Chemistry Sector

Chemistry Sector

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

The **Chemistry Sector** conducts basic and applied research and development to create scientific knowledge and technological solutions that strengthen the leadership in key areas of science related with nuclear sciences and other fields. The Department owes its strength to its versatile capability of **synthesis and characterisation of compounds** and on **the development and application of nuclear and related methods,** as well on a significant number of **analytical and physico-chemical techniques**. Some of the know-how and infrastructures **are unique in the Country or even in the Iberian Peninsula**. These capabilities have allowed to proceed and reinforce research work on well-defined areas: material science, health, environment and cultural heritage.

During 2001, the different research groups have made significant efforts in order to get funds to maintain and improve their research. These efforts have been successfully supported by funding institutions, mainly the National Science Foundation, European Commission and ICCTI (bilateral cooperations). Protocols and Contracts with other private and public institutions and Universities as well as Services have also significantly contributed to the funding of the groups.

We should refer that, among several projects, a large multidisciplinary one on Marine Sciences and Technology is being co-ordinated by this Sector. The ITN team is also responsible for the sedimentary geochemistry studies. Due to its nature and objectives, the Portuguese Government decided to include this project in the *Programa de Apoio dos Laboratórios de Estado (Resolution nº 137/97)*. This decision followed the recommendations of an International Reference Committee, which evaluated the Portuguese State Laboratories.

For application in archaeology and geology, a new luminescence laboratory has been made available and a database concerning archaeological ceramics and related geological materials has been implemented.

An antagonist of 5HT1A subtype serotonergic receptor has been successfully labelled with ^{99m}Tc, using different approaches. The binding affinity and specificity of some of these complexes may be promising for the synthesis of drugs for CNS diseases diagnostic. New building blocks for the labelling of peptides have been synthesized. Their applicability for the development of specific drugs for cancer diagnosis is being explored.

Concerning the most toxic actinides, new research on environmental issues is emerging through the development of new methods for actinide speciation and studies oriented to actinide/lanthanide separation. The first gas-phase ion chemistry studies of transuranium actinides, Np and Pu, by FTICR/MS, have been performed. These studies involved mainly oxidation reactions. An absolute scale for uranium bond enthalpies was established. A catalysis laboratory, unique in the country concerning CO manipulation, achieved operationality.

The synthesis and characterization of materials with unconventional electrical and magnetic properties, namely molecular materials based on *d*-transition metal complexes and intermetallics with f-elements including uranium continued. A Pulse Tube Cryocooler prototype was designed, constructed and the first tests performed in collaboration with CEA-Grenoble.

Due to the highly specialised nature of our research, the Sector has contributed significantly for the training of undergraduated, MSc and PhD students. Postdoctoral staff graduated elsewhere has also been trained in our laboratories and play an important role for the acomplishement of our goals.

Structure of the Sector and Technical staff

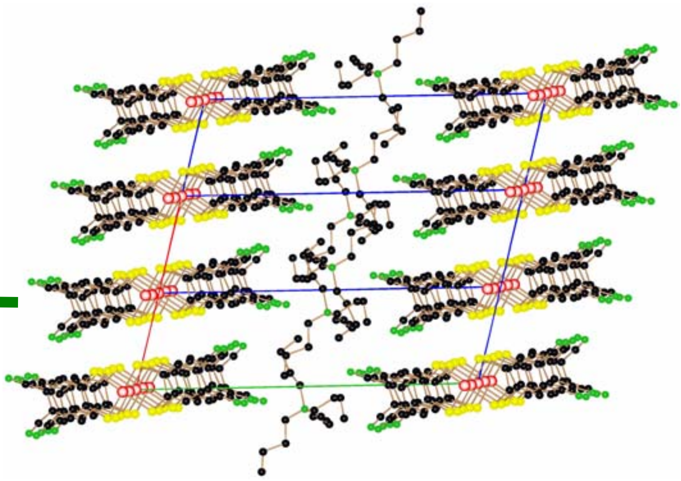
Research groups in the Chemistry Sector

- Solid State (SS)
- Inorganic and Organometallic Chemistry (IOC)
- Inorganic and Radiopharmaceutical Chemistry (IRC)
- Production and Application of Radioisotopes (PARIS)
- Environmental Analytical Chemistry (EAC)
- Cultural Heritage and Sciences (CHS)

Administrative and Technical staff

- Elsa Cristina Flores Gonçalves
- Fernando Rodrigues Almeida
- Isabel Ferro Frazão
- Julieta Pedro Pires
- Maria Bárbara Rufino
- Maria Fátima Marques
- Maria Fernanda Cabrita
- Maria Margarida Costa
- Pedro Miguel Alves Reis

Solid State



Solid State

Manuel Leite de Almeida

The *Solid State Group* in the Chemistry sector 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 powders, EPR spectroscopy, a Mössbauer spectroscopy laboratory, magnetisation measurements by Faraday and extraction techniques and AC-susceptibility measurements, electron transport measurements, heat capacity, 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 by 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 it was started a project aiming at to install facilities for the preparation of thin films with uranium. 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 Tc materials, during a period where almost all main solid state laboratories in the world were involved in this subject. 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.

Students

- I. CATARINO, Teaching Assistant FCT-UNL
- D.BELO, PhD Student, FCT grant
- H. ALVES, PhD Student, FCT grant
- S. RABAÇA, PhD Student, FCT grant
- S. SÉRIO, PhD Student, FCT grant.
- R. MEIRA, BIC PRAXIS XXI
- J. MENDONÇA, BIC PRAXIS XXI
- J. C. DIAS, BIC PRAXIS XXI
- J. MARIA, undergraduate student, FCT-UNL
- A. ROSA, MSc Student, FCUL.
- M. DIEGO, undergraduate student, FCUL.

Technicians

- So far none.

Funding

	$\times 10^3$ PTE
Research Projects:	44656
Total:	**44656**

Publications

Journals:	30 and 4 in press
Conf. Communications:	34
Other Publications:	5

Molecular Metals based on Transition Metal Chalcogenates

H. Alves, R. T. Henriques[1], V. Gama, M. Almeida, E. B. Lopes, I. C. Santos, M. T. Duarte[1],
D. P. Simão[1]

Objectives

Study the physical properties of new families of conducting charge transfer solids based in several organic donors and a series of transition metal dichalcogenates, as a part of the general aim of establishing correlations between structure and physical properties of molecule-based conductors.

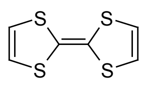
Results

The study of the series of M(dcbdt)$_2$ complexes based on the new ligand *dcbdt* that has been recently synthesised by us[1] was extended to different transition metals M and their structure and physical properties investigated. Partially oxidised complexes, TBA$_2$[M(dcbdt)$_2$]$_5$, where found to occur for most metals[2,3] and particularly those with M=Ni, Au and Cu were caracterised as small gap semiconductors with properties reflecting both variations in the band filling and stacking modulation.

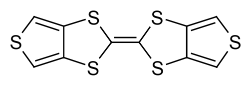
The complexes M(mnt)$_2$ were combined with a series of donors based on TTF fused with thiophenes and their electrical and magnetic properties measured. With the donor DT-TTF were combined different diamagnetic complexes in order to test the strategies for obtaining spin-ladder systems. Spin-ladder behaviour was found with Au(i-mnt)$_2$ while with the Au(cdc)$_2$ a different structure with a spin-Peirels transition at 7 K was observed.

Three different stoichiometries and polymorphs were observed in salts resulting from the combination of Au(pds) with the donor TTF and their physical properties could be related to the structure [4].

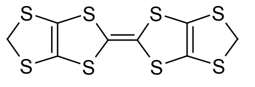
The transport properties of a series of charge transfer salts formed from the donor perylene and polyoxometallate anions, of different charge were characterised and the results related to the different bandfilling [5].



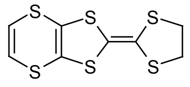
TTF



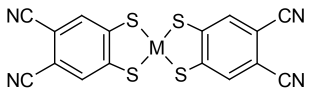
DT-TTF



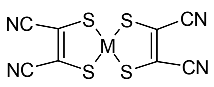
BMDT-TTF



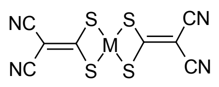
EDT-TTF



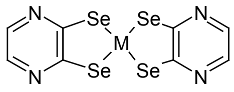
M(dcbdt)$_2$



M(mnt)$_2$



M(i-mnt)$_2$



M(pds)$_2$

Published, accepted or in press work

1. D. Simão, H. Alves, D. Belo, S. Rabaça, E.B. Lopes, I.C. Santos, V. Gama, M.T. Duarte, R.T. Henriques, M. Almeida, H. Novais, "Synthesis, Structure and Physical Properties of Tetrabutylammonium Salts of Nickel Complexes with the New Ligand dcbdt = 4,5-dicyanobenzene-1,2-dithiolate, [Ni(dcbdt)$_2$]$^{z-}$ (z = 0.4, 1, 2)", *Eur. J. Inor. Chem.*, 3119-3126 (2001).
2. H. Alves, D. Simão, E. B. Lopes, D. Belo, V. Gama, M.T. Duarte, H. Novais, R. T. Henriques, M. Almeida, "Structure and Physical Properties of (n-But$_4$N)$_2$[Au(dcbdt)$_2$]$_5$", *Synthetic Metals*, **120** (2001) 1011.
3. M. Almeida, H. Alves, D. Belo, I. C. Santos, E. B. Lopes, V. Gama, R.T. Henriques, D. Simão, H. Novais, M.T. Duarte, A. Pérez-Benítez, C. Rovira, J. Venciana, New Metal Bis-dithiolene Type Complexes for Conducting and Magnetic Materials, *The 56th Yamada Conference "The Fourth International Symposium on Crystalline Organic Metals, Superconductors and Ferromagnets", ISCOM2001*, Hokkaido, Japan, September 10-14, 2001, abstract S59, p.39, invited oral.
4. J. Morgado, I. C. Santos, L. F. Veiros, C. Rodrigues, R. T. Henriques, M. T. Duarte, L. Alcácer and M. Almeida, "Preparation, Structural, Electrical and Magnetic Properties of Tetrathiafulvalene-Au(pds)$_2$ Radical-cation Salts (pds=pyrazine-2,3-diselenolate)", *Jornal of Materials Chemistry*, **11**, 2108-2117 (2001).
5. M. Clemente-Léon, E. Coronado, C. Gimenez-Saiz, C. J. Gomez-Garcia, E. Martinez-Ferrero, M. Almeida and E. B. Lopes, "Organic Inorganic Molecular Conductors Based upon Perylene and Lindquist-type Polyoxometalates", *Jornal of Materials Chemistry*, **11**, 2176-2180 (2001).

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Molecule-based Magnetic Materials

V. Gama, S. Rabaça, D. Belo, R. Meira , R.T. Henriques[1], M.T. Duarte[1], and D.Simão[1]

Objectives

With the study of magnetic molecular materials such as coordination polymers and the metallocenium based charge transfer (CT) salts we aim to achieve a better understanding of molecule based magnets, in particular the crystal-structure magnetic properties relationship.

Results

In case of the M(RR'-DCNQI)$_2$ coordination polymers the main efforts have been related with the synthesis of the compounds and a few more were prepared and are under characterization.

The [M(Cp*)$_2$] based CT salts with the small acceptors, such as DR-DCNQI, (R=Cl, Br Me), [Ni(edt)$_2$], [M(tds)$_2$], (M=Ni, Pt) were found to exhibit crystal structures consisting in an arrangement of parallel 1D alternated stacks, DADADA. In most cases the magnetic behaviour of these compounds is dominated by the intrachain DA FM interactions and at low temperatures metamagnetic (MM) behaviours were observed to occur. This type of transition indicates a strong magnetic anisotropy in these compounds due to the coexistence of AFM intrachain interaction along with FM interchain interactions. The phase diagram obtained for [Mn(Cp*)$_2$][Pt(tds)$_2$] is shown in the figure above. The magnetic behaviour of these compounds was observed to be in good agreement with the predictions of McConnell I mechanism, through the analysis of the crystal structures and spin density calculations.

In case of [M(Cp*)$_2$][Ni(α-tpdt)$_2$], where the acceptor as a larger π system than the acceptors mentioned earlier, the crystal structure consists of alternated layers of acceptors and donors. DA contacts form DADA chains in a plane perpendicular to those layers. MM was observed in case of M=Fe, while in case of M=Mn, FIM ordering occurs at T_C=2.7 K. For M=Cr, a FIM behaviour was also observed.

In case of the CT salts with larger acceptors, structures presented also mixed 1D structural motives. In case of [M(dmix)$_2$] (M=Ni, Pd, Pt) based salts, face-to face pairs of acceptors alternate with side-by-side pairs of donors (AADD), while for [M(Cp*)$_2$][M'(bdt)$_2$], aceptors alternate with side-by-side pairs of donors (ADDADD). In the last compounds there is a net + charge per repeat unit (ADD) that is neutralised by a layer of acceptors. The magnetic behaviour for the [M'(dmix)$_2$] based compounds is dominated by the AA interactions. In case of the [M(Cp*)$_2$][M'(bdt)$_2$] a large variety of magnetic behaviours was observed and MM and FIM transitions were observed, for M/M'=Mn/Ni and Mn/Pt respectively.

As a result from this work the first known FIM ordering in CT molecular salts were obtained.

Published, accepted or in press work

1. S. Rabaça, R. Meira, J. Soares, M.T. Duarte, V. Gama, Structural and Magnetic Characterisation of [Fe(Cp*)$_2$][DR-DCNQI], R=Me and Ph, *Synthetic Metals* 121 (2001) 1828.

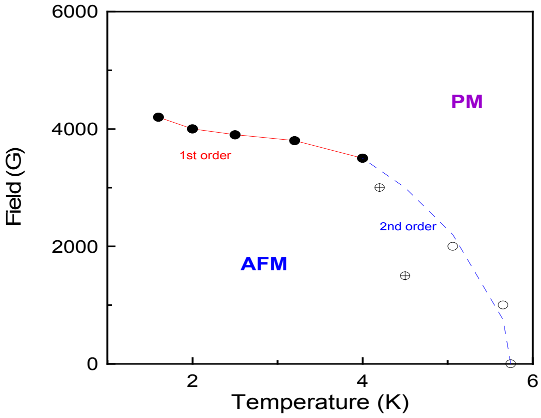

Fig. Magnetic Phase diagram of [Mn(Cp*)$_2$][Pt(tds)$_2$]

2. D. Belo, H. Alves, E.B. Lopes, V. Gama, R.T. Henriques, M.T. Duarte, M. Almeida, A. Pérez-Benítez, C. Rovira, J. Veciana, New dithiothiofene complexes for conducting and magnetic materials, *Synthetic Metals* 121 (2001) 699.
3. S. Rabaça, R. Meira, L.C.J. Pereira, M.T. Duarte, V. Gama, Synthesis, Structural and Magnetic Characterization of the Metamagnet [Fe(Cp*)$_2$]DMe-DCNQI, *J. Organomet. Chem.* 632 (2001) 67.
4. D. Belo, H. Alves, S. Rabaça, L.C. Pereira, M.T. Duarte, V. Gama, R.T. Henriques, M. Almeida, E. Ribera, C. Rovira, J. Veciana, Nickel Complexes, Based on Dithiothiophene Ligands; Magnetic Properties of Metallocenium Salts, *Eur. .J. Inor. Chem.*(2001). In press.
5. S. Rabaça, R. Meira, L.C.J. Pereira, M.T. Duarte, J.J. Novoa, V. Gama, Metamagnetism in Linear Chain Electron-Transfer Salts Based on Decamethylferrocenium and Metal-bis(dichalcogenate) Acceptors, *Inorg. Chimica Acta*. (2001). In press.

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Magnetic interactions in intermetallics based on *f* and *d* elements

J. C. Waerenborgh, A. P. Gonçalves, I. Catarino, G. Bonfait, M. Almeida, S. Sério[1],
C. Cardoso[1], T. Gasche[1], M. Godinho[1], J. A. Paixão[2], M. Ramos Silva[2]

Objectives

Detailed understanding of the role of U on the magnetic behaviour of intermetallics with *d* elements.

Results

The magnetic phase diagram of the series UFe_xAl_{12-x} previously studied for ($4 \leq x \leq 6$) was extended to the extreme compositions x=3 and x=7 which were prepared as single phase samples [1].

The YFe_xAl_{12-x} series crystallizing in the same $ThMn_{12}$-type structure was equally studied and its magnetic phase diagram was compared with the U one. This comparison enabled to put into evidence the significant influence of U in the magnetic properties, favouring the ferromagnetic interactions in the Fe sublattice[1,2]. These conclusions were supported by theoretical calculations based on the density functional theory, which were extended to UFe_5Al_7.

In order to perform these studies the structures of a few AFe_xAl_{12-x} compounds (A=Y, Lu, Tm) were fully characterized for the first time.

Further single crystals of $AFe_{4+\delta}Al_{8-\delta}$, (A=Y, Lu, Er, Nd) suitable for neutron diffraction, were grown and the magnetic structure was investigated. In these compounds random distribution of the muduli of the Fe magnetic moments were deduced from Mossbauer data[3].

The preparation of UFe_xAl_{12-x} compounds containing interstitial hydrogen and the study of their magnetic properties[3] showed an important effect of pressure. The pressure effects and the distributions of Fe magnetic moments on these compounds will be further studied by the ^{57}Fe Mössbauer effect and magnetisation measurements.

The study of the U-Fe-M phase diagrams (M=Sn at 750C and Al at 850C) was completed [5,6]. A new compound UFe_5Sn was characterized and the magnetic properties of U_2Fe_2Sn free from Fe containing impurities were studied [6].

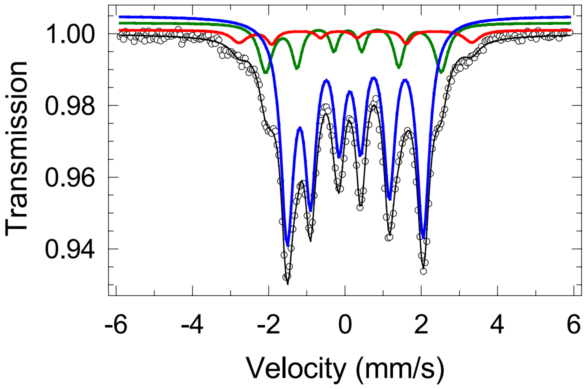

Fig 1 - Mössbauer spectrum of $YFe_{4.2}Al_{7.8}$

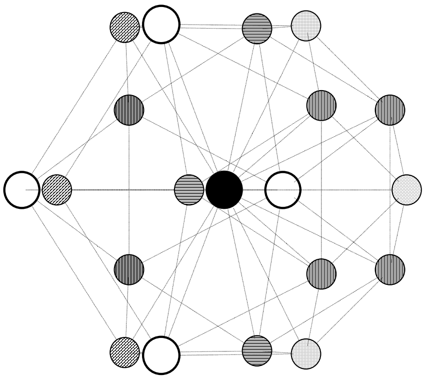

Fig. 2 - U Coordination in UFe_5Sn

Published, accepted or in press work

1. M. Almeida, A. P. Gonçalves, J.C. Waerenborgh, G. Bonfait, I. Catarino, S. Sério, C. Cardoso, M. Cruz, M. Godinho, U/Y intermetallics with Fe derived from the $ThMn_{12}$-type structure, *Rare Earths 2001*, São Paulo, Brasil, 22-26 September 2001, invited oral.
2. I. Catarino, C. Cardoso, J. C. Waerenborgh, A.P. Gonçalves, M.M. Cruz, M. Kuznietz, G. Bonfait, M. Almeida, M. Godinho "Magnetism of the series UFe_xAl_{12-x}", *J. Magn. Magn. Mater.* 226(2001)1120
3. J. A. Paixão, M. Ramos Silva, J. C. Waerenborgh, A. P. Gonçalves, G. H. Lander, P. J. Brown, M. Godinho, P. Burlet "Study of the magnetic structures of $MFe_{4+\delta}Al_{8-\delta}$, M = Lu, Y" *Phys. Rev. B* 63(2001)054410.
4. S. Sério, J.C. Waerenborgh, A.P. Gonçalves, M. Almeida, D. Frouchart, S. Miraglia, M. Godinho "Effect of interstitial hydrogen on UFe_xAl_{12-x}" *J. Alloys Comp.* 317(2001)88
5. H. Nöel, A.P. Gonçalves, Isothermal section at 750ºC of the U-Fe-Sn ternary system, *Intermetallics*, 9 (2001) 473.
6. P. Gonçalves, H. Noël, J. C. Waerenborgh, Crystallographic and magnetic properties of the $U_{2.1}Fe_2Sn_{0.9}$ ternary stannide, *J. Magn. Magn. Mat.*, accepted for publication.

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[2] *Dept. Physics, Fac. Sciences and Technology, Univ. Coimbra, 3004-516 Coimbra, Portugal*

Uranium Based Thin Films

A.P. Gonçalves, M. Almeida, J.C. Waerenborgh, E.B. Lopes, E. Alves[1], G. Bonfait[2], M.R. da Silva[3], M. Godinho[4], M.M. Cruz[4], C. Cardoso[4], S. Sério[4], M.A. Rosa[4], M. Diego[4].

Objectives

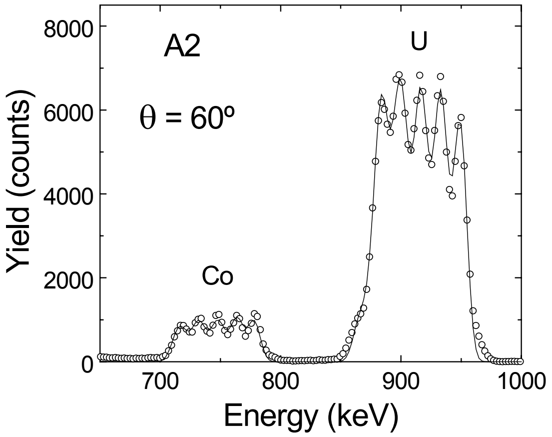
This project aims at:

1. Implementation of a sputtering system dedicated to the preparation of uranium-based thin films and multilayers.
2. The study of the structural, microstructural and physical properties of these films, with emphasis on the magnetic and electrical transport properties.

Results

Continuing the work started in 2000, uranium films were prepared at different conditions (substrate type, substrate temperature, base pressure, etc.) and characterised by Rutherford backscattering spectrometry (RBS), scanning electron microscopy and grazing-incidence X-ray diffraction (GIXRD). The results show an important dependence of crystallinity and morphology on the substrate type and deposition temperature [1-3].

The preparation and characterisation of U/Co multilayers was started. The degree of crystallinity of the samples was determined by GIXRD and the thickness, interfacial roughness and composition of the deposited layers were controlled by RBS. The multilayers were also charaterized by electrical resistivity, AC-susceptibility and magnetization measurements. Preliminary results show that the layers are mainly amorphous, with small amounts of partially disordered U-Co binary phases, and with a roughness of a few tens of Å. The multilayers have a ferromagnetic behaviour, with a saturation magnetisation increasing with the thickness of the layers. [4,5].



RBS spectrum of a U/Co multilayer.

A load-lock system, necessary to maintain the vacuum in the chamber during samples changing was started to be designed.

Communications

1. M.A. Rosa, A.P. Gonçalves, E. Alves, M.R. da Silva, M. Diego, O. Conde, M. Godinho, M. Almeida, Structural and microstrucrural characterization of uranium sputtered films, *31ièmes Journées des Actinides*, Saint-Malo, France, 26-28 April 2001.
2. M. Diego, A.P. Gonçalves, M.R. da Silva, M.A. Rosa, M. Godinho, M. Almeida, Development of a sputtering system for the deposition of U-containing films, *31ièmes Journées des Actinides*, Saint-Malo, France, 26-28 April 2001.
3. M.A. Rosa, A.P. Gonçalves, E. Alves, M.R. da Silva, M. Diego, O. Conde, M. Godinho, M. Almeida, Uranium films prepared by dc sputtering, *Physics of Magnetic Multilayers – Theory and Experiment*, *EGSCM Prague'01*, Prague, June 9-16, 2001.
4. M.A. Rosa, M. Diego, E.B. Lopes, E. Alves, N.P. Barradas, O. Conde, M. Godinho, M. Almeida, A.P. Gonçalves, Structural, magnetic end electrical transport characterisation of U/Co multilayers, *8th Workshop on Magnetism and Intermetallics*, Physics Department, Coimbra University, Coimbra, 17-18 October 2001.
5. A.P. Gonçalves, M. Diego, E. Alves, M.A. Rosa, O. Conde, M. Godinho, M. Almeida, Preparation and study of U/Co multilayers, *Actinides 2001*, Hayama, Japan, November 4-9, 2001.

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Materials for Selective Oxygen Separation Membranes

J.C. Waerenborgh, F.M. Figueiredo[1], D.P.Fagg[1], J.R. Frade[1], M.T. Colomer[2] and J.R. Jurado[2]

Objectives

Improvement of A(Ti,Fe,Mg) O_{3-y} (A = 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

For the first time the structural analysis of $CaFe_xTi_{1-x}O_{3-y}$ containing Fe^{4+} was performed by ^{57}Fe Mössbauer spectroscopy. Besides the concentration of Fe^{4+} the relative amounts of Fe^{3+} coordinated by 6, 5 and 4 O^{2-} were analysed. This study is particularly relevant since 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+}. The high ionic and electronic conductivities of these perovskites depend on the concentration and mobility of the anion vacancies which are directly related to the relative amounts of Fe^{4+} and Fe^{3+} in different coordinations. The results obtained could also explain the differences in the Fe concentration dependence of the electric transport properties of $CaFe_xTi_{1-x}O_{3-y}$ and $SrFe_xTi_{1-x}O_{3-y}$.

A similar study was performed on La substituted $SrFe_xTi_{1-x}O_{3-y}$ perovskites. Substituton 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.

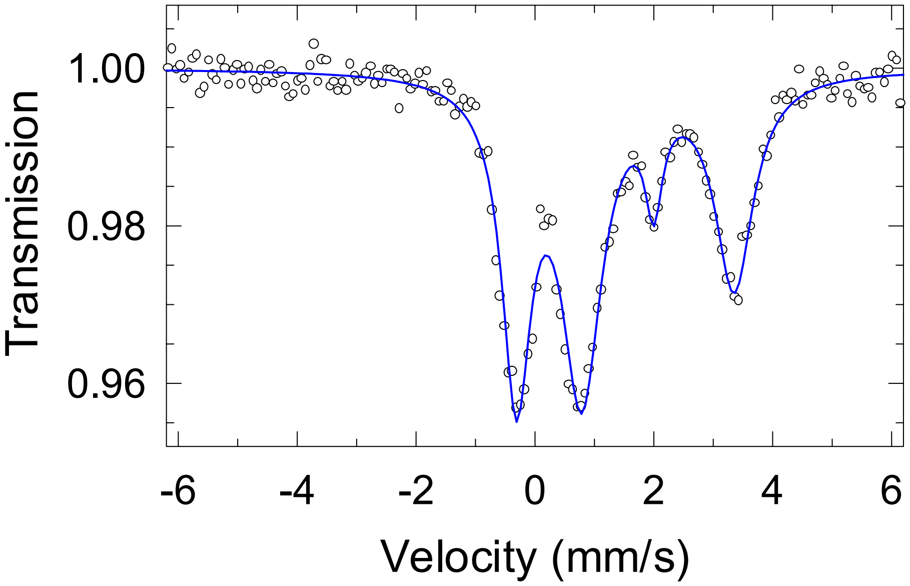

Fig. Mössbauer spectrum taken at 10 K of $CaFe_{0.6}Ti_{0.4}O_{3-y}$. Contributions of Fe^{4+} (red), Fe^{3+} coordinated by 4 (blue) and 6 (green) oxygens are shown slightly shifted, for clarity.

Published, accepted or in press work

1. J.C. Waerenborgh, F.M. Figueiredo, J.R. Frade, M.T.Colomer, J.R.Jurado, Fe^{4+} content and ordering of anion vacancies in partially reduced $AFe_xTi_{1-x}O_{3-y}$ (A = Ca, Sr; x ≤ 0.6) perovskites. An ^{57}Fe Mössbauer spectroscopy study, *J. Phys.: Cond. Mat.* 13(2001)8171.
2. D.P.Fagg, J.C. Waerenborgh, V.V. Kharton, J.R. Frade, Redox behavior and transport properties of $La_{0.5-x}Sr_{0.5-x}Fe_{0.4}Ti_{0.6}O_{3-\square}$ (0< x < 0.1) validated by Mössbauer Spectroscopy, *Solid State Ionics* (in press).

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Mössbauer spectroscopy in Materials Science

J.C. Waerenborgh and 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 temperature range 300-5 K and in external magnetic fields up to 5 T. The expertise developed in ITN is now able to support other national or foreign research institutions.

Last year, besides the applications described in detail for intermetallics, minerals and selective oxygen separation membranes, 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 and in GaN targets. A conversion electron detection system was implemented. 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 Instituto de Ciencia Molecular, Univ. of Valencia, Spain. Training in Mössbauer spectroscopy is given to a *PhD* student of this University.
- Fe distribution in FeCo spinel oxides based on Mössbauer data and the Rietveld refinement of powder diffraction data. Collaboration with the Chemistry Dept. of the Fac. of Sciences of the Univ. Lisbon. Training in powder X-ray diffraction and Mössbauer spectroscopy is given to a *PhD* student of this University.
- The first results on the identification of the Fe-containing phases and determination of the Fe oxidation state in FeMo catalysts were obtained. Collaboration with the Dept. of Chem. Engineering of Instituto Superior Técnico of the Technical Univ. Lisbon.

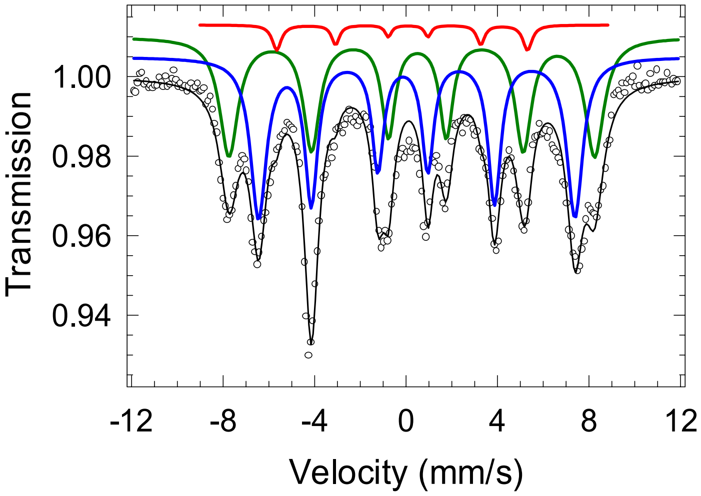


Fig. Mössbauer spectrum of [$CoCp^*_2$][$FeRu(ox)_3$] indicating that the compound is magnetically ordered at 10 K, the Fe electronic spin is S = 2 and the direction of the Fe magnetic moments.

Published, accepted or in press work

1. E. Alves, C. Liu, J.C. Waerenborgh, M.F. da Silva, J.C. Soares, Study of Fe^+ implanted GaN, *Nucl. Instr. Meth. Phys. Res. B* 175(2001)241.

2. E. Coronado, J.R. Galán-Mascarós, C.J. Gómez-García, J.M. Martínez-Agudo, E. Martínez-Ferrero, J. C.Waerenborgh, M. Almeida, Layered Molecule-Based Magnets Formed by Decamethylmetallocenium Cations and Two-Dimensional Bimetallic Complexes [$M^{II}Ru^{III}(ox)_3$]- (M^{II} = Mn, Fe, Co, Cu and Zn; ox = oxalate), *J. Sol. Stat. Chem.* 159(2001)391.

Strongly correlated electrons in 5-f systems

L. C. J. Pereira, A. P. Gonçalves, J. C. Waerenborgh, E. B. Lopes, I. Catarino[1], G. Bonfait[1], M. Godinho[2], M. Almeida.

Objectives

This projects aims at establishing correlation 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.

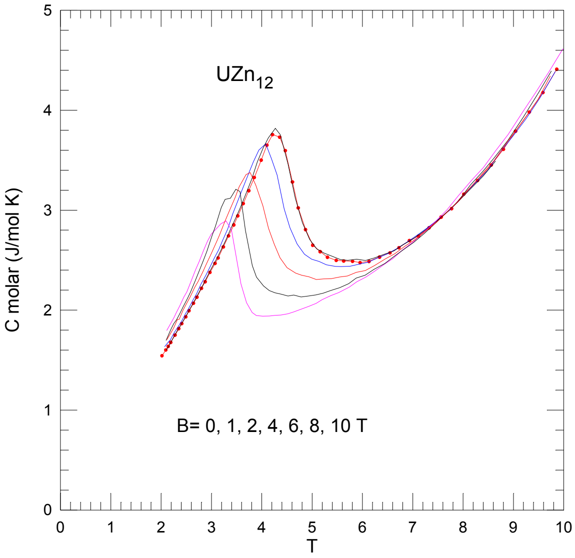
Results

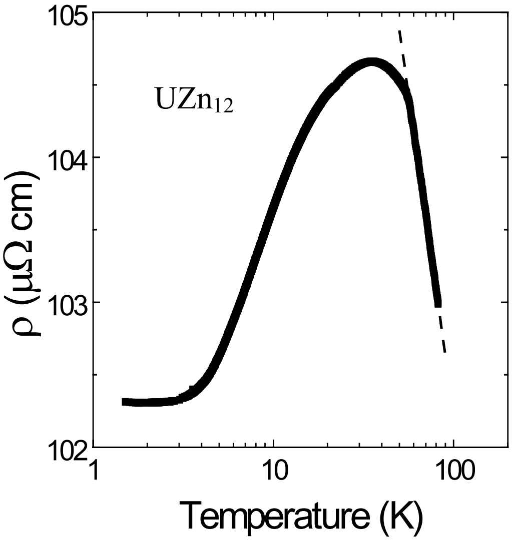
Measurements of electrical resistivity of single-crystalline U_2Pt_2In under pressure ($p \leq 1.8$ GPa) between 0.3 and 300 K were performed in both *a* and *c* directions [2], in order to enlighten the origin of the NFL behaviour. The experimental data already existing from a thorough experimental characterisation pointed to the most plausible scenario being the proximity to a magnetic quantum critical point (QCP) [1]. Our measurements show that U_2Pt_2In is easily driven away from its non-Fermi-liquid state under pressure.

The study of the structural and magnetic properties the alloys like $(U_{1-x}Th_x)_2Pt_2In$ was also pursued in order to probe that QCP scenario, by expanding the lattice of U_2Pt_2In which should result in magnetic order[2, 3]. 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.

UZn_{12} single crystals were prepared for the first time using the high temperature solution growth technique. Single crystal X-ray diffraction experiments confirm the $SmZn_{12}$-type structure and the structure refinement gives a final composition $U_{1.01(1)}Zn_{11.7(1)}$, with a zinc concentration close to the 1:12 ratio.

Muon spin relaxation, magnetisation, specific heat and electrical resistivity measurements show the existence of an antiferromagnetic transition at $T_N = 5.0(2)$ K. A maximum in the electrical resistivity can be observed at ~35 K; pointing to UZn_{12} as a Kondo-type system. A $\gamma = 740$ mJ/molK^2 value can be deduced from the specific heat measurements, clearly classifying UZn_{12} as a heavy-fermion compound.





Published, accepted or in press work

1. P. Estrela, A. de Visser, T. Naka, F.R. de Boer, L.C.J. Pereira, "High-pressure study of the non-Fermi liquid material U_2Pt_2In", *European Physical Journal B*, **23** 449-454 (2001).
2. L.C.J. Pereira, J.C. Waerenborgh, I. Catarino, G. Bonfait, M. Godinho, M. Almeida, "The effect of Th substitution for U in the heavy fermion U_2Pt_2In", *J. Alloys Comp.* **317-318** 419-422 (2001).
3. I. Catarino, L.C.J. Pereira, J.C. Waerenborgh, M. Almeida, M. Godinho, G. Bonfait, "Non-Fermi-liquid behaviour of the $(U_{1-x}Th_x)_2Pt_2In$ solid solutions", *J. Magn. Magn. Mat.* **226-230** 93-95 (2001).

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Magnetotransport in Oxides

J. Maria[1], G. Bonfait[1], M. Godinho[2]

Objectives

In this project we aim at the study of the effects of strong magnetic fields (up to 18 T) on the transport properties of conducting oxides like High Tc superconductors, manganite oxides or superconductors/manganites heterostructures. The results are analysed in complement to other characterisation results such as magnetisation and structure.

Results

The magnetoresistance of several compounds of the family $(La,Ca)_{n+1}Mn_nO_{3n+1}$, synthetised at FCUL, were measured. We showed (Fig. 1) that these compounds could exhibit a magnetoresistance of 90% at 16 T around the metal-insulator transition (Ref. 1).

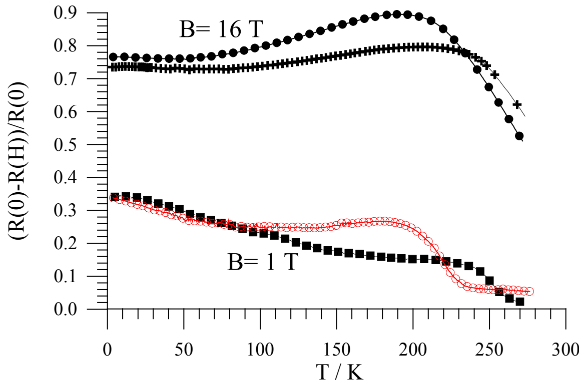

Fig. 1 Magnetoresistance for $La_{1.4}Ca_{1.6}Mn_2O_7$ (crosses) and $La_2Ca_2Mn_3O_{10}$.(circles) annealed at 1373 K at 1 and 16 T

The electrical characteristics of YBaCuO films grown by pulsed MOCVD technique at Vilnius University were measured around the critical temperature in the frame of the EC network MULTIMETOX. The existing rotating sample holder was improved in order to make resistivity measurements on a large angle range (0º-90º) between the magnetic field and the (ab) plane of the films. These measurements showed the very high quality of these films (Tc=93 K, ΔTc=0.3 K). Thanks to the rotating sample holder, the anisotropy ratio was determined using the scaling law valid for anisotropic superconductors, and, was found equal to 7 as in the best single crystals.

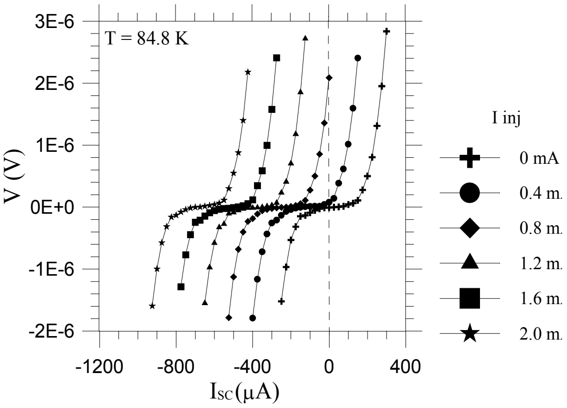

Fig. 2 I(V) curve for various spin injection current. Such curves allow the determination of the critical current reduction due to spin polarisation injection.

The same type of measurements was made on an heterostructure YBCO/Manganites (Spin-Injection device). We showed that despite the absence of an insulator layer between the superconducting and the manganites layer (generally present to avoid interdiffusion during the growth process) the YBCO layer remains superconducting (Tc=90 K). Measurements of critical current (Isc) were done on one heterostructure looking for an effect of the spin polarized injection current (Iinj, Fig 2). The results were negative on the sample measured. New samples are on preparation to try to understand this negative result.

Published, accepted or in press work

1. M. M. Cruz, M. D. Carvalho, A. Casaca, G. Bonfait, F.M. Costa, M.Godinho, "Ruddlesden-Popper versus perovskite phases in manganites", *J. Magn. Magn. Mat.* **226-230**, 800 (2001)
2. B. Vengalis, V. Plaušinaitienė[1], A. Abrutis, Z. Šaltytė, R. Butkutė, V. Petrauskas, J. Maria, G. Bonfait, "Transverse and longitudinal electrical transport properties in HTS/I/FM and HTS/FM Heterostructure*s",* Accepted in Journ. de Physique C4.
3. P. Kovác, I. Hušek, W. Pachla, M. Diantoro, G. Bonfait, J. Maria, K. Frohlich, L. Kopera, R. Diduszko, A. Presz, "Material for resistive barriers in Bi-2223/Ag tapes", *Supercond. Sci. Technol.* **14,** 966 (2001)

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Development of Pulse Tube Cryocoolers

G. Bonfait, I. Catarino[1], J. M. Poncet[2].

Objectives

This project (3 years) aims at the introduction in Portugal of new technique of cryocoolers. The Pulse-Tube Cryocoolers (PTC) are capable to fulfil the low-cost, low-weight, low-size, low-maintenance requirements. Morover they provide also a reduced vibration level, not offered by the usual cryocoolers (Gifford-Mac Mahon, Stirling) which contrary to PTC have moving parts at low temperatures.

This project focuses on the design, construction and test of a "low frequency" (2-7 Hz) PTC allowing a base temperature lower than 30 K and a high cooling power (80 W at 77 K).

One goal of the project is the study the degradation of the performances by the angular position of the PTC. This work will be used to build an optimised to be inserted in a multitechnique surface analysis apparatus existing in CeFiTec (Physics Dept, FCT/UNL) in order to perform Thermal Desorption Spectrometry on a large temperature range and with an high temperature change rate.

Results

The conception and technical drawings of our first prototype were studied in collaboration with the “Service des Basses Températures” of CEA-Grenoble, in France (supported by ICCTI/French Embassy programme). The construction started at ITN at the beginning of 2001. First tests were performed in Grenoble (July 2001) and this Pulsed Tube is now working at ITN since beginning of December and it is installed on a rotating support (Fig. 1).

This system achieved a lowest temperature of 26 K at 3 Hz with a cooling power of 6 W at 40 K. The performance degradation versus the inclination were studied for 3 different frequencies (3 Hz, 5 Hz and 7 Hz). Our results (Fig. 2) show that for an angle smaller than 90º the base temperature remains below 40 K. For angles larger than 90º, the system works better at 7 Hz and the worst performances occur beteween 120º and 150º with a base temperature increasing up to 70 K at 7 Hz. The optimisation of these performances are now under progress.

Fig. 1 The ITN rotating Pulse Tube Cryocooler in 0º position

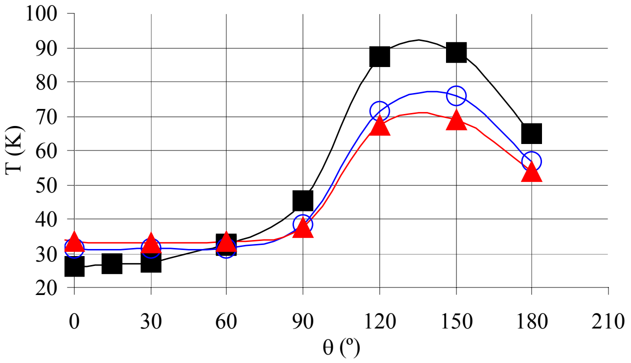

Fig.2 Base temperature versus inclination at 3 Hz (Square), 5 Hz (Circle) and 7 Hz (Triangle).

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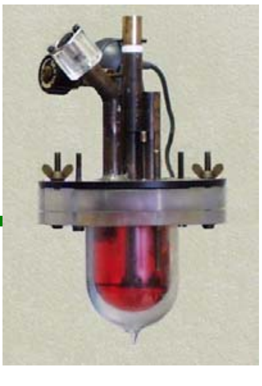
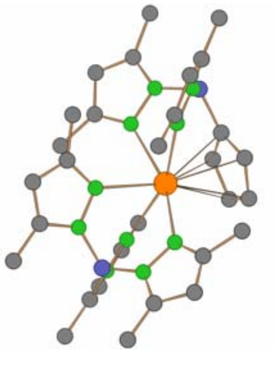
Inorganic and Organometallic Chemistry





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 exploring, through international collaborations, the use of electrospray ionisation (ESI) coupled to FT-ICR/MS to develop methods for actinide speciation in aqueous phase, taking advantage of the ability of ESI to transfer solution species to the gas phase.

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 5f vs 4f 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. Studies on the potential use of thorium and uranium oxides as catalysts for the destruction of volatile chloro-organic compounds and NO_x abatement is also being initiated.

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.

The work made during 2001, described in the following pages, is summarized as follows:

Uranium and lanthanide (III) triazocyclononane complexes were synthesized. These studies with multidentate nitrogen ligands can be relevant for An(III)/Ln(III) separation.

The first gas-phase ion chemistry studies of transuranium actinides, Np and Pu, by FT-ICR/MS have been performed, with a focus on oxidation reactions. From these studies useful thermochemical data could be obtained. The Laboratory of mass spectrometry was adapted for handling toxic actinides.

Characterisation of glasses by laser ablation FT-ICR/MS mass spectrometry, related to studies of vitrification of radioactive waste, was started.

Bond dissociation enthalpies of some new organometallic uranium compounds were determined. This led to an integrated review of all literature data for U(IV) compounds, with the proposition of a unique absolute scale for the energetics of those compounds.

The synthesis of lanthanide compounds involving heteroscorpionate ligands with potential application in Ziegler-Natta catalysis and C-H activation was pursued.

Having in mind the oxidative coupling of methane, the synthesis and characterisation of $LnCu_2$ (Ln= La, Ce, Pr, Nd, Eu, Ho, Tm, Yb, Th, U) intermetallic compounds was performed, and they were used as precursors for the preparation of the corresponding heterobimetallic oxides. A prototype for oxides characterisation by temperature programmed reduction (TPR) was built and is now operational.

CO_2 activation and EXAFS studies with polynuclear lanthanide alkoxides and aryloxides were made.

Gas-phase reactivity studies of thorium and uranium metal and metal oxide ions with C_6H_5Cl were carried out to try to model the decomposition of organochloride compounds over thorium and uranium oxides in condensed phase.

The synthesis in condensed phase of catalysts for the oxidation of chlorohydrocarbon compounds was initiated.

The work made is financially supported by 5 projects of FCT (one approved for 2002), one project supported by an industrial association, SPV, one NATO post-doctoral grant and one PhD grant. Two other projects were submitted (one to the IAEA for 2003-4; another to the FCT is still waiting for evaluation after 2 years).

Inorganic and Organometallic Chemistry

Research Team

Researchers

- A.P.MATOS, Coordinator Researcher, Group Leader
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- J. MARÇALO, Auxiliary Researcher
- J. BRANCO, Auxiliary Researcher
- J.P. LEAL, Auxiliary Researcher
- T.A. GASCHE, Auxiliary Researcher
- J.M. CARRETAS, Assistant Researcher

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- M. A. ANTUNES, PhD student, FCT grant
- B. RAMOS, BIIC grantee, POCTI
- C. DIAS, BIIC grantee, POCTI
- M. SANTOS, BIIC grantee, POCTI
- A.C. GONÇALVES, grantee, SPV
- V. GAFFNEY, grantee, SPV

Technicians

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

Funding

	$\times 10^3$ PTE
Research Projects:	26855
ITN:	-
Other Sources:	400
Total:	**27255**

Publications

Journals:	9 and 2 in press *
Proceedings:	6
Conf. Communications:	13
Internal Report:	1
Other Publications:	1
Theses:	1

* One member of our Group, Ângela Domingos, contributed as crystallographer to another 4 published papers and 1 in press from the Inorganic and Radiopharmaceutical Chemistry Group of the Chemistry sector of ITN.

Uranium and Lanthanide (III) Triazocyclononane Complexes for Actinide/Lanthanide Separation

B. Ramos, A. 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 a class of ligands based on the triazocyclononane ring (TACN). We have tested the complexation of lanthanide and uranium ions by TACN-X$_3$ (X = HCl, SiMe$_2$NPh, SiMe$_2$N^{t}Bu).

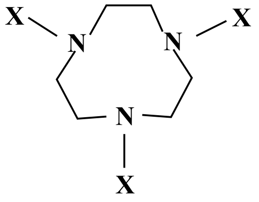

Figure 1 - TACN-X$_3$

Results

TACN-(SiMe$_2$NPh)$_3$ has been synthesized by a published method and the new TACN-(SiMe$_2$N^{t}Bu)$_3$ ligand has been obtained by a similar procedure. Y, Eu and Yb trichlorides react stoichiometrically with the sodium salt of the ligand TACN-(SiMe$_2$NPh)$_3$ to yield complexes of general formula M[TACN-(SiMe$_2$NPh)$_3$] (M = Y **(1)**, Eu **(2)**, Yb **(3)**). Due to the bigger ionic radii of La and U, the analogous reactions of LaCl$_3$ and UI$_3$ results in formation of the adducts M[TACN-(SiMe$_2$NPh)$_3$]THF (M = La **(4)**, U **(5)**). Compounds **1** and **2** were structurally characterized by X-ray diffraction analysis.

In **2** the Eu is nine-coordinate by the three nitrogen atoms of the amine groups, the three nitrogen atoms of the TACN ring and by three interactions with three alternating carbon atoms of the ring. The coordination geometry around the metal centre is tricapped trigonal prismatic.

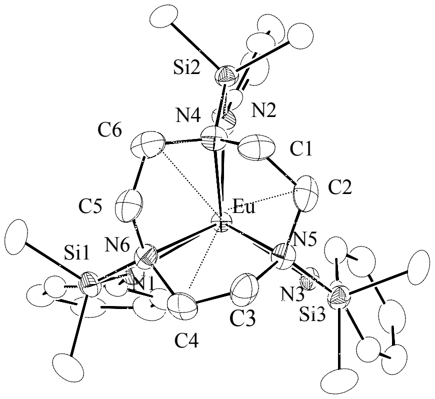

Figure 2 - Molecular structure of **2**

In **1** no interactions between the yttrium and the carbon atoms of the ring are observed and the coordination geometry can be described as trigonal prismatic.

Characterization by ^{1}H NMR spectroscopy indicated fluxional behaviour of the compounds in solution, but by lowering the temperature spectra consistent with the symmetry found in the solid are obtained.

For comparison the complex Eu[TACN-(SiMe$_2$N^{t}Bu)$_3$] **(6)** was prepared and its structure determined by means of X-ray diffraction analysis. The structure is similar to the one determined for **2** and also its solution behaviour.

We intend now to replace the group SiMe$_2$ in TACN(SiMe$_2$NPh)$_3$ by a group resistant to hydrolysis and to study the complexation of the different ions in aqueous solution.

Gas-Phase Ion Chemistry of Lanthanides and Actinides

J. Marçalo, A.P. de Matos, M. Santos,
J.K. Gibson[1], R.G. Haire[1]

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.

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.

The experimental work is based on the use of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS), a technique that is specially suited for the study of the chemistry of ion/molecule systems in the gas phase.

We have also been exploring, through international collaborations, the use of electrospray ionisation (ESI) coupled to FT-ICR/MS to study different aspects of the gas-phase chemistry of Ln and An compounds and to develop methods for uranium speciation in aqueous phase, taking advantage of the ability of ESI to transfer solution species to the gas phase.

Results

The gas-phase reactions of lanthanide ($Ln^+ = La^+ - Lu^+$, except Pm^+) and actinide ($An^+ = Th^+, U^+$) cations with ferrocene, $Fe(C_5H_5)_2$, were studied [1]. The An^+ cations and the majority of the Ln^+ cations reacted by metal exchange, yielding Ln and An biscyclopentadienyl ions $M(C_5H_5)_2^+$, while the less reactive Ln^+ cations formed the “adduct” ions $LnFe(C_5H_5)_2^+$. The product ion distributions observed and the reaction efficiencies obtained in kinetics studies both revealed a close relation with the relative stability of the accessible formal oxidation states of the metal cations. A few thermochemical estimates pertaining to the different species formed in the reactions could also be made. Reactivity studies of Ln, Th and U oxide and hydroxide cations were also performed.

Gas-phase reactivity studies of thorium and uranium metal ions, Th^+ and U^+, and metal oxide ions, ThO^+, ThO_2^+, $Th_2O_3^+$, UO^+ and UO_2^+, with C_6H_5Cl were carried out to try to model the decomposition of organochloride compounds over thorium and uranium oxides in condensed phase. All the ions studied reacted efficiently with C_6H_5Cl mainly by chlorine abstraction.

The first gas-phase ion chemistry studies of transuranium actinides by FTICR-MS have been performed [2]. Reactions of An^+ and AnO^+ (An = Th, U, Np and Pu) with O_2, CO_2, N_2O and NO were studied with a focus on oxidation of transuranium ions. All four An^+ produced AnO^+ for each oxidant under near thermal conditions. The results for Th and U are consistent with previous studies. Formation of AnO^+ from NO suggests that each BDE(An^+-O) exceeds 631 kJ/mol. This is consistent with known values for ThO^+, UO^+ and NpO^+. Experimental values of 618(22) and 682(54) kJ/mol have been reported for BDE(Pu^+-O); the uncertainty in the former value is such that our BDE(Pu^+-O) > 631 kJ/mol is not aberrant. The UO^+ was oxidized to UO_2^+ by NO and CO_2; no other AnO_2^+ were produced with these oxidants. All four AnO^+ were oxidized to AnO_2^+ by N_2O. With O_2, AnO_2^+ appeared for An = U, Np and Pu, suggesting that each of the three BDE(OAn^+-O) exceeds 498 kJ/mol. This is certainly the case for UO_2^+. However, our initial results appear to conflict with literature values for BDE(OPu^+-O) of 261(22) and 249(77) kJ/mol. Data are not available for comparison with the minimum BDE(ONp^+-O) derived from our results.

This work has been complemented by reactivity studies of the same ions with C_2H_4O and H_2O, which led to concurrent results. Bracketing experiments of the ionisation energy of PuO_2 have also been performed, in which a value of 7.0(0.3) eV could be obtained, in conflict with literature values of 9.4(0.5) and 10.1(0.1) eV, but in agreement with our estimate of BDE(OPu^+-O) > 498 kJ/mol.

Published, accepted or in press work

1. M.C. Vieira, J. Marçalo, A. Pires de Matos, Gas-Phase Reactivity of Lanthanide and Actinide Cations with the Archetypal Organometallic Complexes $Fe(CO)_5$ and $Fe(C_5H_5)_2$, *J. Organomet. Chem.* 632 (2001) 126.
2. M. Santos, J. Marçalo, A. Pires de Matos, R.G. Haire, J.K. Gibson, Gas-Phase Oxidation Reactions of Neptunium and Plutonium Ions Investigated via FTICR-MS, *6th European FTICR-MS Workshop,* Kerkrade (The Netherlands), October 2001.

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

A.P.de Matos, J.Marçalo, M. Santos, F. Araújo[1], P. Valério[1]

Objectives

One objective of this project is to develop in ITN know how in glass science to contribute to the research on the waste vitrification processes. The final goal is to study glass samples contaning radioactive elements (actinides and fission products) and to obtain structrural information as well as to investigate the chemical behaviour in lixiviation 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. For the speciation studies necessary to investigate the glass lixiviation 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 characterization and synthesis of glasses two applications are envisaged in collaboration with researchers of other Groups of ITN. A joint project with the Faculty of Fine Arts of the University of Lisbon, was submitted to FCT. The idea is to synthesize new coloured glasses namely, fluorescent glasses by incorporating rare earth oxides in silicate glasses or the "dichroic" glasses made by thin layer deposition of several metal oxides on glasses. ("Multilayer Surface Coating of Glass With Metal Oxides: Characterization by Rutherford Backscattering, X-Ray Fluorescence and FTICR Mass Spectrometry", P.R. Gordo, E. Alves, L.C. Alves, R.C. da Silva, A.P. Gonçalves, J. Marçalo, M.F. Araújo, A. Pires de Matos, in *Proceedings of the 18th International Congress on Glass, San Francisco, California, 1998*, Eds., M.K. Choudhay, N.T. Huff, C.H. Drummond III, The American Ceramic Society, Westerville, Ohio, 1998, p. C4.).

Concerning the characterization of glass objects a collaboration with the Museum of Marinha Grande started, and a set of samples are beeing studied in a joint work with the Environmental Analytical Chemistry Group.

Results

LD-FTICR/MS studies of several silica based glasses were made in order to obtain structural information and to analyse some of the metal oxides present [1]. It was found that negative spectra could easily be obtained for the glass former oxides, and positive spectra for the flux reagents, namely the alkali oxides and lead oxides, and for the colorants, namely the 3d transition elements. Glass containing uranium showed the species U^+, UO^+ and UO_2^+ being U^+ the most abundant ionic species. Glass containing aluminium showed clusters of the series $Si_xAl_yO_{2(x+y)}^-$ represented by SiO_2^-, $SiAlO_4^-$ and $Si_2AlO_6^-$, and only one ion, SiO_3^-, of the series $Si_nO_{2n+1}^-$. Borosilicate glass indicated the presence of the ions $Na_2BO_2^+$, $Na_2BO_3^+$ and BO_2^-. The glass former phosphorous oxide could easily be identified through the species PO_2^- and PO_3^- in a glass containing phosphorus.

The elemental composition of a series of samples of a factory which laborated in Marinha Grande until the nineties, and which belong now to the Glass Museum of Marinha Grande, was obtained by energy dispersive X-ray fluorescence (EDXRF) spectrometry at the Laboratories of the IAEA in Vienna. Multivariate statistical analysis, namely the principal component extraction, simplified the identification of some of the colouring chemical elements, associating them with the different colours of the glass objects. Electronic absorption spectra of all the samples were also made.

Published, accepted or in press work

1. J. Marçalo, M. Santos, A. Pires de Matos, Characterization of Glasses by FTICR Mass Spectrometry, *Proceedings of the XIX International Congress on Glass, Vol 2, Extended Abstracts, Edinburgh, Scotland 1-6 July, 2001*, pp. 216-217.

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[1] Environmental Analytical Chemistry Group, Chemistry Department, ITN.

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) and on the reactions in which they are involved. The study of the energetics of alkaline and alkaline-earth compounds as models for f-element compounds is also carried out, as it has proved to be a quite promising field.

Results

During 2001 several lines were followed to attain the stated objectives. Bond dissociation enthalpies of some new organometallic uranium compounds were determined. This, lead to an integrated review of all literature data for U(IV) compounds, with the proposition of a unique absolute scale for the energetics of those compounds [1]. It should be stressed that the results obtained for U(IV) organometallic compounds on the last decade at IOC group (J.P. Leal, N. Marques, A. Pires de Matos, M.J. Calhorda, A.M. Galvão, J.A. Martinho Simões, Uranium-ligand bond dissociation enthalpies in U(IV) polipyrazolylborate complexes, *Organometallics* **1992**, *11*, 1632; J.P. Leal, J.A. Martinho Simões, Uranium-ligand bond dissociation enthalpies in U(IV) polypyrazolylborate complexes. II, *J. Chem. Soc. Dalton Trans.* **1994**, 2687) represent a substancial amount of the worldwide available results in the literature.

During this year we kept a renewed interest on alkaline [2] and alkaline-earth compounds because they proved to be good models to understand *f*-elements compounds. The *ALKALI 1995*, a database of reaction enthalpies and enthalpies of formation of compounds of those families made at ITN was referred at the *"Survey of Thermodynamic and Kinetic Databases", Nuclear Energy Agency, 1996, p. 14*. The new values obtained until now, and some more programmed for next year will be used for an updated version of such database intended to be ready in two years time.

A new calorimeter, that will allow to make thermal analysis and gas chromatography over the same sample, had its design finished and started to be constructed. It is expected to have the first results in 2002.

Published, accepted or in press work

1. J.P. Leal, N. Marques, J. Takats, Bond Dissociation Enthalpies in U(IV) Complexes. An integrated view, *J. Organomet. Chem.* 632 (2001) 209.
2. Carvalho, V. Cachata, J.P. Leal, Standard Molar Enthalpies of Formation of Li, Na, K and Tl Cyclopentadienyls, *Eur. J. Inorg. Chem.* (2001) 1587.

Lanthanide Compounds with Applications in Ziegler-Natta Catalysis and C-H Activation

D. Roitershtein, B. Monteiro, A. 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.

The project is based on our finding that thermolysis of $Sm(\eta^3\text{-}Tp^{Me2})(\eta^2\text{-}Tp^{Me2})(\eta^5\text{-}Cp)$ led to formation of $Sm(\eta^3\text{-}Tp^{Me2})[HB(3\text{-}5Me_2pz)_2(C_5H_4)]$, a compound in which the Sm is coordinated to a Tp ligand and to a novel, dianionic ligand, $HB(3,5\text{-}Me_2pz)_2(C_5H_4)$, 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 is to investigate if the C-H activation which occurs in $Sm(\eta^3\text{-}Tp^{Me2})(\eta^2\text{-}Tp^{Me2})(\eta^5\text{-}Cp)$ can be extended to other mixed class of compounds to yield other heteroscorpionate ligands.

Results

The synthesis of the new dianionic hydrobis(pyrazolyl)(cyclopentadienyl)borate ligand, $[HB(3,5\text{-}Me_2pz)_2(C_5H_4)]$ was not accomplished due to oligomerization of the Cp anion and formation of pyrazaboles. By using bulkier substituents (C_4Me_4H and 3-^{t}Bupz) it was possible to avoid the side reactions and to get the borane $MeB(C_4Me_4H)(3\text{-}^tBupz)_2$. We have to choose now the conditions for deprotonation of the (C_4Me_4H) ring in order to get the desired borate.

At the same time we have been investigating the possibility of inducing transformations analogous to the one described for $Sm(Tp^{Me2})_2(Cp)$ (I. Lopes, G. Y. Lin, A. Domingos, N. Marques, J. Takats, *J. Am. Chem. Soc.* **1999**, *121*, 8110). The protocol used in the synthesis of $Sm(Tp^{Me2})_2(Cp)$ has been extended to the reactions of $Sm(Tp^{Me2})_2$ with TlC_4H_4P and $Tl(C_9H_7)$. Reaction of $Sm(\eta^3\text{-}Tp^{Me2})_2$ with TlC_4H_4P in THF led to formation of $Sm(\eta^3\text{-}Tp^{Me2})_2(\eta^1\text{-}C_4H_4P)$ **(1)**. When the reaction is run in toluene the compound $Sm(\eta^3\text{-}Tp^{Me2})(\eta^2\text{-}Tp^{Me2})(\eta^5\text{-}C_4H_4P)$ **(2)** is obtained. $Sm(\eta^3\text{-}Tp^{Me2})(\eta^2\text{-}Tp^{Me2})(\eta^5\text{-}C_9H_7)$ **(3)** was obtained in an analogous way.

During our studies on the reactivity of $Sm(Tp^{Me2})_2$ we have found that the alkyls $Sm(Tp^{Me2})_2R$ are unstable due to reduction of the metal centre and subsequent precipitation of $Sm(Tp^{Me2})_2$. However the hydrocarbyls have lifetime long enough to undergo protonolysis with several protic substrates. This procedure allows the preparation of $Sm(Tp^{Me2})_2$ (Y) compounds (Y = OPh **(4)**, CCPh **(5)**, Cp **(6)**, $OC_6H_2\text{-}2,4,6\text{-}^tBu_3$ **(7)**, NPh_2 **(8)**, 3,5-Me_2pz **(9)**) in good yields [1-3].

Published, accepted or in press work

1. I. Lopes, B. Monteiro, G. Lin, Â. Domingos, N. Marques, J. Takats, Samarium(III) Compounds Supported by the Hydrotris(3,5-dimethyl-pyrazolyl)borate Ligand: Synthetic Utility of the Putative, Reduction Prone Sm(III)-Hydrocarbyls, '$(Tp^{Me2})_2SmR$', *J. Organomet. Chem.* 632 (2001) 119.
2. I. Lopes, B. Monteiro, Â. Domingos, N. Marques, Compostos de Samário (III) Suportados Pelo Ligando Borato de Tris(3,5-Dimetil-Pirazolilo): Utilidade dos Hipotéticos Hidrocarbilos $Sm(Tp^{Me2})_2R$” na Síntese de Derivados $Sm(Tp^{Me2})_2Y$, *V Conferência de Química Inorgânica da Sociedade Portuguesa de Química,* Monte Real, Portugal, April 2001.
3. N. Marques, Organo-f-Element Chemistry with Multidentate Nitrogen Ligands, *Rare Earths' 2001*, Campos do Jordão, Brazil, September 2001 (invited lecture).

Catalytic Applications of f-Block Element Intermetallic Compounds

J. Branco, T.A. Gasche, C. Dias,
A.P. Gonçalves[1], J. P. Leal

Objectives

Binary intermetallic compounds of lanthanides or actinides and d transition metals (usually Ni, Cu, Co, Zn) have been found to be catalytically active in a range of reactions. The main goal of this project is to study different AB and AB_2 intermetallic compounds, containing lanthanides and actinides, in order to understand the influence of the f block element (electronic configuration and variation in size) in the chemical behaviour of those compounds. In the work reported here the main objective was to study the oxidative coupling of methane (OCM) to C_2 hydrocarbons (ethane and ethylene), with high ethylene selectivity, using binary intermetallic compounds $LnCu_2$ (Ln = La, Ce, Pr, Nd, Eu, Ho, Tm, Yb) and $AnCu_2$ (An = Th, U) as catalytic precursors.

Results

The synthesis and characterization of $LnCu_2$ (Ln= La, Ce, Pr, Nd, Eu, Ho, Tm, Yb) and $AnCu_2$ (An = Th, U) intermetallic compounds was performed [1]. They were obtained by melting stoichiometric amounts of the elements. The characterization was done by powder X-ray and SEM (Figure 1). All the compounds were homogeneous, crystalline and with only one phase. Heterobimetallic oxides were prepared from these intermetallic compounds by oxidation with a mixture of O_2/N_2. The characterization was made by powder X-ray and temperature programmed reduction (TPR) for which a prototype was built and tested.

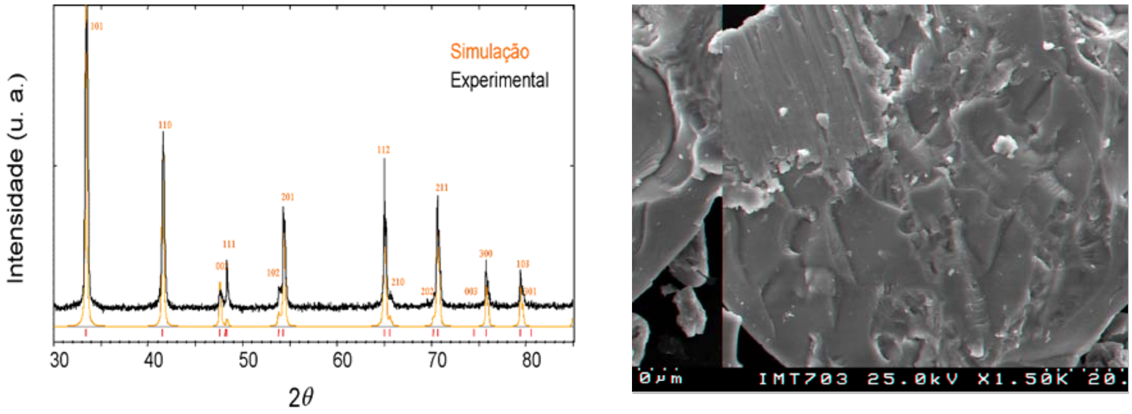

Figure 1 - $LaCu_2$, powder X-ray and SEM.

Published, accepted or in press work

1. C.J. Dias, A.P. Gonçalves, T. Almeida Gasche, J.B. Branco, Síntese e Caracterização de Compostos Intermetálicos Binários do Tipo $LnCu_2$ (Ln= La, Ce, Pr, Nd, Gd, Tm), *V Conferência de Química Inorgânica da Sociedade Portuguesa de Química,* Monte Real, Portugal, April 2001.

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[1] Solid State Group, Chemistry sector, ITN.

Synthesis, Characterization and Reactivity Studies of Lanthanide and Actinide Alkoxides and Aryloxides

J.M. Carretas, J. Branco, J.P. Leal, T. A. Gasche, J. Marçalo, Â. Domingos, A.P. de Matos, M. Epple[1]

Objectives

The applications of lanthanide alkoxides and aryloxides are diverse, ranging from catalysis to synthesis of high purity oxide materials. Uranium and thorium alkoxides and aryloxides have also shown interesting properties. During the last years we have synthesized several alkoxides and aryloxides including some polynuclear species. In this project we are studying the activation of small molecules by this type of compounds, as pure complexes or immobilised surface species. The continuation of this work will be supported by FCT through an approved project: *Immobilised surface rare earth and actinide aryloxides* $[M(OC_6H_2{}^tBu\text{-}2,6\text{-}Me\text{-}4)_3]$*, M= La, Pr, Nd, Sm, Dy, Ho, Er, Yb, Th, U. Activation of small molecules* (CO_2, CH_4, C_2H_6).

Results

The CO_2 activation studies started with well-known and characterized ytterbium aryloxide compounds: $Yb(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)_2.2thf$ (Lappert, M. F., Deacon, B., Hitchcock, P. B., *J. Chem. Soc. Chem. Commun.* (1989) 935) and $[Yb_6(\mu_3\text{-}OH)_4(OC_6H_4\text{-}2\text{-}OCH_3)_2(\mu\text{-}OC_6H_4\text{-}\eta\text{-}OCH_3)_{10}(OC_6H_4\text{-}\eta\text{-}OCH_3)_2]$, the later synthesized and characterized in our group [1]. This preliminary work was completed with the study of two europium alkoxides, “$Eu(OR)_2$, R=Me, Et” (Carretas, J. M., Branco, J., Marçalo, J., Waerenborg, J. C., Marques, N., Pires de Matos, A., *J. Alloys Comp.*, **275-277** (1998) 841). In all cases, we observed the same reactivity pattern: CO_2 insertion into the metal-oxygen bonds. From the IR spectra, the strong OCO symmetric and asymmetric stretches are consistent with the formation of metal carboxylate complexes. Moreover, in the case of the europium alkoxide compounds, υ(OCO) values (1570_{asym}, 1370_{sym} cm^{-1}) are typical of a η^2 complex (bidentate, C_s), whereas for the ytterbium aryloxides these values (1650_{asym}, 1350_{sym} cm^{-1}) are typical of η^1 complexes (monodentate, C_{2v}).

EXAFS studies of these compounds were undertaken and showed that the average metal-oxygen distance changed upon the insertion of CO_2 in the M-O bond. These variations could be correlated with the ones observed in the IR spectra.

Published, accepted or in press work

1. J. Carretas, J. Branco, J. Marçalo, P. Isolani, A. Domingos, A. Pires de Matos, Synthesis and Characterization of Polynuclear Lanthanide Aryloxides, *J. Alloys Comp.,* 169-172 (2001) 323.

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[1] Solid State Chemistry, Faculty of Chemistry, Univ. of Bochum, Germany (CRUP-DAAD funded, 1999-2000; ICCTI-DAAD funded 2002-2003).

Waste Treatment

A.P. de Matos, J. Norte[1], J. Marçalo, J. Branco, J.P. Leal, N. Pinhão[2], A.C. Gonçalves[3], V. Gaffney[3]

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 use of lanthanide, thorium and uranium based catalysts is being considered for oxidation of chlorohydrocarbons and conversion of CO_2 to methanol.

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

Results

The project of the chemical reactor was concluded which involved a series of thermodynamic calculations.

Research is being made in our Laboratories on the conversion of the reaction efluent gases, namely the conversion of CO_2/H_2 to methanol and CO_2/methanol to dimethylcarbonate [1-2]. Oxidation of toxic organic compounds assisted by plasma discharge is also under study.

Gas-phase reactivity studies were made using Fourier transform ion cyclotron resonance mass spectrometry of thorium and uranium metal and metal oxide ions with C_6H_5Cl in order to model the decomposition of organochloride compounds over thorium and uranium oxides in condensed phase.

Published, accepted or in press work

1. A.C. Gonçalves, Obtenção do Metanol a partir do Gás de Síntese, *Report-ITN/SPV*, 34 pp, July 2001.
2. V.J. Gaffney, J. Branco, A. Pires de Matos, Síntese Directa do Dimetilcarbonato a partir do CO_2 e Metanol Utilizando Catalisadores do Tipo $ACl_M/KCl/SiO_2$ ($A=Cu^+$, Cu^{2+}, Ce^{3+}, U^{4+}), *5º Encontro da Divisão de Catálise da Sociedade Portuguesa de Química*, Leiria, Portugal, May 2001.

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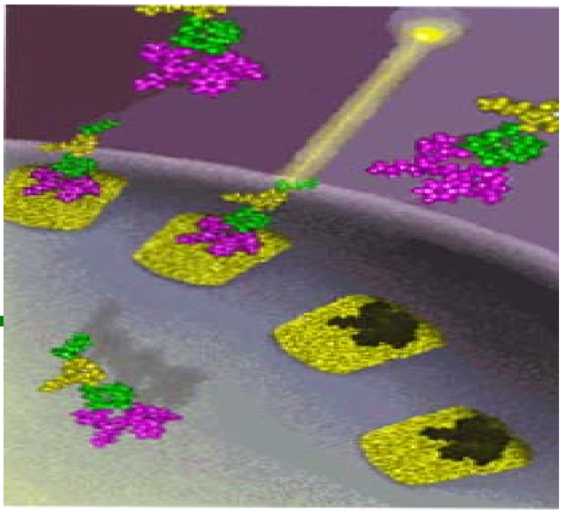
[1] Companhia Industrial de Reciclagem

[2] Inorganic and Organometallic Chemistry

[3] Grantees (Sociedade Ponto Verde)

Inorganic and Radiopharmaceutical Chemistry



Inorganic and Radiopharmaceutical Chemistry

Isabel Santos

The development of specific radiolabelled compounds for diagnostic and therapy became a hot topic. This research area involves the synthesis and characterization of specific radioactive compounds for application in Nuclear Medicine, strongly interested on cancer and on Central Nervous System (CNS) diseases, such as Alzheimer and Parkinson. The development of such drugs implies the labelling of receptor targeting molecules with different radionuclides, using strategies which depend on the nature of the radionuclide. In any case, the pharmacokinetic of such drugs have to be adequate to their application and the biological activity of the targeting molecules has to be preserved.

The Inorganic and Radiopharmaceutical Chemistry (IRC) Group is involved on this subject and the efforts are centered on metal-*d* an *f*-specific radiopharmaceuticals, as well as on halogen-based specific drugs. The ITN, namely the IRC, is the only place in the country which combines expertise and facilities for the synthesis and characterization of organic and inorganic inactive compounds with expertise and facilities for the synthesis, characterization and biodistribution studies of the analogous radioactive compounds (DGS-249/01). The IRC group also profits from the existence in the campus of the Portuguese Nuclear Reactor (RPI), where radionuclides interesting for therapy, namely lanthanides, can be produced. In the group there are also conditions for preparing lyophilized kit formulations under inert, sterile and apyrogenic conditions. To provide these expertise and facilities to National and International Universities, Research Institutes and Companies has been one of the main goals.

During 2001, at the National and International level, close links have been established with other research groups to whom the IRC group has offered its own knowledge. Those groups provided expertise on targeting, synthesis of chemopreventive and chemotherapeutic agents, binding affinity measurements, protonation and stability constants determinations. These achievements are confirmed by five joined research projects funded by FCT, by one bilateral cooperation through ICCTI/DAAD, by our active participation in COST ACTION B12 (Development of New Radiotracers for the *in vivo* Assessment of Biological Functions and Drug Interactions) and in COST ACTION D18 (Lanthanides for Therapy). Some of our facilities have also been useful for International Companies.

The IRC expertise on chemistry, radiochemistry and radiopharmacy has also been successfully used for training new scientists funded by FCT grants: undergraduated, BIC, PhD and Post-Doctoral students. We have also teached Radiopharmacy, January-June, in the Technical Nuclear Medicine Course, at the Escola Superior de Tecnologias da Saúde de Lisboa (ESTeSL). Fifteen students of this course (two weeks each) have been trained in our laboratories. Lectures have been given at the Faculdade de Farmácia of Lisbon and at the Course "Production and Medical Use of Radiopharmaceuticals", in Coimbra. At the International level the IRC participates in the European Radiopharmacy Course, INSTN, and is one of the three users participating in the European Community Shared COST RTD ACTION, submitted in 2001 and approved to start in January 2002.

In the search for novel specific ^{99m}Tc-CNS agents we pursued exploring new building blocks based on poly(mercaptoimidazolyl)borates and containing the moiety $[M(CO)_3]^+$ (M=Re, ^{99m}Tc). Stability studies have been performed and the labelling of a selective antagonist of $5HT_{1A}$ subtype serotonergic receptor (part of WAY 100635) has been successfully achieved, using one of the several synthetic approaches. The same biomolecule was also successfully labelled with ^{99m}Tc complexes containing the fragments $[M(CO)_3]^+$ and $[M(O)]^{3+}$ and stabilized by heterofunctionalized phosphine ligands. In order to compare the different approaches, stability studies, binding affinity measurements and biodistribution studies have been performed.

In the search for novel tumor seeking metal agents suitable for diagnosis and/or therapy we pursued our efforts for synthesizing new building blocks based on Re, ^{99m}Tc and on macrocyclic lanthanide (III) complexes. Promising building blocks have been characterized for Re and Tc, and the coupling of peptides to the framework ligands is underway. For Ln, four different tetraaza-macrocyclic ligands with methylcarboxylate and methylphosphonate pendant arms have been labelled with ^{153}Sm. The best ones will be functionalised and the complexes characterized at the macroscopic level. A new benzo-[14]ane-N4 macrocycle was synthesized and the protonation constants are being measured. Concerning halogen-based drugs, we have succeeded on the synthesis of β–hydroxytamoxifen, which is a key compound for preparing inactive and radioactive halotamoxifen derivatives to be evaluated as chemotherapeutic/chemopreventive and as imaging agents, respectively.

Inorganic and Radiopharmaceutical Chemistry

Research Team

Researchers

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- P. CAMPELLO, Auxiliary Researcher
- J.D.G. CORREIA, Invited Auxiliary Researcher
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- C. XAVIER, undergraduate student
- I. PEREIRA, undergraduate student

Technicians

- A. RODRIGUES, laboratory technician
- E. CORREIA, laboratory technician

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Other Sources:	482
Total:	**29094**

Publications

Journals:	9 and 1 in press
Proceedings:	1
Conf. Communications:	14
Graduation Thesis:	1

*PhD student, since 1997, at Université de Genève, Suisse.

Labelling of CNS Receptor Ligands Based on Re and Tc Carbonyl Complexes with Poly (mercaptoimidazolyl) Borates

R. Garcia, Y.H. Xing, A. Paulo, A. Domingos[1] and I. Santos

Objectives

To apply new building blocks, based on poly(mercaptoimidazolyl)borate Re and Tc carbonyl complexes, in the labelling of CNS-receptor ligands, without altering their biological properties.

Results

The complexes [^{99m}Tc{κ^3-R(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (R = H, Me, Ph) and [^{99m}Tc{κ^3-HB(tim^{Me})$_3$}(CO)$_3$] (tim^{Me} = 1-methyl-2-mercaptoimidazole) have been prepared with high radiochemical yield (> 90%), using low ligand concentrations (10^{-4}-10^{-6}M). Their identity has been confirmed by HPLC comparison with analogous Re complexes. Being small-sized, neutral and lipophilic, these ^{99m}Tc complexes are adequate for the labelling of CNS-receptor ligands. The biomolecules can be attached to the metallic fragment in several ways, namely by direct linkage to the boron atom or through the mercaptoimidazolyl ring. Derivatization of the mercaptoimidazolyl rings with (2-methoxyphenyl)piperazine moieties (part of WAY 100635, a selective antagonist of 5-HT$_{1A}$ sub-type serotonergic receptor) has been investigated, and symmetric and assymetric poly (mercaptoimidazolyl) borates have been synthesized. These functionalized ligands have been labelled with ^{99m}Tc, by reaction with the precursor [^{99m}Tc(CO)$_3$(H$_2$O)$_3$]$^+$, with high specific activity and with high radiochemical purity. The identity of the resulting ^{99m}Tc tricarbonyl complexes has been confirmed by HPLC comparison with analogous Re complexes, which were fully characterized including by X-ray diffraction analysis (Figure 1). The butterfly shaped symmetric functionalized complexes can be useful in the so-called *"bivalent approach"* which, as recently reported, can enhance the selectivity and affinity of the ligands to the putative receptors.

The biodistribution of the novel building blocks and of the functionalized complexes (^{99m}Tc) is under evaluation. The binding affinity of the functionalized complexes (Re) to 5-HT$_{1A}$ receptors will be measured. These studies are expected to allow the establishement of adequate strategies for the further modification of the functionalized complexes, having in mind the optimization of their biological properties.

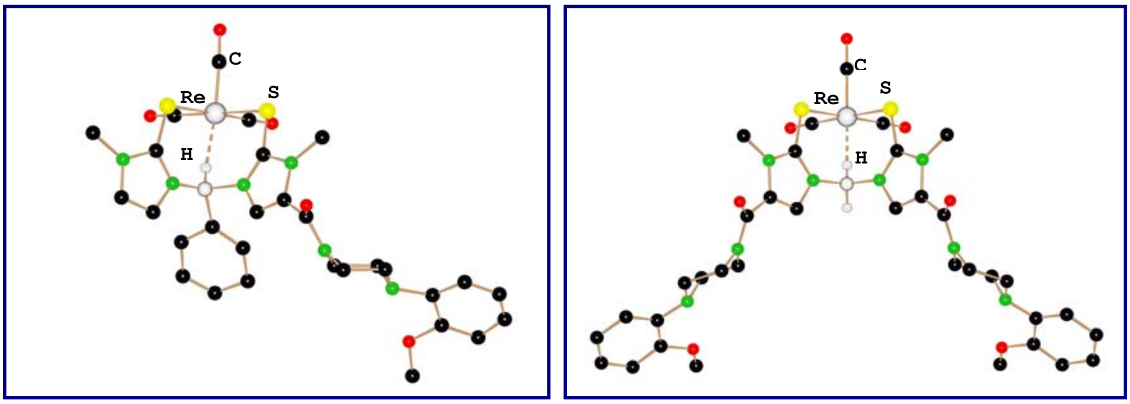

Fig. 1 - Molecular structures of assymetric and symmetric Re tricarbonyl complexes

Published, accepted or in press work

1. R. Garcia, A. Paulo, A. Domingos, I. Santos, Rhenium(I) organometallic complexes with novel bis(mercaptoimidazolyl)borates and with hydrotris(mercaptoimidazolyl)borate: chemical and structural studies, *J. Organomet. Chem.* 632 (2001) 41.
2. R. Garcia, A. Paulo, A. Domingos, I. Santos, R. Alberto, New organometallic labelling tools based on tripodal sulfur donor ligands, *The Tenth European Symposium on Radiopharmacy & Radiopharmaceuticals, Granada, Spain,* 2001, poster
3. R. Garcia, Y.H. Xing, A. Paulo, A. Domingos, I. Santos, Organometallic Re and Tc complexes for the labelling of biomolecules, *V Conferência de Química Inorgânica da SPQ, Monte Real, Portugal, 2001,* poster.

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[1] Inorganic and Organometallic Chemistry Group, ITN.

Labelling of $5HT_{1A}$ Receptor-Binding Ligands Using Heterofunctionalized Phosphines with PNO, PNN and PNS Donor Atom Sets

J.D.G. Correia, C. Fernandes, Â. Domingos,[1] I. Santos, R. Alberto,[2] A. Drews,[3] S. Seifert,[3] H. Spies[3] and R. Syhre[3]

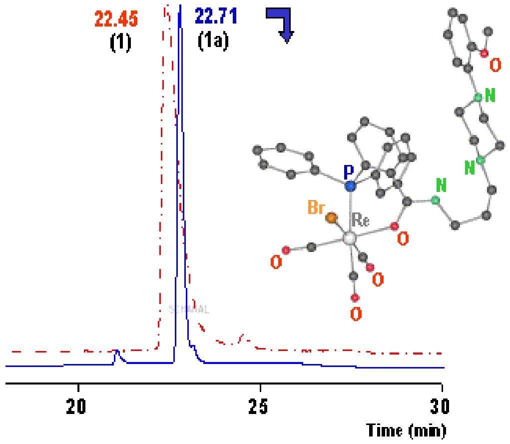
Objectives

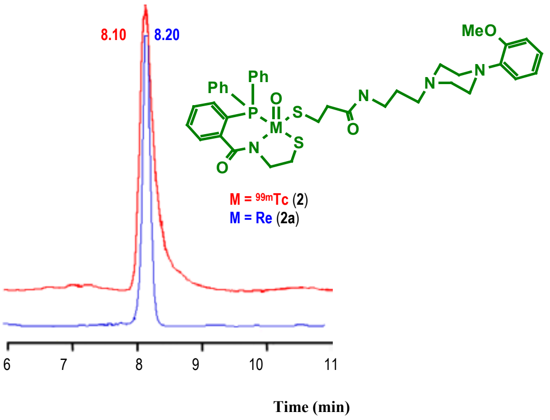
Labelling of CNS receptor ligands (antagonists of the $5HT_{1A}$ sub-class of serotonergic receptors) with ^{99m}Tc complexes containing the moieties *fac*-$[M(CO_3)]^+$ and $[M(O)]^{3+}$, and stabilized by heterofunctionalized phosphines

Results

1. ***Organometallic Approach***: Reaction of the *fac*-$[M(CO_3)]^+$ moiety with N-[4-(3-Aminopropyl)-1-(2-methoxyphenyl)piperazine]-2-(diphenyl-phosphanyl)-benzamide (**HPN-Pip**) yielded the stable complexes $[^{99m}Tc(\kappa^2\text{-HPN-Pip})X(CO)_3]$ (**1**) and $[Re(\kappa^2\text{-HPN-Pip})Br(CO)_3]$ (**1a**). Complex **1**, which is stable for 24h at 37ºC in PBS, was obtained in high radiochemical yield (94,5%), and its identity was accomplished by comparing its radioactive HPLC profile with the UV/Vis HPLC profile of the Re surrogate **1a**. No significant loss of biological selectivity and affinity was found (IC_{50} for the $5HT_{1A}$ receptor: 20±0.1nM; Competitor $5HT_{2A}$: 4680±51nM).

2. ***[3+1] Approach***: The mixed-ligand oxo complexes $[^{99m}Tc(O)(\kappa^3\text{-PNS})(\kappa^1\text{-SPipOMe})]$ **2** and $[Re(O)(\kappa^3\text{-PNS})(\kappa^1\text{-SPipOMe})]$ **2a** were prepared using the heterofunctionalized phosphine 2-(diphenyl-phosphanyl)-*N*-(2-thioethyl)benzamide (**H_2PNS**) as tridentate ligand and the receptor-binding ligand *N*-[4-(3-aminopropyl)-1-(2-methoxyphenyl)piperazine]-*N*-[(3-thio)propiamide] (**HSPipOMe**) as coligand. Complex **2** was obtained in high radiochemical yield (90%) and is stable in saline solution, in PBS and against 1mM glutathione solution (37ºC). However, comparing this approach with the organometallic one, a considerable loss of biological activity was observed for compound **2** (IC_{50} for the $5HT_{1A}$ receptor: 120±1.1nM; Competitor $5HT_{2A}$: 860±51nM).





Published, accepted or in press work

1. J.D.G. Correia, Â. Domingos, I. Santos, H. Spies, Synthesis and characterization of mixed-ligand oxorhenium(V) complexes with new [(PNO/S)(S)] donor atom sets, *J. Chem. Soc., Dalton Trans.*, (2001) 2245.
2. J.D.G. Correia, Â. Domingos, I. Santos, C. Bolzati, F. Refosco, F. Tisato, Synthesis and structural analysis of mono-oxo Re(V) complexes with phosphino-carboxylato ligands, *Inorg. Chim. Acta*, **315** (2001) 213.
3. J.D.G. Correia, Â. Domingos, I. Santos, R. Alberto, K. Ortner, Re Tricarbonyl complexes with ligands containing P,N,N and P,N,O donor atom sets: synthesis and structural characterization, *Inorg. Chem.*, **40** (2001) 5147.
4. J.D.G. Correia, I. Santos, R. Alberto, K. Ortner, H. Spies, A. Drews, Heterofunctionalized phosphines as anchor groups for coupling biomolecules to the fac-[M(CO)3]+ (M = Re, Tc) moiety, *J. Labelled Cpd. Radiopharm*, **44** (2001) 507.
5. C. Fernandes, J.D.G Correia, L. Gano, I. Santos, S. Seifert, R. Syhre, H. Spies. Tc Oxocomplexes with the PNO/S and PNS/S donor atom sets: labelling of a 5HT1A receptor-binding ligand, *J. Labelled Cpd. Radiopharm*, **44** (2001) 518.

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[1] Inorganic and Organometallic Group, ITN.
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[3] Institute of Bioinorganic & Radiopharmaceutical Chemistry, FZ-Rossendorf, Germany

Hydroxyl Silylated Re and ^{99m}Tc "3+1" Mixed Ligand Complexes

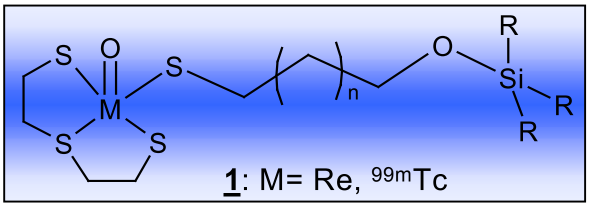
T. Kniess, J.D.G. Correia, C. Fernandes, H. Spies[1] and I. Santos

Objectives

A promising way to increase the lipophilicity of organic compounds is the introduction of silyl groups. It is expected that silylation of biological active molecules would facilitate their transportation in the organism.

Results

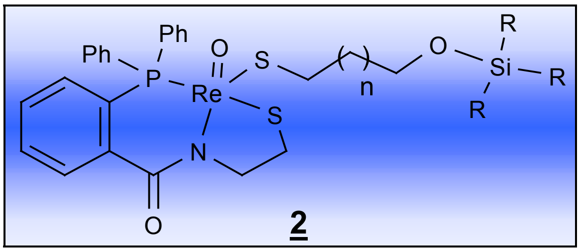
The main goal of this work was the preparation of silylated mixed ligand complexes of the "3+1" type. Using 3-thiapentane-1,5-dithiol (HSSH) as tridentate, compounds of the structure **1** were obtained. The silylated monodenate ligands were synthesised by reacting mercaptoalcohols with trimethyl-, triethyl- and triphenyl-chlorosilane respectively. By using imidazole as catalyst only O-silylation occurred.



1: M= Re, ^{99m}Tc

The precursor chloro(3-thiapentane-1,5-dithiolato)-oxorhenium(V) served as starting material for the Re complexes **1**, that were obtained in 71-80 % yield.
The ^{99m}Tc complexes **1** were prepared via ^{99m}Tc gluconate in aqueous solution. The pH had to be adjusted at about 7 with a phosphate buffer to avoid hydrolysis. The ^{99m}Tc complexes were detected by HPLC at retention times corresponding to the Re compounds. For the triphenyl- and triethyl-silylated ^{99m}Tc complexes labelling yields between 80 and 90 % were found, in any case no hydrolysed products were formed. For the trimethyl-silylated ligands all efforts of labelling were unsuccessful. The trimethylsilyl group was found to be unstable for labelling in aqueous conditions.

The new silylated mixed-ligand Re complexes **2** with the tridentate 2-(diphenyl-phosphanyl)-N-(2-thioethyl)-benzamide (PNS) were synthesised in a one pot procedure by reacting the monodentate silylated ligand, the PNS and the rhenium precursor $[NBu_4][ReOCl_4]$ in equimolar amounts.



2

The products were purified by column chromatography, after lyophilization were grey-green solids obtained in 19-38 % yield. One reason for the relative low yields is the formation of a concurrence product, where the PNS itself reacts as monodentate ligand. This mixed ligand complex with the structure $[ReO(\kappa^3\text{-PNS})(\kappa^1\text{-PNS})]$ was already described.
All Re complexes were full characterised by ^{1}H and ^{31}P MNR spectroscopy and elemental analysis. The ^{1}H NMR spectra of **2** presents four multiplets for the methylenic protons of the chelate, indicating that these protons became diastereotopic after complexation to the metallic center. The signal of the phosphorous shifted in the complex to a value about +20 ppm, comparing to -9 ppm in the free ligand.
Further work to prepare silylated ^{99m}Tc complexes with the PNS ligand is under progress.

Published, accepted or in press work

1. T. Kniess, H. Spies, I. Santos, A. Zablotska, Synthesis of Hydroxyl Silylated Re and ^{99m}Tc "3+1" Mixed Ligand Complexes., *J. Labelled Comp. Radiopharmaceuticals*, in press.

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[1] Institute of Bioinorganic & Radiopharmaceutical Chemistry, FZ-Rossendorf, Germany

New Re and Tc Carbonyl Building Blocks for Labelling Peptides

S. Alves, Â. Domingos,[1] A. Paulo, J. D. G. Correia and I. Santos

Objectives

To find novel chelator systems suitable for preparing hydrophilic building blocks containing the moiety $[M(CO)_3]^+$ (M=Re, ^{99m}Tc), and adequate for labelling peptides, without changing their biological properties.

Results

Several potentially tridentate ligands containing nitrogen and sulphur donor atoms have been synthesized and fully characterized. The capability of these ligands to stabilize the moiety $[M(CO)_3]^+$ has been tested, using different reaction conditions (Figure 1).

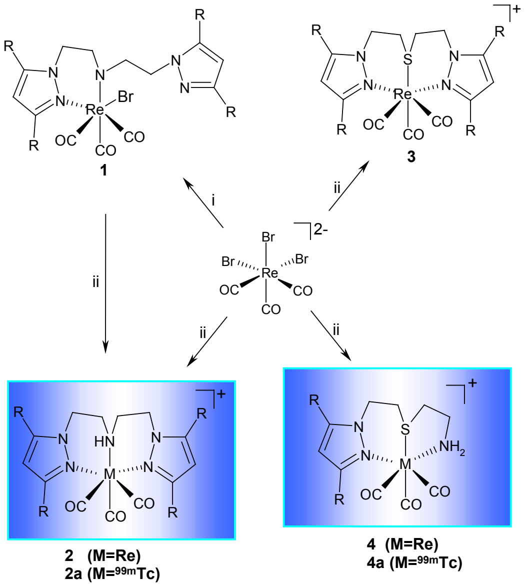
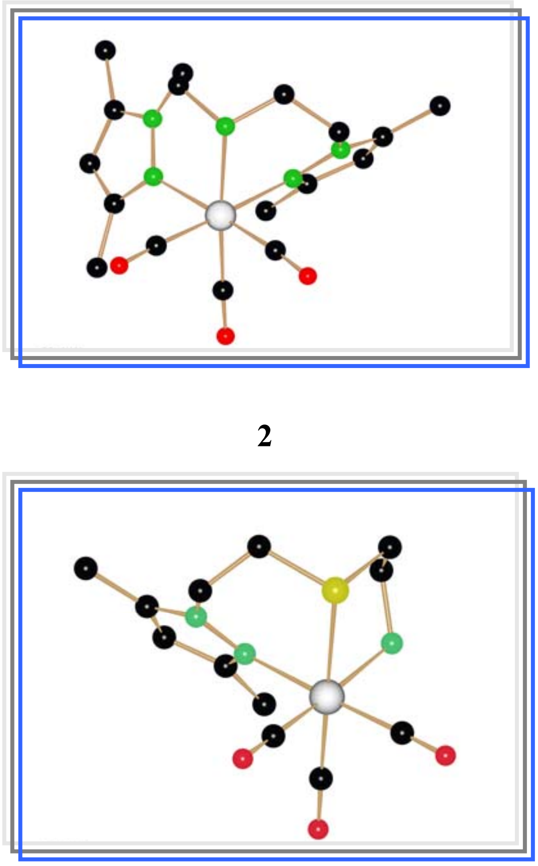


Figure 1 Syntheses of complexes **1-4**: i) MeOH, r.t., 60min; ii) MeOH, reflux, 60 min.

The coordination mode of the ligands, as well as the charge of the compounds have been established by ^{1}H NMR spectroscopy and by X-ray diffraction analysis (Figure 2).

The $[^{99m}Tc(CO)_3(k^3\text{-pzNHpz})]^+$ (**2a**) and $[^{99m}Tc(CO)_3(k^3\text{-pzSNH}_2)]^+$ (**4a**) complexes have been prepared in high yield and with high radiochemical purity, using low concentration of ligands. The identity of the resulting ^{99m}Tc tricarbonyl complexes has been confirmed by HPLC comparison with the analogous Re complexes (Figure 2).



2

4

Figure 2 Molecular structures of $[Re(CO)_3(\kappa^3\text{-pzNHpz})]^+$ (**2**) and $[Re(CO)_3(\kappa^3\text{-pzSNH}_2)]^+$ (**4**)

The nature of these building blocks might open the way to new classes of radiopharmaceuticals, as required for *i.e.* ^{99m}Tc labelled peptides. The targeting molecules, namely peptides, can be coupled to the framework ligand either through the pyrazolyl group or by direct attachement to the primary or secondary amines. Different strategies are being evaluated in the derivatization of the ligands in order to maintain the stability of the compounds as well as the affinity of the peptides for the corresponding receptors.

Published, accepted or in press work

1. L. Gano, S. Alves, A. Domingos, Labelling of proteins and peptides with ^{99m}Tc, *in the Course Production and Use of Radiopharmaceuticals*, Coimbra, 2001, invited.

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[1] Inorganic and Organometallic Chemistry Group, ITN.

Re and Tc Oxocomplexes with SSS/S Donor Atom Sets for Labelling Peptides Using a Derivatised Thioimidazolyl Molecule as Co-ligand

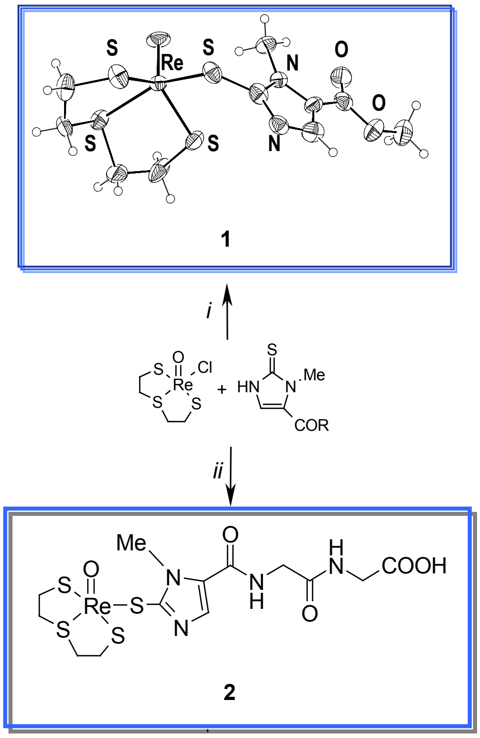
E. Palma, J.D.G. Correia, Â. Domingos,[1] L. Gano, I. Santos

Objectives

Syntheses of Re and Tc [3+2] mixed-ligand oxo complexes, in order to overcome the instability in biological systems of the [3+1] oxocomplexes. The potentially bidentate ligand was a functionalized thioimidazolyl.

Results

By reacting [ReO(SSS)Cl] with methyl(2-mercapto–3-methylimidazol-4-yl)methanoate (**Simz**) or with glycilglycine(2-mercapto-3-methylimidazol-4-yl)methanamide (**SimzCOGlyGly**) the complexes [Re(O)(κ^3-SSS)(κ^1-Simz)] (**1**) and [Re(O)(κ^3–SSS)(κ^1–SimzCOGlyGly)] (**2**) were isolated in good yield, and fully characterized (Scheme 1).

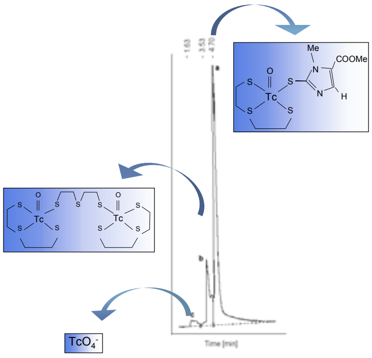


Scheme 1. Syntheses of complexes **1** and **2**: i) CH_2Cl_2/reflux/NEt_3; ii) CH_3CN/reflux/NEt_3.

Published, accepted or in press work

1. E. Palma, J. D. G. Correia, Â. Domingos, I Santos, *V Conferência de Química Inorgânica da SPQ, Monte Real, Portugal, 2001,* poster.

As observed by X-ray structural analysis the functionalized thioimidazolyl coordinates κ^1. The synthesis of the analogous ^{99m}Tc complexes, **1a** and **2a,** was also studied in order to evaluate their stability. The complexes **1a** and **2a**, where obtained in relatively high yield, although with some radiochemical impurities (Scheme 2).



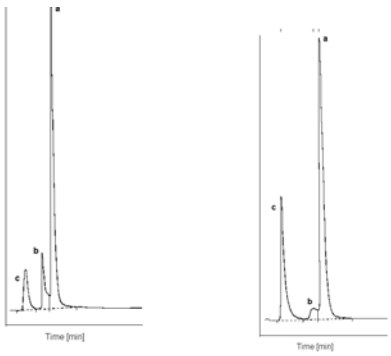
Scheme 2. HPLC (γ -detection) of **1a**.

Stability studies in saline at 37º C revealed that **1a** is stable for at least 1 h, and that after 4h only [$^{99m}TcO_4$]$^-$ is present as an impurity. Further stability and biological studies are underway. Preliminary labelling studies with **SimzCOGlyGly** are also underway.

STABILITY STUDIES

1 hour

4 hours



2. J.D.G. Correia, Re(V) and Tc(V) Mixed-Ligand Oxocomplexes with New [(PNO/S)(S)] Donor Atom Sets for Labeling CNS Receptor Ligands, V Conferência de Química Inorgânica da SPQ, Monte Real, Portugal, 2001, Invited.

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[1] Inorganic and Organometallic Chemistry Group,

Lanthanide Macrocyclic Complexes: Chemical and Radiochemical Studies

M. P. C. Campello, P. Antunes,[1] L. Gano, F. Marques, P. Bacalhau,[1] R. Delgado,[1] I. Santos

Objectives

Find novel tumor seeking agents based on lanthanide macrocyclic complexes.

Results

Four different tetraaza-macrocyclic ligands ([12]ane-N_4, [13]ane-N_4 and [14]ane-N_4), containing methylcarboxylate and methylphosphonate pendant arms have been studied with ^{153}Sm.
After irradiation of natural samarium in the form of $Sm(NO_3)_2$, using the available conditions at the RPI, several ^{153}Sm complexes were prepared using a molar ratio 1:2 (M:L) at pH 6. Radiolabelling yields and *in vitro* stability were determined by ITLC. Labelling efficiencies varying between 70% and 100% were found (Figure 1). The highest and lowest yields were obtained with the macrocycle ligands [12]ane-N_4 containing methylcarboxylate pendant arms and [14]ane-N_4 with methylphosphonate pendant arms, respectively.
The *in vitro* stability of the different ^{153}Sm complexes, at 37º C in physiological conditions, an important requirement for its *in vivo* application, depends on the nature of the macrocyclic ligand. While the complex with the [12]ane-N_4 methylcarboxylate ligand is quite stable, for at least a week in different physiological media, the rate of dissociation increases in physiologic acid medium for the complex containing the methylphosphonate pendant arms. Stability constants and chemical characterization of some of these complexes are underway.

A new benzo-[14]ane-N_4 macrocycle ligand was prepared in order to evaluate its influence on the radiochemical and biological behaviour of the lanthanide complexes. The protonation constants of this benzo-[14]ane-N_4 ligand ($K_i^H=[K_iL]/[H_{i-1}L][H]$) has been calculated by fitting the potentiometric data using the HYPERQUAD program. The values obtained are being confirmed by NMR measurements. After the introduction of pendant arms the stability constants of the complexes formed with different trivalent lanthanide metal ions will be determined. The *in vitro* and *in vivo* behaviour of the more promising radiolanthanide complexes will be also evaluated.

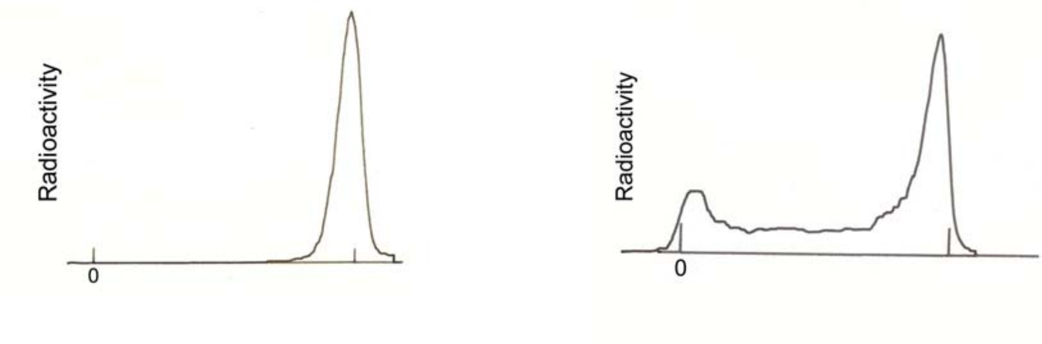

Figure 1. Radiochromatograms of ^{153}Sm complexes.

Published, accepted or in press work

1. P. Antunes, P. Campello, R. Delgado, I. Santos, Lanthanide Complexes of Functionalized Benzotetraaza Macrocycles, *6Th FIGIPS Meeting in Inorganic Chemistry, Barcelona, Spain, 15-20 July*, (2001).
2. P. Bacalhau, Ligandos Macrocíclicos para Aplicações à Medicina: Síntese e Estudos de Alguns dos seus Complexos, *Graduated Thesis,* Setembro, 2001, Faculdade de Ciências e Tecnologia, Universidade do Algarve.

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[1] Instituto de Tecnologia Química e Biológica, Univ.Nova de Lisboa, Oeiras, Portugal

Evaluation of the Genotoxic and Antiestrogenic Potential of Triphenylethylene Derivatives and their Metabolites

M.C. Melo e Silva, M.M. Marques[1], G.G. Costa[1], P.C. Pereira[1]

Objectives

The aim of the present study is the synthesis and evaluation of β-halogenated triphenylethylene derivatives as potentially safer alternatives to tamoxifen, a chemotherapeutic and chemopreventive agent for breast cancer, which has some genotoxic properties.

Results

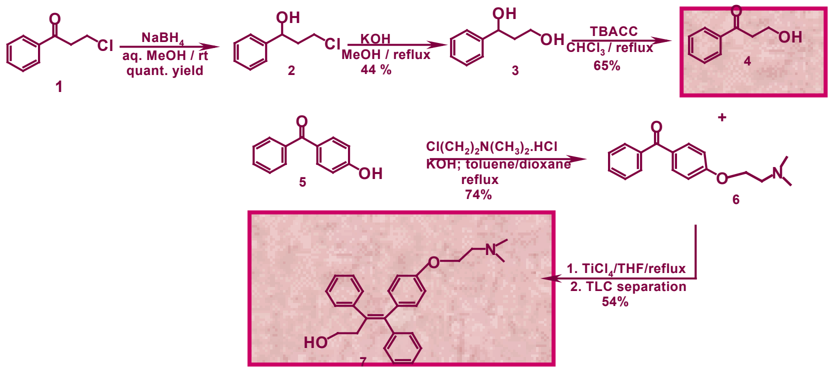
We have explored a synthetic approach to these tamoxifen analogues, involving the crossed reductive coupling of a 4-substituted benzophenone **(6)** with 3-hydroxypropiophenone **(4)** by way of a McMurry reaction, to yield a mixture of diastereomeric E and Z derivatives which can be separated by chromatographic techniques to afford the biologically interesting Z-compound, β-hydroxytamoxifen **(7)**.

4-(2-Dimethylaminoethoxy) benzophenone **(6)** was prepared by alkylation of 4-hydroxybenzophenone **(5)** with 2-dimethylaminoethoxychloride hydrochloride.

3-Hydroxypropiophenone was prepared using 3-chloropropiophenone **(1)** as the starting reagent. Due to the difficulties found in the direct hydrolysis of **1** to **4,** 3-chloropropiophenone **(1)** was previously reduced to the corresponding alcohol **(2)** using $NaBH_4$ as the reductive reagent. The alcohol **(2)** was hydrolysed in alkaline medium to the diol **(3),** which was then oxidised to 3-hydroxypropiophenone **(4)** with previously prepared tetrabutylammonium chlorochromate (TBACC). All the compounds were characterised by NMR. Attempts to prepare **4** directly from **1** are currently being undertaken.

Reversed-phase high performance chromatography provided a very useful method for monitoring the synthesis of **4** from its precursors, as well as the McMurry reaction. The same technique has allowed a suitable control of the separation of **7** from its *E* diastereomer.

Since halogenated triphenylethylene derivatives are suited for radiolabelling, β-hydroxytamoxifen **(7)** will be subsequently halogenated by standard procedures to the corresponding β-halotamoxifen derivatives (e.g. Br, I, F). The potential use of these tamoxifen derivatives as imaging agents for breast cancer will be evaluated by their *in vitro* binding affinities for the estrogen receptor, as well as the *in vivo* tissue uptake of the radioiodinated compound (e.g. ^{125}I) in the target tissues of immature female rats.



Scheme 1. Synthesis of *Z*-β-hydroxytoremifen

Published, accepted or in press work

1. M.C. Melo e Silva, G.G. da Costa, M.M. Marques, Studies Towards the Synthesis of β-Halo Tamoxifen Derivatives", 4º Encontro Nacional de Química Orgânica, 26-28 de Setembro de 2001, Coimbra (poster).
2. P.C. Pereira, M. C. Melo e Silva, G.G. da Costa, M.M. Marques, A New Synthetic Approach to β-Halo-α-Hydroxytamoxifen 4º Encontro Nacional de Química Orgânica, 26-28 de Setembro de 2001, Coimbra (poster).
3. M.C. Melo e Silva, G.G. da Costa, M.M. Marques, HPLC monitoring of the synthesis and purification of β-functionalized tamoxifen derivatives". 2º Encontro Nacional de Cromatografia, 10-12 de Dezembro de 2001, Lisboa (oral).

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[1] Centro de Química Estrutural, Complexo I, IST, Lisboa, Portugal

Uranium (III) Compounds with Boron Containing Ligands

L. Maria, A. Domingos[1] , I. Santos

Objectives

To study the chemistry of uranium (III) with boron containing ligands. To evaluate the effect of the electronic and steric properties of these ligands on the structure of the complexes.

Results

Using dihydrobis(thioimidazolyl)borates, of the type $[H(R)B(tim^{Me})_2]M$ (R=H, Ph), neutral and cationic complexes of U(III) have been isolated and fully characterized: $[UI\{\kappa^3\text{-}H(R)B(tim^{Me})_2\}_2(THF)_2]$ (R=H, **1;** R=Ph**, 2**), $[U\{\kappa^3\text{-}H(R)B(tim^{Me})_2\}_2(THF)_3]^+$ (R=H, **3;** R=Ph**, 4**) As can be seen in Figure 1, in both compounds the metal center is nine coordinated, and the two dihydrobis(thioimidazolyl)borates act as tridentate through the two thione sulfurs and one agostic hydrogen. The nature of compounds **1-4** is completely different from what was obtained with the analogous dihydrobis(pyrazolyl)borates. In this case only more sterically hindered neutral compounds could be stabilized: $[U\{\kappa^3\text{-}H(H)B(3,5\text{-}Me_2pz)_2\}_3]$. In order to prepare less substituted complexes with poly(pyrazolyl)borates we were forced to use either bulkier substituents on the 3-position of the pyrazol rings or ligands of the type hydrotris(pyrazolyl)borates. Examples are the new complexes synthesized and fully characterized: $[UI_2\{\kappa^3\text{-}H_2B(3^tBu,5Me\text{-}pz)_2\}(THF)_2]$, $[UI_2\{\kappa^3\text{-}HB(3,5\text{-}{}^iPr_2pz)_3\}(THF)_2]$, or $[UI\{\kappa^3\text{-}H_2B(3^tBu,5\text{-}Mepz)(3,5\text{-}Me_2pz)\}_2]$. During this year, the chemistry of $[UI_2\{\kappa^3\text{-}HB(3,5\text{-}iPr_2pz)_3\}(THF)_2]$ has also been explored and the new compounds $[UI_2\{\kappa^3\text{-}HB(3,5\text{-}{}^{iPr2}pz)_3\}(bipy)]$ (**5**), $[UI_2\{\kappa^3\text{-}HB(3,5\text{-}iPr_2pz)_3\}(dme)]$ (**6**) and $[UI_2\{\kappa^3\text{-}HB(3,5\text{-}iPr_2pz)_3\}(3^tBu,5MepzH)_2]$ (**7**) were isolated and characterized by NMR, infrared spectroscopy and elemental analysis.

The co-ordinated THF in the complexes $[U\{\kappa^3\text{-}H(R)B(tim^{Me})_2\}_2(THF)_3][BPh_4]$ (R=H (**3**), R=Ph (**4**)) were also easily replaced by neutral coordinating molecules, such as C_5H_5N or CH_3CN. The compounds $[U\{\kappa^3\text{-}H(R)B(tim^{Me})_2\}_2(L)_3][BPh_4]$ (R=H or R=Ph and L= C_5H_5N (**8**) ,CH_3CN (**9**)) were obtained, by stirring for a while, complexes **3** and **4** in the respective solvents. Electron transfer reactions with compounds **3** and **4** are in progress.

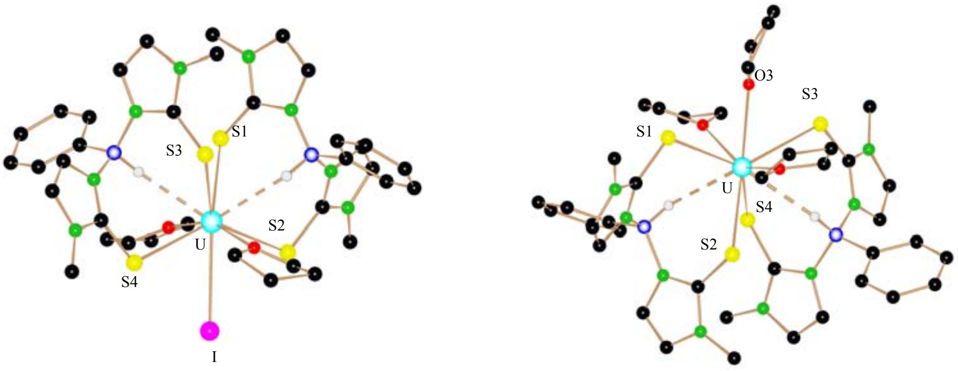

Figure 1: Molecular Structures of the complexes **2** and **4**

Published, accepted or in press work

1. J. Collin, N. Guiseppone, N. Jaber, A. Domingos, L. Maria, I. Santos, Iodo bis bistrimethylsilylamido Lanthanides, *J. Organometallic Chemistry,* **628** (2001) 271
2. L. Maria, A. Domingos, I. Santos, Unique Uranium (III) Cations Anchored by Polydentate Sulfur-Based Ligands: Synthesis and Structurre, *Inorg. Chem.,***27,** (2001) 6863.
3. L. Maria, A. Domingos, I. Santos, Synthesis and structural characterisation of bis[bis(2-mercapto-1-methylimidazolyl) hydroborato] uranium(III) cations, *6th FIGPS, Barcelona, Spain, July 2001, poster.*
4. L. Maria, A.Domingos, I. SantosS, Uranium(III) Complexes: Synthesis and Structural Characterization, V Conferência de Química Inorgânica da SPQ, Monte Real, Portugal, *April 6-7* 2001, poster.

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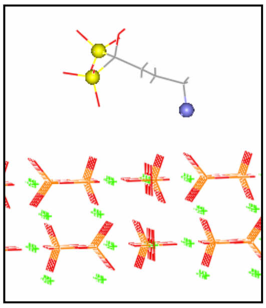
[1] Inorganic and Organometallic Chemistry Group, ITN.

Production and Application of Radioisotopes



Production and Application of Radioisotopes

Maria dos Anjos Neves

The activity of the group is the production of radioisotopes and their biomedical application in colaboration with other research national or international groups. The main goal is the production of radionuclides at the Portuguese Nuclear Reactor (RPI) and their application in the field of new radiopharmaceuticals for therapeutic purposes. Also, to colaborate with other research groups interested on R&D action involving radionuclides and potential radiopharmaceuticals.

Production and Application of Radioisotopes

Research Team

Researchers

- M.A. NEVES (ITN), Group Leader

Students

- H. RAMINHOS, (ITN-FCT grant), MSc Student,

Funding

	$\times 10^3$ PTE
Research Projects:	2600
Total:	**2600**

Publications

Journals:	2 in press
Proceedings:	2
Conf. Communications:	2

Radiopharmaceuticals for bone therapy: a molecular mechanics study

M.A. Neves, L. Gano[1], H. Raminhos, R. Fausto[2], M. Rosado[2], M.C. Costa[3], M.R. Costa[3]

The project "Radiopharmaceuticals for bone therapy: a molecular mechanics study" (PRAXIS /SAU/14036/98) ended on last 30 October. The results are described on communications and papers accepted and submitted for publication, but the main conclusion are:

- Specific interactions play a relevant role in determining the relative ability of bis phosphonates to act as anti-resorption agents.
- The nature of the bisphosphonate-metal complexes do not play a decisive role in hydroxyapatite binding and skeletal uptake, confirming what was previous by others authors.

These conclusions are very important for the design of new bisphosphonates as drugs for bone diseases and as ligands to carrier radioactive metals. Also, it is also possible to conclude that molecular modeling studies are a good approach to evaluate specific interactions between bisphosphonates and hydroxyapatite and then a suitable method to be used in the design of new bisphosphonates with increased pharmacologic activity, and in the design of new bone therapeutic radiopharmaceuticals before *in vitro* and *in vivo* studies. The project was leader by ITN with the collaboration of the Department of Chemistry – University of Coimbra (computational studies), and INETI (bisphosphonates synthesis). ITN participation was in Sm-153 production at RPI, labelling of pamidronate, alendronate and neridronate with Sm-153, radiochemical quality control and *in vitro* and *in vivo* studies. This project has guide us to the proposal of two news projects, presented to FCT: Radiation induced-apoptosis in osteoclastic cells, and Novel indazolebisphosphonates for bone mineral metabolism: synthesis, molecular modelling and pharmacological activities.

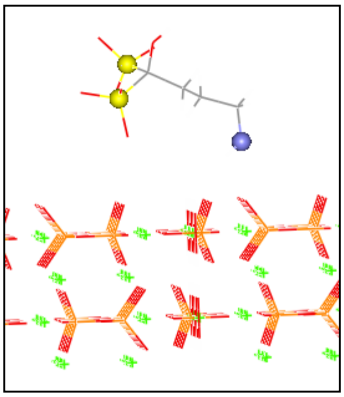


Fig. Spatial view of the minimum energy interaction of alendronate with the 001 surface of hydroxyapatite.

Published, accepted or in press work

1. M. Neves, A. Kling and R. M. Lambrecht Radionuclide production for therapeutic radiopharmaceuticals. *Applied Radiation and Isotopes* (2001). In press.

2. M. Neves, L. Gano, N. Pereira, M.R. Costa, M.C. Costa, M. Chandia, M. Rosado and R. Fausto. Synthesis, Characterization and Biodistribution of Bisphosphonates Sm-153 Complexes: Correlation with Molecular Modelling Interaction Studies. *Nuclear Medicine & Biology* (2001). In press.

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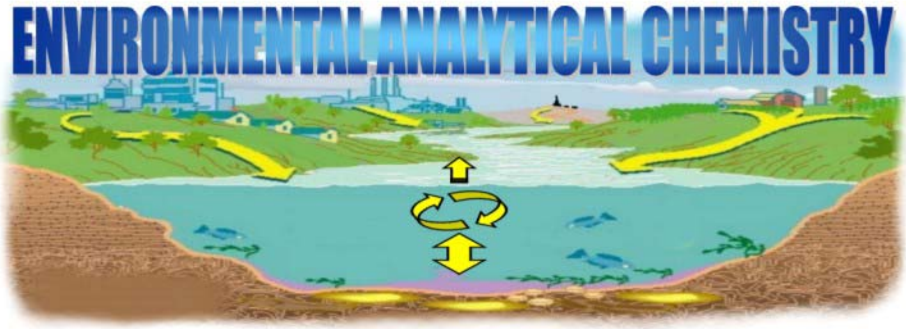
[1] Inorganic and Radiopharmaceutical Chemistry, group, ITN
[2] Chemistry Department, University of Coimbra
[3] Instituto Nacional de Engenharia e Tecnologia Industrial – INETI

Environmental Analytical Chemistry



Environmental Analytical Chemistry

Maria de Fátima Araújo

The **Environmental Analytical Chemistry** research team's main objective is the study of Biogeochemical Cycles of Chemical Elements and Light Isotopes in the Environment. 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. We collaborated with other research teams and Laboratories – the multielemental analyses and light isotopic determination were often shared with partners that contributed with geochronological and mineralogical techniques as well as elemental and ion determinations in liquid samples, primarily directed into the *Environmental and Marine Geochemistry* and *Isotope Hydrology*.

The major domains of research are studies:

1. In sediments of river basins and coastal zones, in order to understand the consequences of the modification of the sediment load carried by large rivers to estuaries and to the continental shelf, due to several anthropogenic activities. These alterations, caused by a wide range of factors, in a seasonal and temporal scale, are responsible for important environmental alterations in the coastal area. Marine organisms from coastal areas have been studied to assess their application as environmental monitors.
2. On the transfer of pollutants from soils to plants in contaminated mining areas, in order to propose remediation strategies.
3. Aiming to contribute to a better understanding of the dynamic evolution response of aquifer systems to Human influences and the climatic evolution. The national network for isotopes in precipitation provides important information for hydrological investigations, relevant for the management and development of water resources.

Another part of our research is aimed at the EDXRF non-destructive analysis of artefacts with museological and archaeological interest, in order to identify their origin, chronology and fabrication processes.

The main achievements of the research on the above mentioned areas included some projects:

1. A multidisciplinary project, "*Consequences of River Discharge Modifications on Coastal Zone and Continental Shelf - (CRIDA)"*, co-ordinated by the EAA Group leader was initialised in October 2001. By decision of The National Science Foundation this project "due to the nature of its scientific objectives" was included in the - Programa de Apoio à Reforma dos Laboratórios do Estado – PLE/8/00. This Program was established by the "resolution n° 133/97" of the Portuguese Government, which defines a set of orientations for the reinforcement and valorisation of the scientific activity in the *"State Laboratories"*. The orientations were adopted following recommendations of the International Reference Committee, which evaluated the Portuguese State Laboratories. The project is focused on the consequences caused by the changes in run-off and sediment load during the last century in the main Iberian river basins.
2. The "Aquifers as archives of palaeoclimate and indicators of future climatic scenarios – Sado/Sines system and Bairrada carsic aquifer" project began, being dedicated to the study of groundwater resources, in two different hydrogeological systems in Portugal. A Coordinated Research Program (CRP) financed by the IAEA "The Isotopic Composition of Precipitation in the Mediterranean Basin in Relation to Air Circulation Patterns and Climate" continued to be developed.
3. The upgrade of some Equipment funded by the projects and services within the group. This includes the upgrade of the Energy-Dispersive X-Ray Spectrometer (X-ray tube, detector and workstation), the SIRA10 for isotopic determinations (workstation and software) and the modification of the mass spectrometer for deuterium determinations.

These financed projects have made it possible to reinforce the research team with new positions of research, Doctoral and Post-Doctoral students.

Besides, due to the available equipment, analytical techniques and expertise within the group, technical services are provided to Universities, Institutes and Public and Private Institutions.

Environmental Analytical Chemistry

Research Team

Researchers

- M.F. ARAÚJO, Auxiliary Researcher, Group Leader
- P.M. CARREIRA, Auxiliary Researcher
- F. VITALI, Post-doctoral reasearcher

Students

- P.G. FERNANDES, PhD Student, FCT grant
- A.C. CORREDEIRA, MSc Student
- L. FERREIRA, graduate student, FCT grant
- A.C. TEIXEIRA, undergraduate student
- A.S. CONCEIÇÃO, undergraduate student
- S.A. GOMES, undergraduate student

Technicians

- P. VALÉRIO, graduate technician
- D. NUNES, graduate technician
- T. BARBOSA, graduate technician, ITN grant
- M.M. CORREIA, laboratory technician

Funding

	$\times 10^3$ PTE
Research Projects:	13792
Services:	1833
Total:	**15625**

Publications

Journals:	2 and 4 in press
Proceedings:	8 and 3 in press
Conf. Communications:	4
Int.Reports:	1
Theses:	1 MSc 3 Graduation

Environmental and Marine Geochemistry
1.a) Geochemistry of Sediments from the Northern Iberian Coastal Area

M. Fátima Araújo, C. Corredeira, T. Barbosa, P. Valério,
J.M. Jouanneau[1], A. Gouveia[2], P.M. Carreira and F. Vitali

Objectives

The work aim to contribute to the understanding of the origin, dispersal pathways and modification of the sediment load carried by the large Iberian river basins draining to the Portuguese shelf.

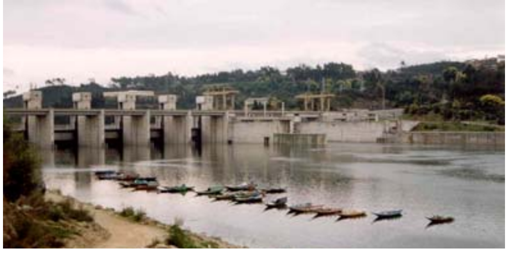


Fig. 1 – *Crestuma* dam in *Douro* river.

Results

Statistical evaluation of the shelf sediment database allows the identification of elements with similar behaviour and to distinguish different sediment types along the shelf and evaluate their origin[1]. The chemical composition of dated fine sediments could not identify any recent records of Human activities. To assess the influence of those river basins in the fine sedimentary formations, elemental distribution patterns of selected sediments collected at these formations were compared with estuarine fine sediments. Chemical composition of the clay/silt size fraction of superficial sediments collected at the main river basins draining the northern Portuguese shelf were utilised to characterise the sedimentary material that reaches the shelf. Results evidence the differences on the chemical signatures and anthropogenic influences of the studied basins[2].

Results on the lithogenic and rare earth elements of fine sediments indicate similarities between the Douro sediment composition and the Douro and Galicia sedimentary deposits. Sediment provenient from the Galician hinterland is trapped in the Galician Rías[3]. The sediments deposited on the shelf are remobilised by waves and storms. Fine-grained sediments are transported northwards of their main sediment sources by poleward flowing bottom currents[4]. They are deposited in the Douro and Galicia Mud Patches, which lie in areas that act as sediment traps. The geochemical study the fine sediments adjacent to the Rias showed that sediment deposition is dependent on continental, biogenic and geomorphological influences in the Galician continental shelf[5].

Research work will be mainly developed under the research contracts recently initiated:

1. PLE/08/00 "Consequences of River Discharge Modifications on Coastal Zone and Continental Shelf" (CRIDA). This project aim at the evaluation of the consequences caused by the changes that occurred during the last decades in the Douro, Tejo and Guadiana river basins. The main objectives are: a) determine the natural balance of rivers in pre-industrial times; b) what the consequences of alterations; and c) make suggestions concerning legislation of river basins, including estuaries and adjacent shelves and coastlines.
2. PLE/12/00 "Late Quaternary Environmental Changes from Estuarine and Continental Shelf Sediments" (ENVI-CHANGES). The objectives are the identification of the environmental changes (natural and man-induced) at the Minho and Douro estuaries and in the adjacent shelf, which have occurred during the Late Quaternary (since 18,000 BP).

Published, accepted or in press work

1. M.F. Araújo, J.M. Jouanneau, P. Valério, T. Barbosa, A. Gouveia, O. Weber, A. Oliveira, A. Rodrigues, J.M.A. Dias, Geochemical tracers of northern estuarine sediments on the shelf, *Progress in Oceanography*, (2001) In press.
2. M.F. Araújo, R. Marques, F. Rocha. Geoquímica da fracção fina de sedimentos dos rios Minho, Lima, Cávado, Ave e Douro, *VI Congresso de Geoquímica dos Países de Língua Portuguesa e XII Semana de Geoquímica*, Faro, Portugal (2001) 506.
3. C. Corredeira, M.F. Araújo, A. Gouveia, J.-M. Jouanneau. Caracterização de sedimentos finos da plataforma continenal Minho/Galiza, *VI Congresso de Geoquímica dos Países de Língua Portuguesa e XII Semana de Geoquímica*, Faro, Portugal (2001) 501.
4. J.M.A. Dias, J.-M. Jouanneau, M.F. Araújo, T. Drago, C. Garcia, R. Gonzalez, A. Oliveira, A. Rodrigues, J. Vitorino, O. Weber, Present day sedimentary processes on the Northern Iberian shelf, *Progress in Oceanography* (2001) In press.
5. C. Corredeira. Caracterização química de sedimentos finos da Plataforma Continental Minho/Galiza (2001). *MSc. Thesis in "Ecology, Management and Modeling of Marine Resources"*, IST.

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

[2] PCC group, ITN.

1.b) Selective Elemental Bio-accumulation in Marine Sponges from the Berlengas Natural Park - Western Portuguese Coast

M. Fátima Araújo, A.S. Conceição, T. Barbosa, M.T. Lopes[1] and M. Humanes[2]

Objectives

Marine sponges are sedentary and unselective filter-feeding metazoans, which are nowadys represented by more than six thousand species with the Demospongiae being the most representative, inhabiting all aquatic environments. Due to their way of feeding, by filtering large amounts of water, these benthic organisms are particularly exposed to pollutants.

This work aims at the investigation of marine sponges collected at the Berlengas Islands as environmental pollution monitors. These islands constitute a National Park with controlled access and low signal of anthropogenic influences, being a nearly ideal habitat to evaluate a possible selective bio-accumulation.

Fig. 1 - Marine sponges and *Berlengas* Islands National Park.

Results

Sediment chemical composition evidenced the existence of high Ca levels, low Si and confirmed the absence of any trace metal contamination at the region. Sponge composition showed low Si contents, even in the siliceous specimen. Certain high elemental contents determined in some species indicated a clear selective bioaccumulation of some trace elements, such as Ni, Zn and As, which is not dependent on local influences. Despite sponges demonstrate to selectively accumulate considerable amounts of particular trace metals even when their levels are considerably low in the surrounding environment. This study demonstrates that the application of marine sponges as environmental pollution indicators has to be securely controlled. In fact, to deduce whether or not the elements accumulated have an anthropogenic origin or are the consequences of a bioaccumulation of essential elements as a natural process required by these organisms for their metabolism and growth (an article was submitted in October to be published in the *X-Ray Spectrometry*).

Published, accepted or in press work

1. A.S. Conceição. Bioacumulação selectiva de elementos químicos em esponjas marinhas. *Graduation thesis in Technological Chemistry*, Universidade de Lisboa (2001) 79p.

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[1] *D.* Z. A. Faculdade de Ciências da Universidade de Lisboa, Campo Grande 1749-016 Lisboa, P-Portugal.

[2] *Dept. Chemistry* and Bioquímica. Faculdade de Ciências da Universidade de Lisboa, Campo Grande 1749-016 Lisboa, P-Portugal.

1.c) Study of Dispersal Pathways and Transfer of Pollutants from Soils to Plants in Contaminated Mining Areas

Mining activities are ancient in Portugal, developed at least, since the Roman occupation. Generally, the ore is extracted in deep mines and its processing produces large amounts of waste rock and tailings, which contain chemicals and residues, characterised by high concentrations on heavy metals. The erosion of the spoil heaps by wind and water results in permanent pollution of the surrounding terrestrial and aquatic ecosystems. This leads to the emergence of large areas, where the soils are highly enriched in toxic elements, with low pH and poor nutritional conditions, causing the scarcity of vegetation.

A potential solution for this problem is the use of plants, usually as a part of reclamation programs, with flora resistant to these extreme conditions.

I. Elemental Uptake and Root-leaves Transfer in *Cistus ladanifer* L. Growing in a Contaminated Pyrite Mining Area (Aljustrel-Portugal)

P.M. Alvarenga[1], M. Fátima Araújo and J.A. Silva[2]

Objectives

Soils at the contaminated Aljustrel mining area, situated at SW Portugal in the Iberian Pyrite Belt and *Cistus ladanifer L.*, an autochthonal aromatic bush, were investigated to quantify the most relevant elements present in soils and in the plant, and to evaluate the possibility of phytoremediation of that area, particularly concerning the elements of higher pollutant potential.

Fig. 1 – Contaminated mining area in *Aljustrel*.

Results

Our results suggest that the C. ladanifer has developed selectivity in metal uptake and translocation. Although the soil presented a highly heterogeneous metal composition, the plant largely succeeds in preventing the metals in excess in the soil (Cu, Zn and Pb) from reaching toxic levels in the leaves. On the other hand, they allow the essential metals (Mn, Zn and to a certain extent Cu) to be captured in sufficient amounts. This provides indication of the C. ladanifer capacity to resist in unfavourable soil conditions, highly enriched in toxic elements[1] (an article was sumitted to be published in *The Science of the Total Environment*).

Published, accepted or in press work

1. P.M. Alvarenga, M.F. Araújo, J. Silva. Avaliação da possibilidade de utilização da Esteva (*Cistus ladanifer L.)* numa estratégia de fitorremediação na zona mineira de Aljustrel, *Congresso Internacional Sobre Património Geológico e Mineiro*, Beja, Portugal (2001) 129.

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[1] Escola Superior Agrária de Beja, Rua Pedro Soares, 7800-295 Beja, Portugal.

[2] Centro de Química Estrutural, I.S.T., Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.

II. Dispersal Pathways of Contaminants and Transfer to Plants System in the *Urgeiriça* Uranium Mill Tailings

M. F. Araújo, T. Barbosa, M.J. Madruga[1] and I. Faria[1]

Objectives

Contaminants such as radionuclides, heavy metals and organic pollutants that come from wastes and subproducts of the chemical processing in uranium mining and milling are a motive of concern since they contaminate the environment.

The chemical characterization of soils/wastes and plants growing along the different dams, locate in this mining region were investigated to evaluate the dispersal pathways and transfer of heavy metals to the plants. Plant and superficial soil samples were collected in 5 dams in the Urgeiriça mine area. Aerial parts (leaves) were collected in autochthonal shrubs (*Cytisus sp.*) and in plants utilised to revegeteted the taillings: pines (*Pinus pinea*) and eucalyptus (*Eucalyptus globolus*).

Results

Results have shown significant levels of contamination on soils from the oldest dams particularly in Cr, Cu, Zn, Pb and U. Downcore distribution of elements in soils reveals high variations on the chemical composition, due to the heterogeneity of the deposited wastes. Plants studied have developed different selective metal uptake. They behave as accumulators for Mn - an essential element; indicators/excluders for Zn, *Cytisus sp.* is accumulator and *Pinus pinea* and *Eucalyptus globolus* are indicator/excluder. All species behave as excluders for Pb and U.

Published, accepted or in press work

1. M.F. Araújo, T. Barbosa, M.J. Madruga, I. Faria. Dispersão de contaminantes e sua transferência no sistema solo/planta nas escombreiras da mina de urânio da Urgeiriça. Congresso Internacional sobre Património Geológico e Mineiro, Beja, (2001) 131.

Fig. 2 – Contaminated mining area in *São Domingos*.

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[1] DPSRN, ITN.

2. Isotope Hydrology

2.a) Aquifers as Archives of Paleoclimate and Indicators of Future Climatic Scenarios. Sado-Sines System and Bairrada Carsic Aquifer

P.M. Carreira, P.A. Fernandes, M.O. Silva[1], D. Nunes and M.A. Marques da Silva[2]

Objectives

Groundwater management and protection is nowadays a major problem and modelling techniques are fundamental for a proper use of these natural resources.

Through an isotopic and physical chemical characterization of groundwater samples from the Sado-Sines System, we intend to model a dynamic evolution response in time of the system since the Late Glacial maximum (Pliocene) to present apparent groundwater flow velocities are giving information about the aquifer response to the sea level changes and reflected in the chemical composition evolution of the groundwater.

The isotope data obtained in the groundwater samples from the shallow and deep system enable a reconstruction of the hydrodynamic response of the system to dramatic changes of climate.

Results

The stable isotope (^{2}H and ^{18}O) contents are being used in the identification of the salts contamination sources in groundwater (sea water intrusion and/or brine dissolution) from Setubal and Grandola area.

Results can be used to understand aspects related to the social-economical and environmental impacts. Amongst others, the problem related with good quality water supply to the population, industry and agriculture would be carefully studied, taking into account the delimitation of recharge protection zones, identification of groundwater salinization (seawater intrusion mechanisms) and determination of residence time. On the other hand, a comparison of the Sado-Sines system characterized by a long residence time, with the Bairrada Carsic aquifer (fast circulation) will allow to assess the influence of climatic variations in precipitation, along hydrological cycles since Pliocene to present and predict future climatic scenarios.

The hydrochemical data obtained in the different campaigns allowed the determination of hydrochemical index and saturation index of calcite, dolomite and gypsum[1]. The analytical results were used on the characterization of the groundwater evolution along the main flow paths, supporting the available piezometric information. In the northern region, ^{14}C determinations on the Total Dissolved Inorganic Carbon (TDIC) allowed the identification of palaeowaters[2]. The radiocarbon content together with stable isotopes show to be an important tool in the identification of salt origin in the groundwater.

Published, accepted or in press work

1. P.G. Fernandes, P.M. Carreira, M. Oliveira da Silva. A hidrogeoquímica na definição do modelo hidrodinâmico do sistema aquífero da bacia do Sado, *VI Congresso de Geoquímica dos Países de Língua Portuguesa e XII Semana de Geoquímica*, Faro, Portugal (2001) 435.
2. P.G. Fernandes, P.M. Carreira, D. Nunes, M. Oliveira da Silva. Use of hydrochemistry and isotopes as tracers in the Sado-Sines sedimentary basin (S Portugal), *XXXI International Association of Hydrogeologists Congress*, New Approches Characterizing Groundwater Flow, Munich, Germany (2001) 65.

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[1] Depart. Geologia, FCUL

[2] Depart. Geociência, U.A

2.b) National Network for Isotopes in Precipitation

P.M. Carreira, L. Gourcy[1], M. Fátima Araújo, D. Nunes, P. Valério, T. Barbosa and S. Gomes

Objectives

Portugal through ITN/Environmental Analytical Chemistry 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 use as tracers of the isotopic composition of past and present precipitation, giving an opportunity for climate and water studies, all these information are very relevant for water resources inventory, planning and development.

Results

The isotope distribution in space and time can be related to a number of environmental parameters, which characterise not only the source region but also a given sampling site. Seasonality, amount of precipitation, altitude dependence, continentality, the role of local temperature, together with the source specific fractionation between ^{18}O and ^{2}H, all contribute to the isotope content of precipitation.

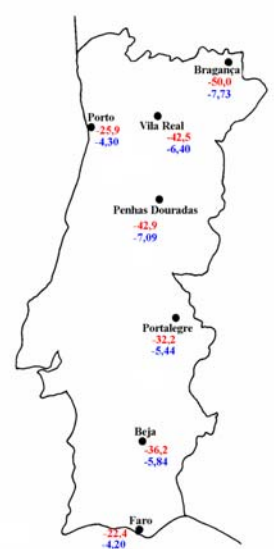

Fig. 1 – Isotopic (^{18}O and ^{2}H) variation of precipitation in Portugal.

CRP – daily events: rain and vapour isotopic composition study in Lisbon area

Under the Coordinated Recharge Programme of the I.A.E.A. "*Isotopic composition of precipitation in the Mediterranean Basin in relation to air circulation patterns and climate*", ITN participation include the determination of "daily events: rain and vapour isotopic composition study in Lisbon area". The EAC Group used the existent database of Portuguese stations and some conclusions were already achieved:

1. Relation between the isotopic composition ($\delta^{18}O$ and $\delta^{2}H$) with the amount of precipitation:
   $\delta^{18}O = (-0.01 + 0.003)\ Pp + (-4.46 + 1.36)$
   $\delta^{2}H = (-0.08 + 0.02)\ Pp + (-27.28 + 9.34)$
2. Relation between the isotopic composition of precipitation and temperature:
   $\delta^{18}O = (0.21 + 0.02)\ T + (-8.59 + 1.07)$
   $\delta^{2}H = (-1.23 + 0.16)\ T + (-51.56 + 7.91)$
3. The isotopic gradient with the altitude of the meteorological stations is the following:
   $\Delta\delta^{18}O = -0.2\ ^{o}/_{oo}$ / 100 m and $\Delta\delta^{2}H = -1\ ^{o}/_{oo}$ / 100m

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

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).

Published, accepted or in press work

1. S.A. Gomes, P.M. Carreira, D. Nunes. Estudo do comportamento isotópico (^{2}H e ^{18}O) das águas de precipitação em Portugal Continental, *VI Congresso de Geoquímica dos Países de Língua Portuguesa e XII Semana de Geoquímica*, Faro, Portugal (2001) 542.
2. S.A. Gomes. Estudo do Comportamento Isotópico das Águas de Precipitação em Portugal através da Técnica de Espectrometria de Massa. *Graduation thesis in Technological Chemistry*, Universidade de Lisboa (2001) 145p.
3. I.A.E.A. Isotopic composition of precipitation in the Mediterranean basin in relation to air circulation patterns and climate (RC-826) Finnal Report (2001).

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[1] Isotope Hydrology Section - IAEA

2.c) Thermomineral CO_2 –Rich Waters - N Portugal

P.M. Carreira, J.M. Marques[1], D. Nunes

Objectives

During the last decades, we have witnessed an increase worldwide interest on the exploitation of low temperature geothermal resources. Low temperature geothermal systems and cold carbon dioxide waters are linked in many parts of the world.

On the Portuguese mainland a great number of hot (76ºC) and cold $HCO_3/Na/CO_2$ rich mineral waters flow from natural springs and drill wells. They are mainly associated with important NNE-SSW faults. Several geochemical and isotopic studies were carried out with the aim to identify groundwater origin, altitude of recharge and underground flow paths.However most recently the environmental isotopes are being used in the identification of the source of the CO_2 in these waters, that could be associated to a deep-seated (mantle) origin or to a limestone dissolution mechanism.

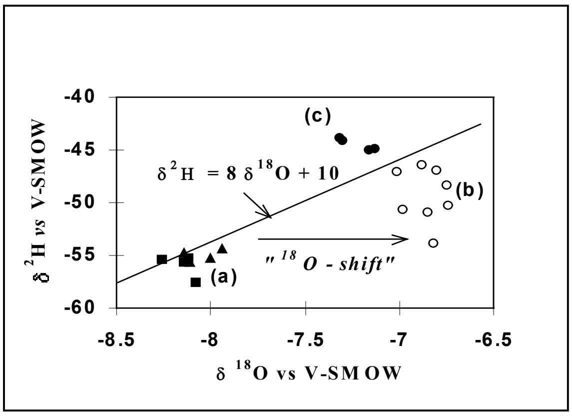

Fig. 1 - ^{18}O and ^{2}H variation in the thermomineral waters.

Results

The differences in the isotopic composition between Vilarelho da Raia / Chaves group and Vidago / Pedras Salgadas group has been interpreted as the result of different recharge altitudes. Based on the ^{18}O values an isotopic gradient was establish for this region around –0.26 ‰ for ^{18}O per 100 m of altitude. All these thermomineral waters are meteoric percolating at great depth and then emerge, as thermal waters in a discharge area at lower altitude. The Chaves group with an issue temperature of 76ºC presents some tritium in their composition.

The low temperature and the systematic presence of tritium in Vidago, Pedras salgadas cold mineral waters seems to indicate that in contrast to Chaves hot waters, the chemistry of these cold CO_2-rich mineral waters is mainly related to water rock interaction favoured by the presence of CO_2 in a low temperature (shallow) environment. Recent $\delta^{13}C$ data ($-6.0<\delta^{13}C>-1.0$ ‰ versus V-PDB) seems to indicate that the lightest $\delta^{13}C$ values can be derived mainly from a deep-seated (mantle) source. The carbon dioxide could be transported from its deep source (mantle) to the surface.This involves a migration as a separate gas phase and incorporation in the infiltrated meteoric waters. This hypothesis is supported by the fact that the $\delta^{18}O$ and $\delta^{2}H$ data related to the studied hot and cold CO_2-rich mineral waters do not show any evidence of mixing with magmatic waters. The fact that most of the studied hot and cold springs are located near faults indicates that those tectonic features must have access to deep levels in the study area.

Published, accepted or in press work

1. P.M. Carreira, J.M. Marques, L. Aires-Barros. A problemática da datação por 14C em águas gasocarbónicas, *VI Congresso de Geoquímica dos Países de Língua Portuguesa e XII Semana de Geoquímica*, Faro, Portugal (2001) 698.

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

3. Non-Destructive Analysis of Archaeological and Museological Objects

3.a) Study of the Origin, Chronology and Fabrication Processes of Pre-Historical Metallic Artefacts

M. Fátima Araújo, A. Teixeira, A.A. de Melo[1], P. Valério, L. de Barros[2] and A.C. Sousa[3]

Objectives

The investigation of production, circulation and consumption of metal artefacts from the Calcolithic till the Late Bronze and Iron Age Culture groups. The chemical characterisation of two collections of artefacts excavated in two archaeological sites (*Penedo do Lexim-Mafra* and *Almaraz-Cacilhas)* located at the Estremadura has been carried out, under the protocol between ITN and IPA.

Our main objectives are the establishment of the technical conditions of the metallic artefacts production and circulation. The large amount of artefacts available with rather variable chemical composition, the findings of foundry and the identification of distinct metallurgical operations (e.g. crucibles) is giving a remarkable contribution to the understanding of the historical dynamics of a long period in the Pre-History of Central Portugal.

Results

Both collections present typological, chronological and compositional distinct characteristics indicating different smelting processes. Artefacts collected in Penedo do Lexim have rather simple forms and their chemical composition indicate a Prehistorical occupation with characteristics of the Calcolithic (Cu with As impurities), Late Calcolitic or Early Bronze Age (Arsenical copper), Bronze (bronzes) and Late Bronze Age (bronzes with addition of considerable amounts of Pb1)).

Artefacts found in *Quinta do Almaraz* excavations (since 1988) present typological and compositional attributes, which indicate that they have been produced during the Bronze Age, Late Bronze Age and Early Iron Age. It is worth to note that the typology/composition of pre-historical artefacts have become more elaborate with the evolution of the metallurgical technology. Nevertheless, all the bronze artefacts found at *Almaraz* have similar typological characteristics (applications), although the rather different chemical composition indicated the existence of two different metallurgical techniques. Metallic remains on the interior of crucibles clearly identified the existence the metalllurgy of gold and the extraction of silver by cupellation. The Phoenician introduced this technology and the Iron Age in the region[1].

An integrated study integrated of all the available data published about a palstave found *Quarta-Feira* mine (*Sabugal, Guarda*) at a depth of twelve meters, in a broad archaeometallurgical perspective. The palstave is referred to in the scientific literature as one of the most important prehistoric finding which can be directly related with mining exploration in the Portuguese territory. The chrono-typological characteristics and the chemical composition of the palstave are discussed taking into account the existent technology to extract specific metals from the available mineral resources of that period[2].

Fig. 1 – Archaeological artefact.

Published, accepted or in press work

1. A.A. Melo, H. Alves, M.F. Araújo. The pre-historical bronze palstave of the Quarta-feira mine, *British Archaelogical Report* (2001) In press.
2. A.C. Teixeira. Caracterização de Metais e de Ligas Metálicas Pré-históricas – Aplicação da Técnica de Espectrometria de Fluorescência de Raios-X Dispersiva de Energias. Graduation thesis in Technological Chemistry, Universidade de Lisboa (2001) 85p.

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[1] Museu Nacional de Arqueologia, Praça do Império, Lisboa.
[2] Museu Municipal de Almada.
[3] Museu Municipal de Mafra.

3.b) Modern Coloured Glasses from Marinha Grande

P. Valério, A. Markowicz[1], M.F. Araújo and A.P. de Matos[2]

Objectives

Colour in glasses can be obtained through the addition of polyvalent transition metals (e.g. Cr, Co and Cu) or rare earth ions with unpaired electrons in 3d or 4f orbitals, respectively. Other sources of colour include the formation of metal or semi-conductor colloidal particles. The major chemical elements determined can identify the type of glassware and possibly also the original raw materials used during the glass manufacture. Furthermore, the different colouring elements, i.e. major or minor chemical elements or combination of chemical elements responsible for the different colours of the analysed glasses, were also identified.

Results

The way of obtaining the exact glass colour and tonality is through experimental trials. In these, both the technological features of the glass manufacture (melting and redox conditions) and the use of different compounds (e.g. colorants, decolorants and opacifiers) are studied. The analysed glass objects are two experimental sample sets of coloured glass from a famous glass factory, *Fábrica de Vidros da Marinha Grande*, which had manufactured between 1748-1994. The samples belong to the Glass Museum of Marinha Grande, a city with one of the largest concentration of glass industries in Europe. The experimental work was carried out within the technical co-operation project IAEA TC/POR/7/003, at the Instrumentation Unit (IAEA Seibersdorf Laboratories) under the supervision of A. Markowicz.

The results of EDXRF measurements of the two collections of coloured glasses from Marinha Grande, revealed the use of sand (mainly SiO_2 and Fe_2O_3 as an impurity) and limestone (CaO) as the major glass raw materials. Some chemical elements (K, Ti, Cr, Mn, Fe, Ba and Pb) can be used to distinguish between the two glass collections. The lower content or even the absence of these elements in the samples belonging to the first set, are probably due to the use of superior raw materials in the glass production (e.g. use of more pure sand imported from Belgium). All glasses from the second set contain higher percentages of Pb. Nevertheless, even in those samples the concentration is relatively low and Pb presence is probably due to careless choice of cullets added to the raw materials. The statistical analysis of the EDXRF results, based on the principal components extraction, allow the association of some chemical elements with different colours (Cr: green glasses; Co and Cu: blue glasses; Se and Nd: purple glasses; Fe and Mn: brown glasses). An article was submitted in October to be published in the *X-Ray Spectrometry*.

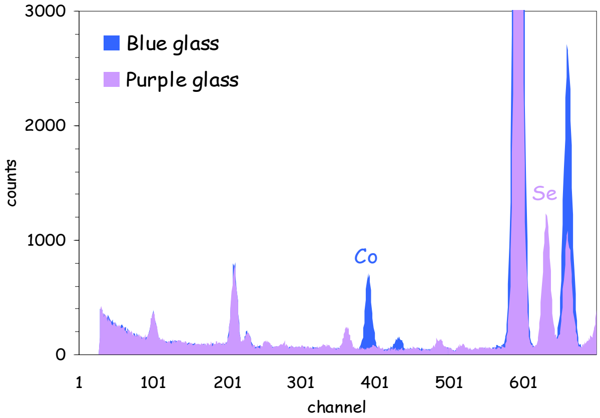

Fig. 1 – EDXRF spectra of blue and purple glasses.

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[1] Instrumentation Unit. IAEA Seibersdorf Laboratories, A-2444 Seibersdorf, Austria.

[2] QIO group, ITN.

Services

The facilities available and the expertise within the members of the research team are often requested to provide services to Universities, Laboratories and Public and Private Institutions, either as analytical results or as consultants. The main analytical requests involve the following facilities:

Energy-Dispersive X-Ray Fluorescence Spectrometry

Multielemental analysis (e.g. quality control, environmental monitoring) and non-destructive analysis (e.g. archaeometry). Inside this area several services have been provided to *Hovione*, *Museu de Marinha* and *Valorsul*.

Mass Spectrometry for Light Isotopes and Tritium Dating

Determination of light isotopes ($^{2}H/^{1}H$, $^{13}C/^{12}C$ and $^{18}O/^{16}O$) in waters and sediments and tritium (^{3}H) determination in water samples. Several services were provided to *Laboratório Nacional de Engenharia Civil*, *Universidade de Aveiro*, *Instituto Superior Técnico* and *Companhia de Indústria e Serviços Mineiros e Ambientais*.

Cultural Heritage and Sciences

Cultural Heritage and Sciences

M. Isabel Prudêncio

The "Cultural Heritage and Sciences" (CHS) research group is mainly directed to the protection, conservation and enhancement of the Portuguese cultural patrimony through the application of scientific approaches, specially 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 and luminescence dating (TL-OSL). The good performance of these laboratories is a major objective, with the maintenance of excellent quality in the results obtained to serve the national and international communities. This is obtained through periodic comparisons with international standards and laboratories. These methods allow the chemical characterisation of materials and the chronologies establishment, consisting on the research-working basis of the group.

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). These studies also support environmental projects through the geochemical natural background knowledge, in order to evaluate anthropogenic influences.

Beyond financed research projects in collaboration with other national laboratories and universities, a significant part of the research activities of the CHS group is directed to end users through the ITN-IPA (Instituto Português de Arqueologia) protocol. Also contracts/services are made with other private or public institutions (IPPAR, EDIA, Valorsul, Petrogal, Robbialac, City Halls, etc).

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

1 - Movable Cultural Assets;
2 - Absolute Dating;
3 - Immovable Cultural Assets;
4 - INAA - Development and applications
5 - ^{57}Fe Mössbauer spectroscopy in Geology and Archaeology

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

1 - **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. The ITN - IPA protocol played a very important role in the increment in this field. A database of ceramics and related raw materials was implemented, and will be available in the internet in a near future.

2 - **Absolute Dating** - development, implementation and application of dating units (radiocarbon and luminescence) serving the archaeological and geological communities. In this field also the ITN-IPA protocol contributed to the archaeological research.

3 - **Immovable Cultural Assets** - identification of the causes and mechanisms of degradation of stones contributing to the protection of historical buildings and monuments made of igneous rocks. Especial attention is paid to the study of the interaction between the stone, the building materials, the pollutants and the percolating solutions.

4 - **INAA - Development and applications**: environmental monitoring studies and quality control of trace elements contents in industrial materials.

5 - **^{57}Fe Mössbauer spectroscopy in Geology and Archaeology**: this method (available at the Solid State group of ITN) has been applied in research fields of the CHS group, such as the study of ancient ceramics and of monument stones. Crystalchemistry characterization of Fe-containing minerals using this technique was also developed and is presently an important tool that contributes to geological research projects from other institutions.

Final Remark: the maintenance and increment of all those activities will only be achieved with the assurance of the increase of the permanent staff, by contracting the already trained competent grant-holders - post-doctoral and technicians (65 % of the team; permanent staff: 2 researchers and 2 technicians).

The **consolidation of the scientific research and its application to the conservation and enhancement of the Portuguese cultural heritage** is a long-term goal of the CHS group, as well as the increase of the interaction between ITN and public institutions to solve problems of cultural assets.

Cultural Heritage and Sciences

Research Team

Researchers

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

Students

- A. GOMES, MSc Student
- A. GASPAR, MSc Student
- R. MARQUES, ITN grant
- D. FRANCO, undergraduate student, ITN grant
- G. CARDOSO, undergraduate student, ITN grant

Technicians

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

Funding

	$\times 10^3$ PTE
Research Projects:	7831
ITN:	11675
Other Sources:	7260
Total:	**26766**

Publications

Books:	1
Journals:	1 and 5 in press
Proceedings:	5 and 6 in press
Conf. Communications:	28
Other Publications:	2
Museum Exhibitions:	3
Theses:	2 MSc

Movable Cultural Assets
Ancient Ceramics Production, Technology and Provenance

M.I. Dias, M. I. Prudêncio, M.A. Gouveia, J.C. Waerenborgh[1] and A.C. Valera[2]

Objectives

This research domain aims to contribute solving problems requested by the archaeological scientific community concerning movable cultural assets, such as ceramics. Several chronologies of ceramics are studied, from the pre-history to the medieval times. 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

Database -Ceramic and Geological Materials Record

A database is running concerning ceramic and geological materials inventory files. The ceramic record presents a very detailed macroscopic characterisation of each object, with its archaeological context, photo and geographical localisation of the corresponding site, linked to the analysis file (Fig. 1). In this latter file are present all the available results of each technique - INAA, XRF, XRD, OM, SEM, PIXE, Mössbauer, etc. An inventory file of potential raw materials connected to each archaeological site, and geographicaly localized, is also linked with the ceramic files, as well as, with another one containing geological materials results for all the used techniques. So, we have available in our lab a complete macroscopic description, location, chronology, chemical/mineralogical composition and possible provenance of each analysed ceramic object entered ITN, in addition to its raw material. Our purpose is to put this database available worldwide in the internet.

Fornos de Algodres Project

The data set of chemical and mineralogical results of Fornos de Algodres pre-historical settlement network (Fig. 2) was enlarged for ceramics of a third archaeological site (Malhada), as well as for the related raw materials. Chemical differences in pottery allowed the definition of several pottery groups according to its composition and the establishment of a correlation between some of the pottery analysed, its typological group and local clay samples, but in some specific cases different origins for raw materials is suggested.

INVENTÁRIO - CERÂMICA

ID
3

Registo Arqueológico
7125

Registo ITN
PRD -03

Data de Entrada
Dezembro de 200

Arqueólogo Responsável
Miguel da Silva, Carlos Valera

Projecto
Protocolo ITN-IPA

Sítio Arqueológico
Povoado de Perdigões

Região
Reguengos de Monsaraz

Cronologia
Neolítico Final-Calcolítico do Sudoeste

UE
90

Sector
x=471,28/y=722,17/z=231,79

Descrição / Tipologia
Forma 8.2 - Recipientes tipo saco, de corpo troncocónico sobre uma base hemieelipsoidal de tendência aplanada. Os indices de abertura variam entre 53 e 64 e os de profundidade entre 73 e 94. Os volumes variam entre 209 e 1122 cm3.

Bordo ☐
Parede ☐
Base ☐
Asa ☐

Outro
Fragmento de Bojo pertencente ao

Área explorada (em cm2
10,5

Estado de Conservação
Bom

Tratamento da Superfície Externa
Normal

Tratamento da Superfície Intern
Normal

Cor (Munsell) Externa
5Y

Cor (Munsell) Interna
5Y

Ambiente de Cozedura
Redutor

Técnica de Fabrico da Forma
Manual

Decoração ☐

Decoração - Técnicas

PASTA - Consistência
Média

PASTA - Textura
Heterogénea - Fina

ELEMENTOS NÃO PLÁSTICOS ☑

ENP - Origem
Mineral

Quartzo ☐
Feldspatos ☑
Micas ☑
Carbonatos ☐
Materiais Vulcânicos ☐

Outro ENP

Forma ENP
Sub-Rolados

Granulometria ENP
Fina

Quantidade ENP
Pouca

Distribuição ENP
Irregular

Espessura Maior e Menor (cm)
0,8

Observações
Sepulcro 1-Uso Funerário

Nº Irradiação Curta

Data da Irradiação Curta

Fotografia

Nº Irradiação Longa
6ª Irradiação Longa de 2001

Data da Irradiação Longa
26/01/2001

Localização Geográfica

Fig. 1 – Example of records from the CHS Database

Fig. 2 - Field work at Fraga da Pena archaeological site.

Bracara Augusta Project

The roman ceramics production technology from Bracara Augusta – FCT Project - ended this year with an important contribution to the establishement of the identification of compositional ceramic groups and its relation with typological archaeological classification. Provenance and production technologies were ascertained. Two master theses were fulfilled.

ITN-IPA Protocol Projects

The running projects in 2001 (ITN-IPA protocol) were:

1 – "Pottery production in occidental neighbourhood of Islamic Lisbon". Archaeologist: J. Bugalhão

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[1] Solid State Group, Chemistry sector of ITN

[2] GAFAL archaeologist (C.M. F. Algodres)

2 – "Roman Ceramics from S. João de Perrelos (V.N. Famalicão)". Archaeologist: Felisbela Leite
3 – "Muslums and christians in the Arrabida Peninsula: the Palmela Castle and its rural surrounds." Archaeologist: I. Fernandes
4 – "Funeral environments in the Perdigões settlement: ceramics from the late Neolithic - SW Chalcolithic". Archaeologist: M. Lago and A.C. Valera.

Interesting results were obtained with the several running projects in 2001. Special attention should be made to the chemical results obtained for the roman ceramic production centres of Peniche, Tagus and Sado. An important distinction was established between the studied production centres, by using geochemical fingerprints (Fig. 3).

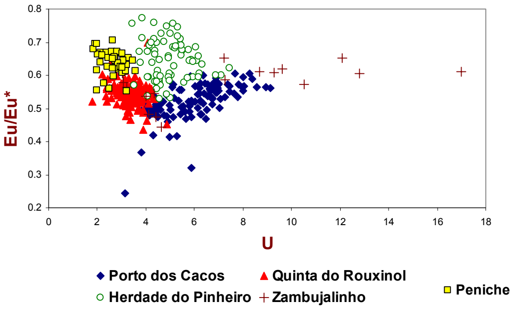

Fig. 3 - Production centers distinguished by the use of geochemical fingerprints.

The Perdigões site is a large Calcolithic settlement, occupied during the late 4th - 3rd millenium B.C. in the Reguengos de Monsaraz region, in South of Portugal. The pottery includes all the typical morphologies of the Late Neolithic and Calcolithic of the South West of the Iberian Peninsula and that there are clear differences between the funerary and the domestic recipients. 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.

IPPAR Projects

The running project in 2001was:

- Project 1.4 - *The archaeological materials from fortified and islamic sites in the south of Iberian Peninsula* within the "Acção-Piloto cooperação Portugal, Espanha e Marrocos sobre ordenamento do território e património cultural. Sub-programa - SA1 - Investigação, inventariação e troca de experiências.

Within this project the CHS group performed the archaeometric study of ceramics from the portuguese sites classified as "National Monuments": Castelo de S. Jorge (Lisbon); Sé de Lisboa; Convento de S. Francisco de Santarém; Castelo de Alcácer do Sal.

The archaeometric study developed to ceramics of those national monuments became particularly interesting, as it was the first realized to islamic times in those regions, and 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. Also interesting was the recognition of the importation from the same production center of all the red painted ceramics belonging to the different studied sites, like those of Lisbon and of Alcácer do Sal. The other ceramics from the latter site point to the use of different raw materials, with particular features, such as the presence of pyroxenes, analcime and amphiboles in some ceramics. Ceramics from Santarém are the more chemical and mineralogical homogeneous, indicating the use of the same type of raw materials.

Published, accepted or in press work

1. M.I. Dias, M.I. Prudêncio, M.A. Gouveia, Arqueometria de cerâmicas islâmicas das regiões de Lisboa, Santarém e Alcácer do Sal (Portugal): caracterização química e mineralógica. *GARB - Sítios Islâmicos do Sul Peninsular*, IPPAR/MC e Junata Da Extremadura - Consejaría De Cultura (Eds.), IPPAR, Lisboa (2001) pp. 257-281.
2. M.I. Dias, M.I., Prudêncio, J. Raposo, M.A. Gouveia, F. Fabião, A. Guerra, J. Bugalhão, A.L. Duarte, A. Sabrosa, Caracterização química por AAN dos tipos de ânfora de um centro de produção do estuário do Tejo: Quinta do Rouxinol (Portugal). *Proceedings do IV Congreso Nacional de Arqueometria*, Valencia, Espanha. (2001). In press.
3. M.I. Dias, M.I. Prudêncio, R. Morais, M.A. Gouveia, Caracterização química de cerâmicas de Bracara Augusta: produções locais e importações da Bética. *Proceedings do IV Congreso Nacional de Arqueometria*, Valencia, Espanha (2001). In press.
4. M.I. Prudêncio, Dias, M.I., Geoquímica de materiais argilosos na região de Braga e sua implicação em estudos de proveniência de cerâmicas arqueológicas. *Actas do VI Congresso de Geoquímica dos Países de Língua Portuguesa e XII Semana de Geoquímica*, Faro, (2001) pp. 452-456.
5. M.I. Dias, M.I. Prudêncio, Gouveia, M.A, Geochemical study of clay materials in Fornos de Algodres region (Central Portugal) in an archaeometric view. *Proceedings of the 12th International clay Conference and 3rd International Symposium on Activated Clays*, Argentina. (2001). In press.

Absolute Dating - Radiocarbon Unit

M.I. Prudêncio and R. Marques

Objectives

The good performance of this dating laboratory is a compromise assumed by ITN in the ITN-IPA protocol. In this context the two institutions promoted in the archaeological community the use of the radiocarbon unit in ITN, and some projects were financed by IPA.
Also the geological community is aware of the good performance of this laboratory incrementing during 2001 the request for analysis.

Results

The increase of the radiocarbon unit output was a major achievement in 2001. This was only possible due to the excellent work of the ITN grant collaborators (Dr. Rosa Marques; Guilherme Cardoso). Seventy samples of geological, hydrogeological and archaeological nature were received at the radiocarbon laboratory, supporting projects and PhD tesis.

Absolute Dating - Luminescence Dating Laboratory

D. Richter, A. Zink and M. I. Prudêncio

Objectives

The main objective of the Luminescence Dating Laboratory is the application of luminescence dating techniques (TL, G-OSL, IRSL, B-OSL) in order to assist archaeologists and geologists in establishing chronologies. In addition, fundamental studies on the luminescence properties of minerals, which could be exploited for dating application, will be a vital part of the work.

Results

The luminescence dating laboratory was set up and is now equipped for dating application. The main piece of equipment, the Risoe D-15 Luminescence Reader (Fig. 1), was checked for its limits and capabilities in blue (diodes), green (halogen lamp) and IR (laser) stimulation, as well as by heating. It was found that the equipment is versatile and meets the requirements for luminescence dating as well as for fundamental research, f.e. linear modulation etc. The attached $^{90}\mathrm{S}/^{90}\mathrm{Y}$-beta-source was calibrated using a SAR (single aliquot) protocol against an international standard.
To investigate the external dose rates in situ, a portable NaI(TL) gamma spectrometer was calibrated by international reference blocks, and a new method of dosimetry based on the B-OSL properties of α-Al_2O_3:C (TLD-500) was developped.

In order to assure the quality of dating results, the luminescence dating laboratory participates in international comparisons. Samples of a brick, quartz sediment, loess and heated flint, which are either part of an interlaboratory comparison, or which had been dated in other laboratories were obtained and their processing for dating started.

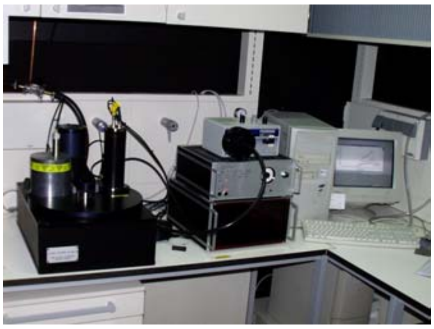

Fig. 1 - Risoe D-15 Luminescence Reader at ITN luminescence laboratory.

The blind tests on the samples mentioned above will be finished, and as a result the laboratory will be fully operational in early 2002.
The beta sources of the laboratory will be calibrated against national standards present at ITN, in order to establish the laboratory’s independency.
Apart from the development of a dating method for heated quartzite based on the study of its luminescence properties, the extension of luminescence detection in the IR region is anticipated.
The focus of the Luminescence Dating Laboratory is currently on the archaeological application, but includes the dating of geological deposits as well. The potential of the methods especially in Quaternary Geology will be disseminated, in order to provide a wide basis for partial funding of the laboratory.
Current projects:

- Thermoluminescence dating of heated quartzite and silex from the Middle Palaeolithic site of Gruta da Oliveira, Almonda. (Archaeologist: Joao Zilhao)
- Thermoluminescence dating of heated silex from the Middle Palaeolithic site of Caldeirão. (Archaeologist: Joao Zilhao)

- OSL dating of sediment from the Lagar Velho (Lapedo) stratigraphy. (Geoarchaeologist: Diego Angelucci; archaeologist: Francisco Alves)
- INAA analysis and TL dating of pottery and heated silex form the Megalithic site at Vale de Rodrigo, Alentejo, Portugal. (joint project of the CHS-group within the ITN-IPA protocol; Archaeologist: Feline Kalb)
- Middle Palaeolithic and Mesolithic sites at Alqueva. Dating archaeology and landscape by luminescence at three locations (Sapateiros 2, Barca do Xeres, Porto Meirinho 1). (Archaeologist: Joao Pedro Cunha Ribeiro, Francisco Alves)
- Chronometric dating of Aïn Hummal and Nadaouiyeh Aïn Askar (archaeologist: Prof. LeTensorer (University Bales, Switzerland), funded by a travel grant from the Leakey Foundation (USA) to DR.
- Luminescence characterization of Ordovician quartzite from Douro-Co*f* region (Archaeologist: Thierry Aubry)
- OSL dating of sediment from the Palaeolithic site Vale da Porta. (archaeologist: Miguel Almeida)

Measurement of the environmental gamma dose rate in archaeological sites

D. Richter and A. Zink

Objectives

In luminescence dating the environmental gamma dose rate needs to be measured. Due to the frequent inhomogeneity of sediment, especially in archaeological sites, such measurements have to be done in situ. For this purpose, two different methods were established for the luminescence dating laboratory:

- portable gamma spectrometry for instant dose measurement
- dosimeter system for long term measurement, which could include seasonal variability

A portable gamma spectrometer (NanoSpec-Target) and α-Al_2O_3:C (TLD-500) dosimeter pellets were purchased after careful consideration and testing.

The portable gamma spectrometer (NanoSpec-Target electronic), which allows the measurement and calculation of either the main natural radioactive element concentrations (U, Th, K), or of a total gamma dose rate, was calibrated versus doped blocks, which serve as unofficial international standards in luminescence dating.

In order to allow the measurement of the environmental gamma dose rate in sites where the use of the large gamma spectrometer probe (8 cm diameter) is not possible, a dosimetry system based on α-Al_2O_3:C (TLD-500) pellets was developped. These require holes of less then 1.5 cm in diameter. As the travel dose from the site to the laboratory has to be recorded as well, the dosimeters needed to be easily and reproducibly reset under unfavourable conditions outside of the laboratory.

Results

A first calibration of the portable gamma spectrometer was performed at the Gif-sur-Yvette (Paris, France) luminescence laboratory using two calibration blocks: a K-doped vat and an infinite depth soil equivalent block of bricks. To define the stripping factors, which are needed for peak count rate evaluation, a further calibration with separate K-, U- and Th-doped blocks was performed at the RLAHA, Oxford, UK. Based on theses calibrations, the gamma dose rate can be measured, using the instant count rate, the global count rate, a partial count rate (E>500keV) and the K, U, Th - peak count rate. The standard deviation between the different methods is of around 6-7 %. The global count rate gives the best precision results with ca. 1 % uncertainty, while for the peak count rate method it is estimated to ca. 9 %. In application either of the methods can be used, due to the large uncertainty on the stability of the dose in the past, which has to be accounted for by an estimated error of at least 10 %. The gamma spectrometer was used in various projects on dating of archaeological sites in Portugal (Fig. 2).

In contrast to the common application of α-Al_2O_3:C (TLD-500) as thermoluminescence dosimeter (TLD), stimulation by blue light was chosen because of increased sensitivity and the potential way of easily resetting the dosimeters with blue diodes. A simple portable device was built in order to enable the use as a dosimeter at greater distances and travel time from the laboratory. It was found, that the recycling of α-Al_2O_3:C pellets is excellent, as well as it's linear dose range from a few µGy to several mGy (Fig. 3).

Short exposure to a variety of light sources did not affect the luminescence from a small dose, which allows the handling of pellets under not well defined artificial light conditions outside the laboratory for zeroing before insertion or recording the travel dose. α-Al_2O_3:C (TLD-500) measured with blue stimulation are therefore much easier to use then any other available dosimeter system at similar sensitivity.

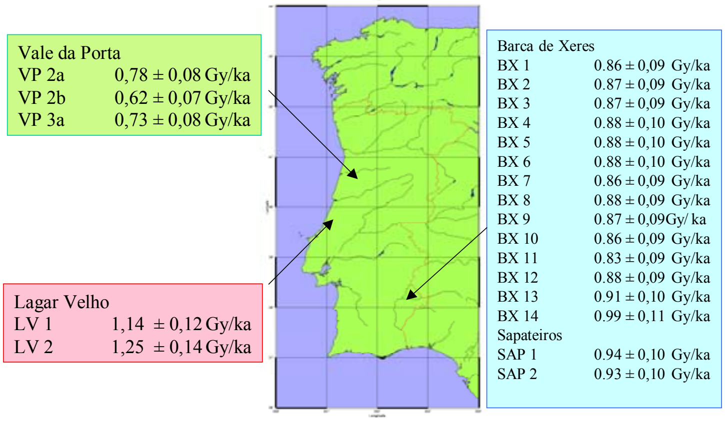

Fig. 2 Gamma spectrometry results of selected sites in Portugal.

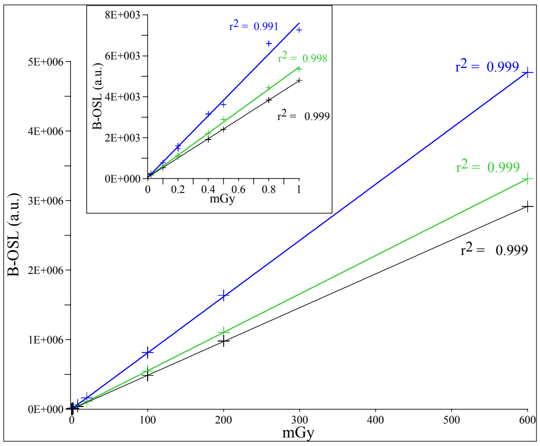

Fig. 3 Sensitivity and linearity of dosed Al_2O_3:C with green stimulation (G-OSL).

Immovable Cultural Assets
Historical Buildings and Monuments

M.I. Prudêncio, M. Nasraoui, M.A. Gouveia and J.C. Waerenborgh[1]

Objectives

This research domain contributes for the detailed characterisation of the prevailing degradation state of the igneous rocks in historical buildings and monuments, as well as the responsible mechanisms, with the identification of the main decay agents. A better definition of preservation actions will be a major objective of the research results and interpretations. This research has been supported by FCT and ICCTI.

Fig. 1 The cathedral of Évora (UNESCO classified monument).

Results

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

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

1- Mineralogical/Geochemical Approach (Learning from the past)

The identification of the different types of stones was the first and a fundamental step of the study of degraded Évora stones. The geochemical and mineralogical transformations occurring during the degradation process, has involved different degrees of mobility of the chemical elements, and consequently hide some of the primary characteristics of the precursor materials from which the monument was built. The results show that a geochemical approach via appropriate elements can allow clear granitic stones discrimination relative to their primary characteristics. The results obtained show that at least two main types of granite were used for the construction and restoration of the Évora Cathedral.

2- Salt phases occurrence (Learning from the present)

Salts from the upper and the lower part of the cathedral, as well as from the cloister have been collected. Their compositions were characterised by chromatography. In addition, the mineral identification was performed by XRD. Clear texture differences between the studied samples were observed by SEM. In addition to the study of salt samples, simulation experience of granite/fluid interactions were realised.

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 contribution of geochemistry and 57Fe Mössbauer spectroscopy. *Proceedings of the VIº Congresso de Geoquímica dos Países de Língua Portuguesa & XII semana de Geoquímica,* Universidade do Algarve, Portugal. (2001). pp 649-652.

2. M. Nasraoui, M.J. Trindade, M.I. Prudêncio, M.A. Gouveia, J.C. Waerenborgh, M.O. Figueiredo, T. Silva, Whole rock classification and geochemical variation of the stones of the Sé of Angra do Heroísmo and of the rocks of a surrounding quarry (Terceira Island, Azores, Portugal). *Proceedings of the VIº Congresso de Geoquímica dos Países de Língua Portuguesa & XII semana de Geoquímica,* Universidade do Algarve, Portugal. (2001). pp 653-655.

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Instrumental Neutron Activation Analysis
Development and applications

M.A. Gouveia, M.I. Prudêncio and M.I. Dias

Objectives

Instrumental neutron activation analysis is a well-established method within this group since the seventies. Based on the use of the nuclear research reactor (unique in the Iberian Peninsula), this analytical method (complemented with other methods) supports most of the research activities of the CHS group and is also used by other ITN researchers. Public and private institutions requested often CHS group for services, considering the high performance of the chemical analysis that it allows.

Some of the activities concern environmental monitoring studies and quality control of trace elements in industrial materials.

So, as main objectives, besides the application to the cultural heritage research domains and the services already established in contracts, we intend to increment the development of the INAA application to other scientific areas, making our know-how more profitable to the community.

Results

The INAA is fundamental for the research activities of the group, allowing determine trace elements, especially Rare Earth Elements, which are excellent geochemical fingerprints.

Regular services have been done to environmental control and industry, namely the chemical characterisation of environmental samples in the vicinity of an urban solid residues power plant (CTRSU, S. João da Talha) for Valorsul, fuel and catalyzer samples for Petrogal and painting samples for Robbialac.

It's important to enhance the work developd so far to the Valorsul, and the new established contract this year. It includes the enlargement of the number of samples around the central, the number of analysed elements, as well as, monitoring the chimney filters, so a more accurate evaluation of the pollutants contribution of this central may be established. Valorsul invited us to public presentations in order to present our results to be discussed within the scientific community, and also the local population of the neighborhoods and local authorities. One of the most relevant results concerns the soils concentration of Zn, Pb and B, which are the elements that present more content variations, specially the Pb case (Fig. 1). For all the cases the element levels were higher at the surface than at deeper levels.

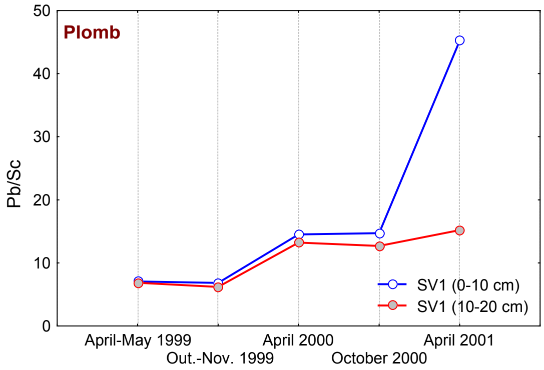

Fig. 1 Pb contents normalized to Sc in the soils near the CTRSU since April 1999.

The quality of the analytical procedures of INAA is periodically controlled through the analyses of international standards and inter-calibrations with other laboratories, in order to maintain and increment the good performance of the laboratories.

Application of INAA to other scientific research areas also occurred, like the collaboration with the Pharmaceutical Univ. of Lisbon to measure the organically bound mercury in biological samples.

A significant number of chemical analyses were performed in 2001, most of them were ancient ceramics, soils and sediments, in a total of 650 samples irradiated.

Published, accepted or in press work

1. M.A. Gouveia, M.I. Prudêncio, M.F. Araújo, M.C. Freitas, M.I. Dias, P. Valério, A.P. Marques, "Programa de monitorização de elementos traço na envolvente à CTRSU de S. João da Talha", Valorizar os resíduos. Monitorizar o ambiente. Efeitos da central de tratamento da Valorsul. *Resumos técnicos dos programas de monitorização*. Ed. Valorsul, Valorização e tratamento de resíduos sólidos da área metropolitana de Lisboa (Norte), S.A., (2001) pp. 9-10.

2. M.A. Gouveia, M.I. Prudêncio, M.F. Araújo, M.C. Freitas, M.I. Dias, P. Valério, A.P. Marques, "*Valorizar os Resíduos Monitorizar o Ambiente - Monitorização de Elementos Traço*", Ed. Valorsul - Valorização e tratamento de resíduos sólidos da área metropolitana de Lisboa (Norte), S.A.(2001)pp.1-21

^{57}Fe Mössbauer spectroscopy in Geology and Archaeology

J. C. Waerenborgh[1], M. Nasraoui, E. Bilal[2], A. Mateus[3], J. Figueiras[3] and M.I. Prudêncio

Objectives

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.

Mössbauer spectroscopy has been applied in research fields of the CHS group. ITN also promotes the application of this technique to support geological research projects from Portuguese Universities. Collaboration with foreign research institutions is also active.

Results

Ancient Ceramics production technology

Mössbauer spectra of a few sherds of the late roman grey ceramics from Braga were taken. The preliminary results suggest a first firing in open air at temperatures higher than 800ºC-900ºC followed by prolonged heating in a reducing atmosphere at similar temperatures.

Historical Buildings Conservation

The Fe^{3+}/Fe^{2+} ratio determined from the Mössbauer data of whole samples from the granitic stones of Sé de Évora together with other geochemical indexes showed that at least two main types of granite were used for the construction of the monument.

Crystalchemistry characterization of minerals:

- Pyrochlore: for the first time, Mössbauer spectra of natural pyrochlores were published. The quadrupole splitting of Fe^{3+} in this mineral structure (Fig.1) was found to be exceptionally high. Furthermore, the knowledge of the Fe^{3+}/Fe^{2+} ratio retrieved from the spectra, provided useful information on the geochemical history of the studied geological complexes.

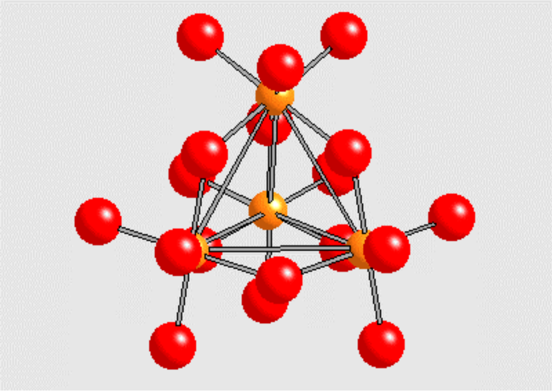

Fig.1 Coordination of Fe^{3+} (●) with unusually high quadrupole splitting, in the pyrochlore structure.

- Tourmaline: the Fe^{3+}/Fe^{2+} ratio and the distribution of Fe^{2+} in tourmalines with different colours from S.José, Minas Gerais, Brazil, have been studied by Mössbauer spectroscopy in collaboration with the École des Mines of St.Étienne.
- Cr-spinels: the differences in the magnetic ordering temperatures allowed the characterization of different types of Cr-spinels from the Beja-Acebuches Ophiolite complex (SE Portugal) using a single Mössbauer absorber, thus avoiding the need to separate them physically, which would have been virtually impossible in the present case. The results were compared to those obtained for other Cr-spinels and, for the first time in the case of natural Cr-spinels, the increase of their magnetic ordering temperatures with their oxidation degree, resulting from natural processes, was discussed in terms of the magnetic exchange interactions between the Fe cations.

Published, accepted or in press work

1. M. Nasraoui, J. C. Waerenborgh, Fe speciation in weathered pyrochlore-group minerals from Lueshe and Araxá by ^{57}Fe Mössbauer spectroscopy, *Can. Mineral* 39 (2001) 1073.
2. 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.* (2001). In press.
3. 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*. (2001). In press.

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