, $\text{Cu}(\text{mnt})_2$ and $\text{Cu}/\text{Au}(\text{pds})_2$, were selected to be combined with the donor DT-TTF in order to test the possibility of obtaining similar spin-ladder systems [1,2].



While with $\text{Au}(\text{i-mnt})_2$ an isostructural compound, with a magnetic spin-ladder behaviour similar to that of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ was found, with $\text{Au}(\text{cdc})_2$, two different crystal phases were obtained depending on the experimental conditions: a mixed-valence molecular compound $(\text{DT-TTF})_2\text{Au}(\text{cdc})_2$ and a radical ion salt with 1:1 stoichiometry $(\text{DT-TTF})\text{Au}(\text{cdc})_2$. [3] The last one is the thermodynamically more stable crystal phase as it is obtained in a wide range of experimental conditions. The mixed valence salt has a crystal structure and physical properties distinct from $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$. The electrical and magnetic properties of these two phases were fully characterised.

With $\text{Cu}(\text{mnt})_2$ a compound isostructural to $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ was obtained, but the study of its electrical and magnetic properties showed an unexpected transition at 233 K with no spin-ladder behaviour.

The new $\text{Cu}(\text{pds})_2$ and $\text{Au}(\text{pds})_2$ complexes were prepared and characterised for this project [4]. The



Bidimensional network of S...S interactions in $(\text{DT-TTF})_4[\text{Au}(\text{pds})_2]_3$.

compounds obtained by combination of these complexes with the DT-TTF present however a quite different stoichiometry: $(\text{DT-TTF})_4[\text{Au}/\text{Cu}(\text{pds})_2]_3$. [5] The Au and Cu compounds present related structures and a series of 1st and 2nd, order phase transitions currently under characterisation.

Published, accepted or in press work

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3. J.C. Dias, J. Morgado, H. Alves, E. B. Lopes, I.C. Santos, M.T. Duarte, R.T. Henriques, M. Almeida, X. Ribas, C. Rovira, J. Veciana, "Magnetic and electrical properties of $(\text{DT-TTF})_4[\text{Au}(\text{pds})_2]_3$ ", *Polyhedron*, accepted.
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5. X. Ribas, M. Mas-Torrent, C. Rovira, J. Veciana, J.C. Dias, H. Alves, E.B. Lopes, M. Almeida and K. Wurst, "Molecular compounds based on DT-TTF and $\text{Au}(\text{cdc})_2$ complex. Structural, magnetic and electrical properties", *Polyhedron*, accepted.

¹Departamento de Engenharia Química, Instituto Superior Técnico, Universidade Técnica de Lisboa.

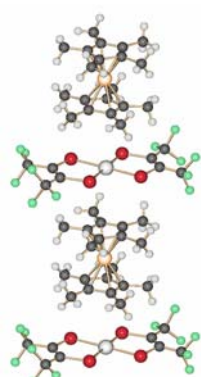
Molecule-based Magnetic Materials

V. Gama, S. Rabaça, D. Belo, R. Meira, L.C.J. Pereira, R.T. Henriques¹, M.T. Duarte¹, D. Simão¹

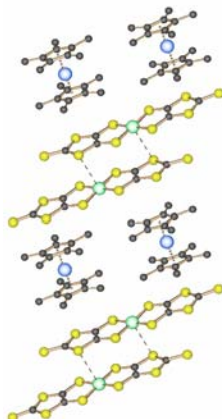
Objectives

The main goal in this work is to achieve a better understanding of the properties of molecule-based magnets, namely the structure-magnetic properties relationship either in molecular crystal, as metallocenium based charge-transfer salts, or in extended 3D networks, as coordination polymers.

Results



$[\text{Cr}(\text{Cp}^*)_2][\text{Pt}(\text{tds})_2]$, the first $[\text{Cr}(\text{Cp}^*)_2]^+$ based CT salt to exhibit MM



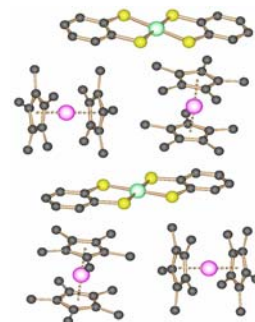
$[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{dmit})_2]$. A FM transition was observed in the $[\text{Mn}(\text{Cp}^*)_2]$ analogue.

The analysis of the structure of $[\text{M}(\text{Cp}^*)_2]$ based CT salts revealed the existence of a clear correlation between the size of the acceptors and the type of crystal structure. In case of the smaller acceptors, the crystal structures consist of arrangements of parallel 1D alternated stacks, DADADA. For the salts with large metal-bis(dichalcogenate) acceptors, the structure consists also on arrangements of alternated chains, but two different motives were observed: pairs of side by side donors, DD, alternate with face to face pairs of acceptors, AA, DDA ADDAA; or with an acceptor, In case of the CT salts exhibiting the simple alternated chain motive, strong intrachain FM interactions were

observed to coexist with weaker AFM interactions, which lead to the observation of metamagnetic transitions for many of these compounds.

For the CT salts with large acceptors a variety of magnetic behaviors were observed. For these salts besides the spin polarization in the donors a spin polarization exists also on the large acceptors, which leads to a competitions between FM and AFM interactions, which is responsible for the magnetic behaviors observed in these compounds. As a result from our efforts in the study of these type of compounds (2000 and 2001 reports; ref 2) a review on the magnetic properties and on the structure-magnetic properties relationship is in press (ref 1)

In case of the $\text{M}(\text{RR}'\text{-DCNQI})_2$ coordination polymers, the main efforts concern the study of electrochemically prepared materials. The magnetic behavior is consistent with the existence of acceptor dimers with AFM coupling leading to relatively weak magnetic interactions between the metallic centers. Magnetic transitions related with AFM coupling between those centers were observed at temperatures of the order of 10 K. These results suggested that AA interactions should be avoided or severely minimized. In this sense efforts are being done through the replacement of the acceptor substituents by bulkier groups and also in the use an alternative synthesis, such as the direct reaction between the metal carbonyls or iodides and neutrals acceptors.



$[\text{Mn}(\text{Cp}^*)_2][\text{Pt}(\text{bdt})_2]$, the first CT salt to exhibit FIM.

Published, accepted or in press work

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2. S. Rabaça, I.C. Santos, M.T. Duarte, V. Gama, Structural and Magnetic Characterisation of $[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{dmio})_2] \cdot \text{THF}$, *Synthetic Metals* (2002) in press.

3. T. Avilés, A. Dinis, J.O. Gonçalves, V. Félix, M.J. Calhorda, A. Prazeres, M.G.B. Drew, H. Alves, R.T. Henriques, V. Gama, P. Zanello, M. Fontani, Synthesis, X-ray structures, electrochemistry, magnetic properties, and theoretical studies of $[\text{CoX}_2(\text{dppfO}_2)]$ ($\text{X}=\text{Cl}, \text{I}$) and the novel polymeric chain $[\{\text{CoI}_2(\mu\text{-dppfO}_2)_n\}]$, *J. Chem Soc. Dalton Trans.* (2002) in press.

¹ Departamento de Engenharia Química, Instituto Superior Técnico, Universidade Técnica de Lisboa.

Magnetic and electrical transport properties in intermetallics based on *f* and *d* elements

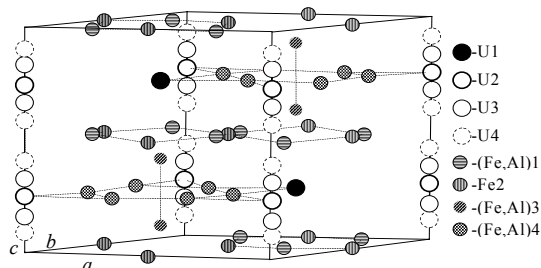
J.C. Waerenborgh, A.P. Gonçalves, L.C.J. Pereira, E.B. Lopes, I. Catarino¹, G. Bonfait¹, M. Almeida, S. Sérgio², C. Cardoso², T. Gasche², M.M. Cruz², M. Godinho²

Objectives

Detailed understanding of the role of U and of the rare-earths on the magnetic and electrical transport behaviour of intermetallics based on *f* and *d* elements.

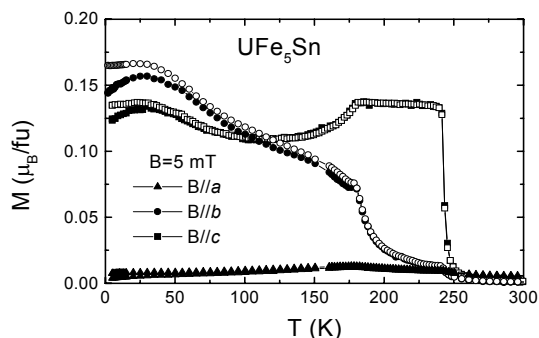
Results

The $\text{U}_2\text{Fe}_{12}\text{Al}_5$ compound, crystallizing in a structure derived from the $\text{Th}_2\text{Ni}_{17}$ -type, was studied [1]. A ferromagnetic-type transition is observed at $T_C = 295$ K, significantly lower than the T_C observed in other $\text{R}_2\text{Fe}_{12}\text{Al}_5$ compounds. A comparison between the Fe occupation factors points to a decisive influence of the number of the magnetic nearest-neighbours on the Curie temperature of this family of compounds. The $\text{UFe}_{12}\text{Al}_5$ spontaneous magnetization is also significantly lower than the observed for $\text{R}_2\text{Fe}_{12}\text{Al}_5$ ($\text{R} = \text{Y}$ and Ce), due to the decrease of the Fe magnetic moments, probably related with the strong hybridisation between Fe and U. $\text{U}_2\text{Fe}_{12}\text{Al}_5$ has a uniaxial anisotropy, with *c* as easy axis. The need of



Unit cell of $\text{U}_2\text{Fe}_{12}\text{Al}_5$

high order anisotropy constants for the correct description of the magnetization points to an important U contribution to the magnetism and to a coupling between the Fe and the U sublattices up to temperatures close to T_C , which can influence the T_C . Millimetre size UFe_5Sn single crystals were grown in order to study the magnetic transitions previously detected in powder samples at 248 K and 178 K [4]. An anisotropic magnetic behaviour is observed in this compound, the transition at 248 K being associated



Temperature dependence of the magnetization for a UFe_5Sn single crystal

with ferromagnetic ordering of iron moments along the *c* axis, while the transition at lower temperature is associated with a reorientation towards *b*. Mössbauer data show that this reorientation is concomitant to the ordering of the Fe2 sites, which in a large proportion remain paramagnetic between the two transition temperatures.

Preliminary results on compounds with a general $\text{U}_x\text{Fe}_6\text{Sn}_6$ formula, derived from FeSn , were obtained in 2002. The ^{57}Fe Mössbauer data showed that the presence of U did not change the uniaxial magnetic anisotropy of FeSn . Furthermore the magnetic ordering temperature increased with the U content.

The study of intermetallics with ThMn_{12} -type structure was mainly concentrated in the $\text{YFe}_x\text{Al}_{12-x}$ and $\text{UFe}_x\text{Al}_{12-x}$ systems. The compounds where Y carries no magnetic moment allow the investigation of the magnetic behaviour of the Fe sublattice when isolated from an *f*-sublattice. Mössbauer spectra showed that the dependence of the hyperfine parameters on the crystallographic site and on the number of Fe nearest neighbours in the Y intermetallics ($4.2 \leq x \leq 5$) is similar to that previously observed in the U analogs. A few Fe atoms however show a negligible magnetic hyperfine field. Preliminary pressure studies were made on the UFe_5Al_7 compound, showing that the ThMn_{12} -type structure is maintained up to 26 GPa [3].

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¹ Departamento de Física, Fac. Ciências e Tecnologia, Universidade Nova de Lisboa.

² Departamento de Física, Fac. Ciências, Universidade de Lisboa.

Study of ternary phase diagrams based on *f* and *d* elements

A.P. Gonçalves, O. Sologub, P. Salamakha, L.C.J. Pereira, J.C. Waerenborgh, H. Noël¹, M. Almeida

Objectives

Study of (*f*-element)-(*d* metal)-X ternary phase diagrams. Identification and synthesis of new ternary intermetallic compounds based on *f* and *d* elements.

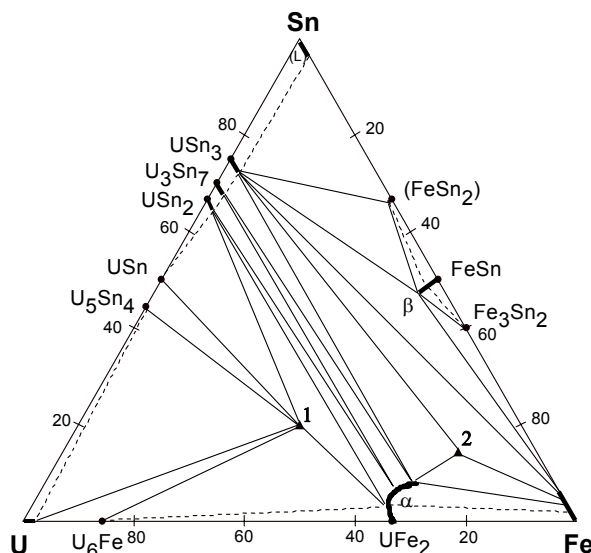
Results

The knowledge of the phase relations in a ternary system gives fundamental informations for the preparation of single-phase samples and the single crystal growth.

A review entitled "Rare Earth–Antimony systems" was submitted for publication in the "Handbook on Physics and Chemistry of Rare Earth" [1]. This work presents the current data on the phase diagrams, crystal structures and physical properties of binary, ternary and quaternary antimonides with the R elements (R=Sc, Y, and the lanthanides).

The systematic investigation of the U-Fe-Al system has continued in 2002. As a result, the $\text{U}_2\text{Fe}_{12}\text{Al}_5$ compound, previously identified, was prepared as single phase. These samples were used in the detailed characterization of the $\text{U}_2\text{Fe}_{12}\text{Al}_5$ crystallographic and magnetic properties.

During the study of the U-Fe-Sn ternary phase diagram, performed in 2000-2001, several new compounds were identified. After obtaining $\text{U}_{2.1}\text{Fe}_2\text{Sn}_{0.9}$ polycrystalline samples free from Fe containing impurities, UFe_5Sn single crystals were grown by the top seed solution growth method from a liquid phase with a UFe_4Sn nominal composition. These crystals were used in the study of the UFe_5Sn magnetic anisotropy. Samples with $\text{U}_x\text{Fe}_6\text{Sn}_6$ nominal compositions were also investigated. These solid solutions are derived from the FeSn binary compound by insertion of U. It was observed that the maximum allowed U concentration was 0.6 U atoms per formula unit, in contrast with the correspondent rare-earth compounds, where RFe_6Sn_6 compounds can be obtained.



Isothermal section at 750°C of the U-Fe-Sn ternary system

A systematic study of the Dy-Fe-Sn phase diagram has started in 2002. Different ternary compositions were prepared and the DyFe_6Sn_6 compound was already identified in this system by powder X-ray diffraction.

During the investigation of the R-(Ni,Pd,Pt)-B systems we found two ternary RNi_4B and RPt_4B phases (R=La-Nd), which crystallize in two different structure types, the CeCo_4B and NdNi_4B -type, respectively [5]. The influence of the lanthanoid and transition metals on the crystal chemistry and physical properties of these two boride series was studied. Preliminary studies were done on the ternary Y-M-B (M=Pd,Pt,Ir,Os) systems, using X-ray single crystal and powder diffraction. The investigation of the crystal structure was performed for several ternary borides, namely, $\text{Y}_2\text{Pd}_{14}\text{B}_5$, $\text{YPd}_3\text{B}_{0.5}$, $\text{YPt}_3\text{B}_{0.5}$, YIr_3B_2 , and YOs_3B_2 .

Published, accepted or in press work

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

Uranium Based Thin Films

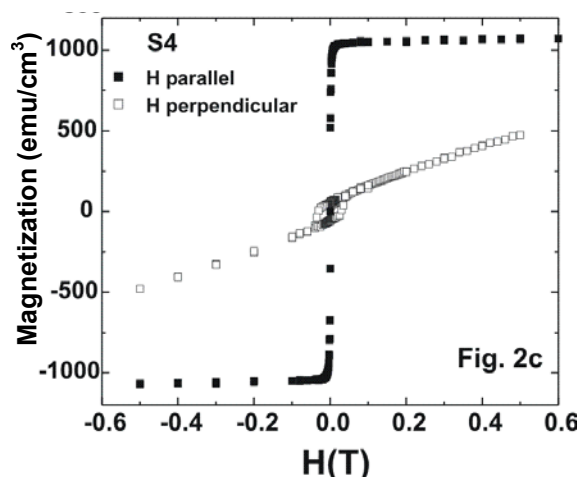
A.P. Gonçalves, M. Almeida, J.C. Waerenborgh, E.B. Lopes, E. Alves¹, N.P. Barradas², G. Bonfait³, M.R. da Silva⁴, M. Godinho⁵, M.M. Cruz⁵, M.A. Rosa⁵

Objectives

This project aims the implementation of a sputtering system dedicated to the preparation of uranium-based thin films and multilayers and the study of the structural, microstructural and physical properties of these films, with emphasis on the magnetic and electrical transport properties.

Results

Design of a load-lock system, necessary to maintain the vacuum in the chamber during samples changing, and a new substrate holder, that can be heated up to 700°C, were designed. Some of the pieces necessary to install these new equipments were purchased, and others were started to be constructed at the ITN workshop.



With the objective of expanding the studies on 2D systems containing uranium, U/Co multilayers with layer thickness ranging from 50 to 200 Å were recently prepared by dc magnetron sputtering onto glass. The multilayers were characterized by Grazing-Incidence X-Ray Diffraction (GIXRD) and Rutherford Backscattering Spectrometry (RBS). Magnetization measurements, performed with a SQUID magnetometer, showed that the multilayers have a ferromagnetic behaviour, with the magnetic signal increasing with the thickness of the layers. The analysis of the magnetic anisotropy evidenced an easy magnetic direction in the film plane with large anisotropy fields, which increase with the thickness of the layers and suggests a positive contribution of surface anisotropy to the effective anisotropy K_{eff} .

Further work

Installation of the load-lock and a new substrate holder in the sputtering system.

Deposition and characterization of uranium and U/Co multilayers and preparation of U/Fe multilayers.

Published, accepted or in press work

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¹ Nuclear Solid State Physics Using Ion Beams Group, ITN.

² Operation and Exploitation of the Reactor, Dosimetry (RPI) and Reactor Calculations, ITN.

³ Departamento de Física, Fac. Ciências e Tecnologia, Universidade Nova de Lisboa.

⁴ Departamento de Física, Instituto Superior Técnico, Universidade Técnica de Lisboa.

⁵ Departamento de Física, Fac. Ciências, Universidade de Lisboa.

Materials for Selective Oxygen Separation Membranes

J.C. Waerenborgh, F.M. Figueiredo¹, D.P.Fagg¹, V.V. Kharton^{1,2}, J.R. Frade¹

Objectives

Improvement of $A(\text{Ti,Fe,Mg})\text{O}_{3-y}$ ($A = \text{Sr, Ca}$) materials in what concerns the applicability as electrochemical membranes for oxygen separation and/or reactions of partial oxidation. This is expected to lead to better sensors and electrodes for solid oxide fuel cells.

Results

The applicability of the $A(\text{Ti,Fe,Mg})\text{O}_{3-y}$ ($A = \text{Sr, Ca}$) perovskites derives from their high ionic and electronic conductivities. These properties are due to the ability of these oxides to accommodate anion vacancies to keep electric neutrality when Ti^{4+} is replaced by Fe^{3+} . In practical applications these materials are subjected to relatively high temperatures in atmospheres where the oxygen fugacity is in equilibrium with a non-zero concentration of Fe^{4+} .

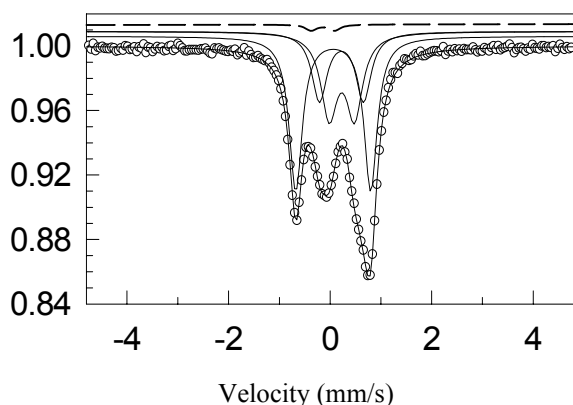


Fig. Mössbauer spectrum of $\text{CaFe}_{0.4}\text{Ti}_{0.6}\text{O}_{3-y}$. Contributions of Fe^{4+} (broken line), Fe^{3+} coordinated by 4, 5 and 6 oxygens are shown slightly shifted, for clarity.

^{57}Fe Mössbauer spectroscopy allows the determination of the concentration of Fe^{4+} as well as the relative amounts of Fe^{3+} coordinated by 6, 5 and 4 O^{2-} . $\text{CaFe}_x\text{Ti}_{1-x}\text{O}_{3-y}$ and La substituted $\text{SrFe}_x\text{Ti}_{1-x}\text{O}_{3-y}$

Published accepted or in press work

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perovskites were studied. Substitution of Sr by La is known to improve the stability of these phases which

have excessively high thermal expansion coefficients and high reactivity with substrate materials at elevated temperatures [1,2].

The influence of the microstructure on the performance of these materials was investigated. Mössbauer spectra showed that larger grains are associated to higher fractions of disordered oxygen vacancies in the bulk of the grains and since the oxygen permeation flux was found to decrease with increasing average grain size a faster oxygen transport and surface exchange at the grain boundaries was suggested. Higher permeation fluxes are therefore expected in nano-sized polycrystalline ceramics [3].

Studies of intergrowth $\text{Sr}_4\text{Fe}_6\text{O}_{13\pm\delta}$ phase, in combination with the structure refinement from X-ray and neutron powder diffraction data, showed that the point defects formed due to oxygen nonstoichiometry variations are accumulated in the non-perovskite layers, built of oxygen-iron polyhedra with pentacoordinated Fe cations

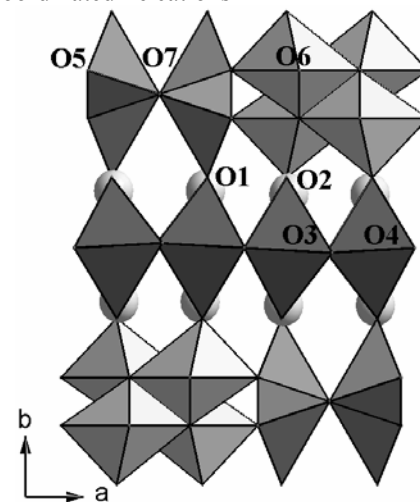


Fig. View of $\text{Sr}_4\text{Fe}_6\text{O}_{13\pm\delta}$ lattice along c axis.

of Fe in $\text{CaTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ and its relation to oxygen stoichiometry and ionic conductivity, *Solid State Ionics*. (in press).

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¹ Departamento de Engenharia Cerâmica e do Vidro, UIMC, Universidade Aveiro.

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

Mössbauer spectroscopy in Materials Science

J.C.Waerenborgh, M. Almeida

Objectives

Application of Mössbauer spectroscopy in research projects from Portuguese and foreign Universities and support to other national research institutions who are presently developing their own Mössbauer facilities.

Results

A Mössbauer spectroscopy laboratory has been developed in ITN for the last 20 years in order to support local research projects. γ -ray transmission and backscattering as well as conversion electron Mössbauer spectra may presently be obtained. γ -ray spectra may be taken with the sample in the 300-5 K temperature range and in external magnetic fields up to 5 T. The expertise developed in ITN has been, in the last years, able to assist other national or foreign research institutions.

During 2002, besides the applications described in detail for intermetallics, minerals, selective oxygen

separation membranes and molecular metals under the corresponding headings of this annual report, the Mössbauer effect has been applied to the study of several materials:

- Identification of the crystallographic sites occupied by Fe and of the Fe-containing phases formed by Fe implantation in Al. Collaboration with the ITN group of Nuclear Solid State Physics using ion beams.
- Magnetic properties of Fe in layered molecule-based magnets. Collaboration with the Univ. of Valencia, Spain.
- a structural and morphological study of the FeCo_2O_4 and CoFe_2O_4 spinels prepared by a low-temperature coprecipitation method has been undertaken. Collaboration with the Chemistry Dept. of the Fac. of Sciences of the Univ. Lisbon.



Fig. Mössbauer spectroscopy facility.

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Strongly correlated electrons in 5-*f* systems

L.C.J. Pereira, J.C. Waerenborgh, A.P. Gonçalves, I. Catarino¹, E.B. Lopes, G. Bonfait¹,
M. Godinho², M. Almeida.

Objectives

This project aims at establishing correlations between the crystal structure of intermetallic compounds with 5-*f* elements and the unusual physical properties (heavy Fermion, spin fluctuations etc.) derived from the existence of narrow 5-*f* bands nearby or at the Fermi level.

Results

The efforts to characterize experimentally the origin of the NFL behaviour in U_2Pt_2In , one of the rare stoichiometric material with non Fermi-Liquid (NFL) behaviour at ambient pressure, were improved. Electrical resistivity under hydrostatic pressure ($p \leq 1.8$ GPa) taken on a single-crystalline sample for a current in the tetragonal plane [1] have shown that the temperature below which the Fermi-liquid T^2 -term is observed increases with pressure as $T_{FL} \sim (p - p_c)$ where p_c is a critical pressure (see figures 1, and 2). This provides evidence for the location of U_2Pt_2In at an antiferromagnetic quantum critical point (QCP) [1].

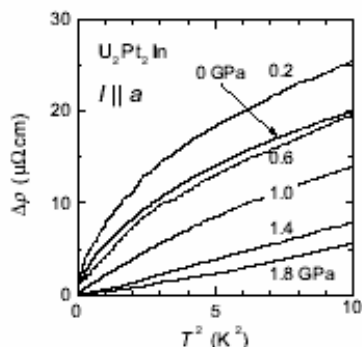


Fig.1- Resistivity under pressure measured along the *a*-axis of single crystalline U_2Pt_2In .

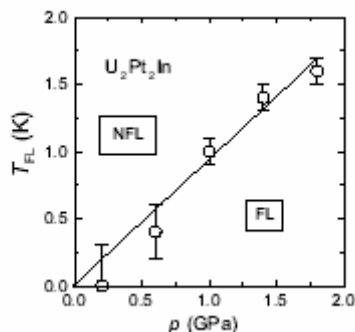


Fig.2 - T_{FL} vs p for single crystalline U_2Pt_2In determined from resistivity data for $I//a$. Solid line separates the NFL from the FL regime. The linear behaviour is consistent with the presence of an antiferromagnetic QCP at zero pressure.

The large residual resistivity values brings about the question whether such NFL is due to Kondo disorder. However, the rapid recovery of the FL behaviour under pressure as probed by the resistivity data at $I//a$ does not support this scenario. Since the compressibility is isotropic, pressure is expected to result in the further broadening of the distribution of Kondo-temperatures and thus the concurrent NFL behaviour would prevail [1].

The study of the structural and magnetic properties of the alloys like $(U_{1-x}Th_x)_2Pt_2In$ was also pursued in order to probe that QCP scenario. Specific heat measurements carried out on samples ($0 \leq x \leq 0.1$) do not show any evidence for magnetic order down to 2 K which was interpreted as a consequence of the *f*-electron lattice dilution when U is replaced by Th. In order to look for significant changes on the magnetic properties of $(U_{1-x}Th_x)_2Pt_2In$ system with the variation of x , the synthesis of solid solutions with higher Th concentration ($x = 0.2, 0.3, 0.5$ and 1) was undertaken. The phase analysis performed by powder X-ray diffraction have shown a mixture of different phases with no presence of the former U_3Si_2 type structure. As the synthesis for all the compounds were made following the same method it seems that the tetragonal 2:2:1 structure that was present for $0 \leq x \leq 0.1$ is no longer stabilized when the concentration of Th is higher. Besides the unidentified phases, $UPtIn$ and UPt were also present in these compositions as in some $x \leq 0.1$ cases. Magnetization and AC-susceptibility measurements confirmed their presence, with magnetic transitions at 15 K ($UPtIn$) and 27 K and 19 K (UPt).

Published, accepted or in press work

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¹ Departamento de Física, Fac. Ciências e Tecnologia, Universidade Nova de Lisboa.

Development of Pulse Tube Cryocoolers

G. Bonfait¹, I. Catarino¹, J.M. Poncet²

Objectives

The cryogenic engineering is fundamental for many new technologies (metrology, superconducting electronics, low energy detectors, space sciences, medical instrumentation, physical and material sciences) but will be useful only if low-cost, low-weight, low-size, low-maintenance cryocoolers become available. The new Pulse-Tube Cryocoolers (PTC) fulfil these requirements because, contrarily to usual cryocoolers (Gifford-Mac Mahon, Stirling), they do not need moving parts at low temperatures and consequently are mechanically simpler, very reliable and work with reduced vibration level.

This project introduced this technique completely new in Portugal, focusing on a "low frequency" (2-7 Hz) PTC. It is based on a powerful compressor and allows a base temperature inferior to 30 K and high cooling power (80 W at 77 K) and one of the objective is to optimized the performances of such cryocoolers working in non vertical position in spite of the performances of this type of PTC are known to be significantly reduced when not working with cold finger in the lowest position.



Fig. 1: The ITN Pulse Tube in the worst position (150°)!

Results

The performance of the Pulse Tube built in 2001 (see Activity report 2001) in collaboration with Service des Basses Températures (CEA-Grenoble) has been significantly improved and was measured as a function of the angle between 0° (cold finger in the

lowest position) and 180°. Our system (U-configuration, double orifice) achieves a lowest temperature of 28 K at 3 Hz with a cooling power about 16 W at 40 K in the vertical position.

Our results, obtained after optimization at 0°, 12 W, are displayed on Fig. 2:

1) below 90°, the base temperature is not significantly modified by the inclination, strong changes occurring for angles larger than 90°.

2) the worst configuration does not correspond to the 180° inclination but to angles between 120° and 150°.

3) In this angle range, the increase of the operating frequency leads to a significant reduction on the base temperature as well as on the cooling power.

The slopes dT/dP ($\approx 1\text{ K/W}$) are found to be not very sensitive on the inclination angle (figure 4), except for the 3 Hz operating frequency where it increases from 1 K/W at 120° to 1.4 K/W with $V_2=1.5/500$ and to almost 2 K/W for $V_2=2/500$.

An optimisation of the valve apertures leads to quite significant improvements of these performances (Close symbols on figure 2): for instance, with 12 W dissipated on the cold finger, a temperature as low as

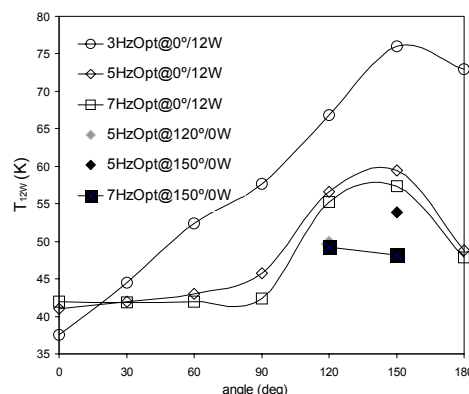


Fig. 2: The temperature achieved with 12W vs the angle, before and after optimization.

45 K is achieved in the 150° position, almost 30 K better than the results obtained in the "classical" configuration of work (3 Hz, optimized at 0°). A similar work will be performed in the next future to study the influence of the Length/Diameter ratio on the performances of a low frequency PTC as a function of inclination.

Published, accepted or in press work

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¹ Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa.

² Service des Basses Températures, EA-Grenoble, France.