

# Inorganic and Organometallic Chemistry

*Joaquim Marçalo*

The activities of the Group encompass the synthesis, characterization and reactivity studies of inorganic, organometallic and intermetallic compounds of the actinides and lanthanides. The main objectives of the work are to understand the role of the electronic structure and the size of the f-elements in the properties of their compounds, and to find new applications for these elements. Chemical properties are evaluated by stoichiometric reactions and by homogeneous and heterogeneous catalytic studies. Gas-phase ion chemistry studies, using advanced MS techniques, are undertaken with the same goal. Energetics is also examined using calorimetry, thermal analysis and MS.

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

Gas-phase chemistry/mass spectrometry studies expanded in 2011. ESI-QIT/MS was used to investigate several aspects of the coordination chemistry of lanthanides and actinides, and a few fundamental gas-phase properties of these elements, including size, effective charge and oxidation state stability. New thorium species, namely, polysulfide ions and cluster carbide ions were synthesized and characterized by LDI-FTICR/MS.

The investigation of the organometallic chemistry of the actinides continued. New Th(IV) and U(IV) complexes with  $[\text{salan-R}_2]^{2-}$  (R = Me, <sup>t</sup>Bu) ligands, notably, the alkyl derivatives  $[\text{An}\{\text{salan-}^t\text{Bu}_2\}_2(\text{CH}_2\text{SiMe}_3)_2]$ , were prepared and characterized. Studies on the chemistry of U(III) anchored on the  $\{\text{tacn-Me}_2\text{SiN}(\text{Na})\text{Ph}\}$  ligand were restarted and the reactivity with redox-active substrates explored. Collaboration with the Solid State Group was initiated to study the magnetic properties of uranium complexes.

In a collaboration with CICECO, U. Aveiro, several new materials were synthesized, namely, uranyl and uranyl-Eu MOFs with phosphonate ligands, and layered lanthanide hydroxides (LLHs) of Eu and Tb with intercalated 2,6-naphthalene-dicarboxylate anions, and their luminescence properties are under study. The magnetic properties of a Dy LLH and its intercalation product with 2,6-naphthalene-dicarboxylate anions were evaluated, in a collaboration with the Solid State Group.

The study of important environmental issues such as the activation and valorisation of CH<sub>4</sub> and CO<sub>2</sub> as valuable C1 feedstocks continued. For the first time, the conversion of CH<sub>4</sub> using N<sub>2</sub>O as oxidant either for the production of syngas or C2 hydrocarbons over f-block elements based catalysts, namely, over KCl-LnCl<sub>3</sub> (Ln = La, Ce, Sm, Dy, Yb) eutectic molten salts, was studied and published. A new work plan was started that comprises the synthesis of binary intermetallic compounds nanoparticles, containing, in particular, f-block elements, and the study of their catalytic behavior for the elimination of primary gaseous pollutants such as CO<sub>2</sub> and N<sub>2</sub>O.

The study of the energetics of organic, inorganic and organometallic molecules was pursued. The ThermoInfo database ([www.therminfo.com](http://www.therminfo.com)) underwent an upgrade of its structure and soon is expected to include some 20 000 new entries. The experimental study of alkaline, alkaline-earth, silicon and lanthanide polyalkoxides continued as well as the study of some of their properties.

Collaborations continued with other research groups within and outside ITN in different areas. Of note is the continued collaboration with OMNIDEA (AeroSpace Technology and Energy Systems) Lda..

A significant part of the activity of the Group was the training of research students. Some of the Group members were involved in undergraduate and post-graduate university teaching. The financial support for the work was mostly from FCT, via research projects and Ph.D. and Post-Doc grants..

## Research Team

### Researchers

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N. MARQUES, Princ. (Retired)

## Mass Spectrometry Studies of the Coordination Chemistry of Lanthanides and Actinides

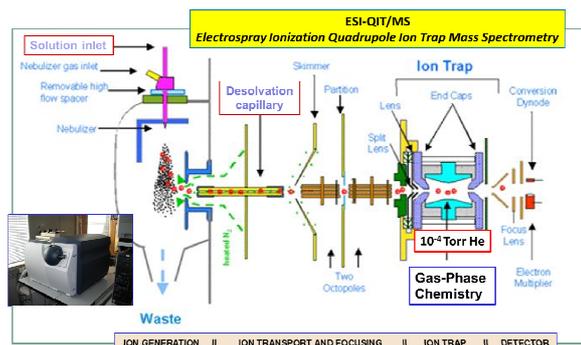
J. Marçalo, J. M. Carretas, A. F. Lucena, C. Lourenço, B. Monteiro, L. Maria, I. Paiva, J. K. Gibson<sup>1</sup>, M. C. Michelini<sup>2</sup>, L. Berthon<sup>3</sup>

### Objectives

The coordination chemistry of the lanthanides (Ln) and actinides (An) is a topic of current interest as related to Ln/An separations within advanced nuclear fuel cycles. We intend to explore the differences and similarities in the chemistry of trivalent Ln and An at a fundamental level, contributing to the clarification of An(III)/Ln(III) selectivity in Ln/An separations. We also expect to widen the knowledge of the physical and chemical properties of elementary actinide species which is essential to enhance the fundamental understanding of these elements

### Introduction

Electrospray ionization quadrupole ion trap mass spectrometry (ESI-QIT/MS) is used to investigate several aspects of the coordination chemistry of lanthanides and actinides. These studies range from the characterization of new f-element complexes to the examination of fundamental gas-phase properties of lanthanides and actinides [1]. The experimental



studies are accompanied by theoretical calculations of selected systems.

### Results

(1) The complexation of the new neutral ligands bis- and tris[3-(2-pyridyl)pyrazolyl]methane to Ln(III) and Am(III) nitrates and chlorides was probed. MS spectra showed that displacement of the anions did not occur for nitrate, as only  $[M(\text{NO}_3)_2\text{L}]^+$  ions were formed, while for chloride formation of  $[\text{MClL}]^{2+}$  ions could be observed. Collision induced dissociation (CID) in the QIT indicated a tetradentate coordination mode for both ligands.

(2) The relative affinity of N- and O-donor bases to Ln(III) and Am(III) ions in the gas phase and in solution was assessed. Competitive CID experiments in the QIT, involving  $[M(\text{NO}_3)_2(\text{L}^1)(\text{L}^2)]^+$  ions, where L were mono- and bidentate heterocyclic N-donor bases or monodentate O-donor bases, revealed the relative gas-phase affinities of the bases and the relevant gas-phase factors behind the observations. Comparison of the relative intensities of

$[M(\text{NO}_3)_2(\text{L}^1)_2]^+$  and  $[M(\text{NO}_3)_2(\text{L}^2)_2]^+$  ions in MS spectra indicated different relative affinities of L that may result from a combination of solution and gas-phase properties of the L bases.

(3) The size/effective charge of Ln(III) and An(III) ions in the gas phase was evaluated. Solutions with pairs of Ln(III), Y(III), Pu(III) and Am(III) nitrates or chlorides readily yielded, in the negative ion mode,  $[\text{M}^1\text{M}^2\text{X}_7]^-$  species. CID experiments in the QIT resulted in the preferential formation of  $[\text{MX}_4]^-$  for the smaller, more charge dense metal ions. Intriguingly, in the gas phase, Y(III) appears to be closer to Gd(III) than to Ho(III) in terms of ionic size/effective charge, while both Pu(III) and Am(III) seem to be closer to their Ln(III) congeners.

(4) CID experiments in the QIT involving  $[(\text{UO}_2)\text{MX}_n]^-$  ions, where M = alkaline-earth metal (n = 5) or lanthanide (n = 6), and X = nitrate or chloride, allowed to examine the effective charge of U in the uranyl ion ( $\text{UO}_2^{2+}$ ) in the gas-phase. Preferential formation of  $[(\text{UO}_2)\text{X}_3]^-$  for the cases of the alkaline-earth metals and the larger Ln was observed. These results indicate that, in the gas phase, the uranyl ion is more similar to a trivalent metal ion than to a divalent, in agreement with solution chemistry studies and theoretical calculations.

(5) The relative stability of the III/IV oxidation states of Ln and An ions in the gas phase was investigated. CID of  $[\text{M}(\text{NO}_3)_x]^-$  ions in the QIT, where M = Sc, Y, Ln, produced  $[\text{M}(\text{O})(\text{NO}_3)_3]^-$  for M = Ce, Pr, Nd and Tb (Ln with more accessible oxidation state IV), while  $[\text{M}(\text{OH})(\text{NO}_3)_3]^-$  ions dominated for most of the remaining metals; the much smaller Sc yielded both fragment ions. In the cases of Pu, Am and Cm, all having an accessible oxidation state IV, only  $[\text{M}(\text{O})(\text{NO}_3)_3]^-$  ions were observed. Gas-phase reactions with the background water present in the QIT were examined in detail to unravel the diverse behavior of the f-element ions and the formation of  $[\text{M}(\text{OH})(\text{NO}_3)_3]^-$  by hydrolysis of  $[\text{M}(\text{O})(\text{NO}_3)_3]^-$ .

### Published work

J. Marçalo, A.F. Lucena, C. Lourenço, B. Monteiro, L. Maria, J.M. Carretas, P. X Rutkowski, J.K. Gibson, Mass Spectrometry of Rare Earths—From Compound Characterization to Fundamental Gas-Phase Properties, XXIV. *Terrae Rarae 2011*, Karlsruhe, Germany, October 2011.

P. X Rutkowski, M.C. Michelini, T.H. Bray, N. Russo, J. Marçalo, J.K. Gibson, Hydration of Gas-Phase Ytterbium Ion Complexes Studied by Experiment and Theory, *Theor. Chem. Acc.* 129 (2011) 575-592.

<sup>1</sup> Lawrence Berkeley National Lab. (Berkeley, CA, USA). <sup>2</sup> U. Calabria (Arcavacata di Rende, Italy).

<sup>3</sup> CEA-Atalante (Marcoule, France).

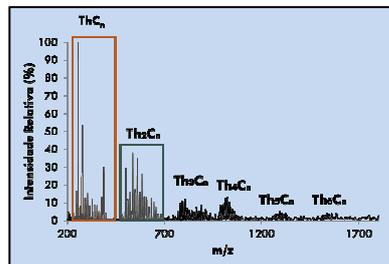
**Gas-Phase Chemistry and Thermochemistry of Elementary Actinide Molecules**

*J. Marçalo, C. C. L. Pereira, A. F. Lucena, A. Pires de Matos, A. P. Gonçalves, J. K. Gibson<sup>1</sup>, L. Andrews<sup>2</sup>*

Gas-phase chemistry studies, using advanced mass-spectrometry techniques (LDI-FTICR/MS and ESI-QIT/MS), are conducted to search for new elementary actinide species and reactions, and investigate their chemical and thermochemical properties.

We used FTICR/MS to study the reactions of  $An^{2+}$  ions ( $An = Th, Np, Pu, Am, Cm$ ) with COS; in the case of  $Th^{2+}$ , the sequential formation of  $ThS_n^{2+}$  ions, with  $n = 1-4$ , was observed. Theoretical studies performed by C. J. Marsden (Univ. Paul Sabatier, Toulouse, France) indicated that the Th polysulfides, as the previously studied U analogues, are mostly of the metallacycle type.

A  $ThC_4$  compound, obtained by high-temperature synthesis, was investigated by LDI-FTICR/MS and formation of  $Th_mC_n^+$  cluster ions, for  $m = 1-6$ , was observed.  $ThC_4$  was also studied by matrix-isolation spectroscopy at the U. Virginia but no neutral  $ThC_x$  species could be identified.



<sup>1</sup> Lawrence Berkeley National Lab. (Berkeley, CA, USA). <sup>2</sup> U. Virginia (Charlottesville, VA, USA).

**f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands**

*L. Maria, M. A. Antunes, B. Monteiro, E. Mora, A. Cruz, J. Marçalo, J. M. Carretas, N. Marques, I. C. Santos, L. C. Pereira<sup>1</sup>, M. Almeida, M. Mazzanti<sup>1</sup>*

The main goal of this research is to develop new coordination environments for the f-elements, with the purpose of creating new reactive centres with unusual reactivity patterns, providing the opportunity to study fundamental organometallic chemistry and also to synthesize new compounds with potential interest in organic synthesis and catalysis.

In this context, the study of the coordination chemistry of the diamino bis(phenolate) ligands  $[salan-R_2]^{2-}$  ( $H_2salan-R_2 = N,N'$ -bis(2-hydroxybenzyl-3,5-di-R)-1,2-dimethylamino-methane;  $R = Me (L_1), ^tBu (L_2)$ ) toward the actinides Th and U was continued. This family of ligands allowed the stabilization of mono and bis-substituted complexes of the type  $[An\{salan-R_2\}Cl_2Y]$  ( $An = Th, U; Y = dme, bipy$ ) and  $[An\{salan-R_2\}_2]$ . Reactivity studies of  $[An\{salan-^tBu_2\}Cl_2Y]$  were performed, showing that this system is able to stabilize the monomeric alkyl complexes  $[An\{salan-^tBu_2\}_2(CH_2SiMe_3)_2]$  for both Th and U (Fig. 1). The formulation of the actinide complexes was based in NMR

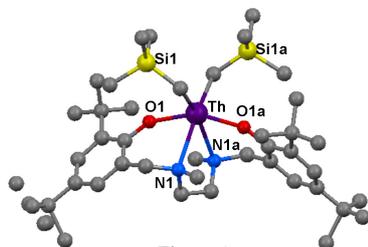


Figure 1

experiments, ESI-QIT/MS and X-ray diffraction analysis.

Studies on the coordination chemistry of U(III) anchored on a functionalised triazacyclononane (tacn) ligand,  $\{tacn-Me_2SiN(Na)Ph\}$ , were restarted. Some years ago we found out that the U(III) complex  $[U\{tacn-Me_2SiN(Na)Ph\}]$  (**1**), which displays a trigonal prismatic coordination sphere with a free axial coordination position, was a good platform to access higher oxidation states. Thus, we started to explore the electron transfer reactions of **1** with redox-active substrates such as organic azides and azobenzene.

Aiming at the study of the magnetic properties of uranium complexes, particularly in terms of single-molecule-magnet behavior, we have initiated a project in collaboration with the Solid State Group of UCQR. In this context, the cationic U(III) compound  $[U(Tp^{Me_2})_2(bipy)]^+$  was prepared and structurally characterized.

<sup>1</sup> INAC, CEA-Grenoble (France).

**f-Element-Based Luminescent and Magnetic Materials**

*C. C. L. Pereira, B. Monteiro, J. Marçalo, L. C. Pereira, M. Almeida, D. Ananias<sup>1</sup>, F. A. A. Paz<sup>1</sup>*

In a collaboration with CICECO of U. Aveiro, several materials were synthesized with the aim of studying their photophysical and photochemical properties. Metal-Organic Frameworks (MOFs) based on uranyl and uranyl-europium with phosphonate ligands, and layered lanthanide hydroxides (LLHs) of general formula  $Ln_8(OH)_{20}Cl_4 \cdot nH_2O$  ( $Ln = Eu, Tb$ ), with 2,6-naphthalene-dicarboxylate anions intercalated inside the gallery are presently being evaluated as luminescent materials (Figure 1).

The magnetic properties of a dysprosium LLH and its intercalation product with 2,6-naphthalene-dicarboxylate anions were also evaluated, in a collaboration with the Solid State group of UCQR-ITN.

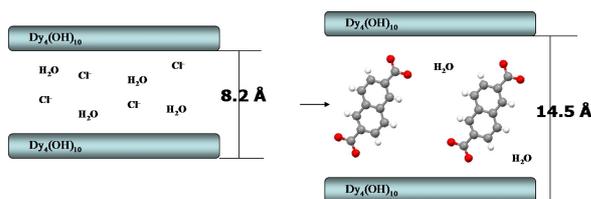


Figure 1

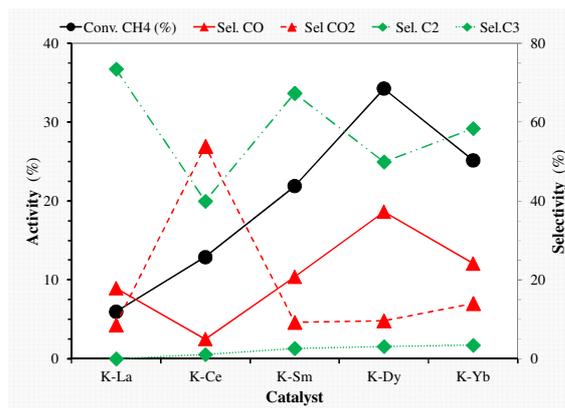
<sup>1</sup> CICECO, U. Aveiro.

***f-Block Elements as Catalysts for the Elimination of Primary Gaseous Pollutants (CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>)***

 J. B. Branco, A. C. Ferreira, T. Almeida Gasche, A. Rego<sup>1</sup>, A. Ferrara<sup>1</sup>, A. P. Gonçalves

We continue to study important environmental issues such as the activation and valorisation of methane and carbon dioxide as valuable C1 feedstocks, namely through the catalytic partial oxidation of CH<sub>4</sub> (POM reaction) using O<sub>2</sub> or N<sub>2</sub>O as oxidant. The study of the partial oxidation of methane (POM) over KCl-LnCl<sub>3</sub> (Ln=La, Ce, Sm, Dy, Yb) eutectic molten salts was undertaken. The main reaction products were hydrocarbons (> 70%, except for K-Ce).

The catalytic performance is clearly dependent on the rare earth ions properties and the factors that seem to contribute to the variation of the activity and selectivity along the lanthanide series are the mobility and the oxidative character of the rare earth trivalent ions in the potassium chloride melt. The activity increases with the molten salts eutectic melting temperatures and the selectivity to hydrocarbons decreases with the oxidative character of rare earth ions. To our knowledge, this is the first time that POM was studied over chloride based rare earth molten salts.

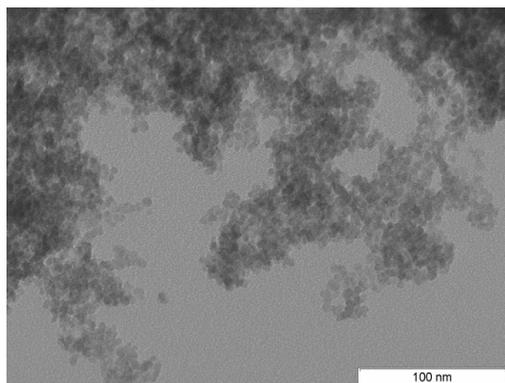


<sup>1</sup>Technical Univ. of Lisbon/IST, IN and Centre for Molecular Physical Chemistry.

**Binary Intermetallic Compounds Nanoparticles: Synthesis and Catalytic Behavior**

 J. B. Branco, A. C. Ferreira, T. Almeida Gasche, J. P. Leal, A. Rego<sup>1</sup>, A. Ferrara<sup>1</sup>

A new work plan that comprises the synthesis of binary intermetallic compounds (IC) nanoparticles containing, in particular, f-block elements and the study of their catalytic behavior for the elimination of primary gaseous pollutants such as carbon dioxide and nitrous oxide was started in 2011. This approach will enable the synthesis of nanoparticles at temperatures significantly lower than those used by traditional high temperature solid state chemistry and, predictably, with different chemical and physical properties. Moreover, the combination of the unique properties of the f elements with the ability to control the shape and size of the nanoparticles will bring benefits to the expected catalytic properties of these materials. Several approaches were already tried, such as the polyol and bioreduction methods. Nanoparticles of Cu, La, LaNi, LaCu<sub>2</sub>, SmCo<sub>5</sub> and DyFe<sub>3</sub> were obtained. XRD, SEM and TEM measurements were performed to characterize the ICs.

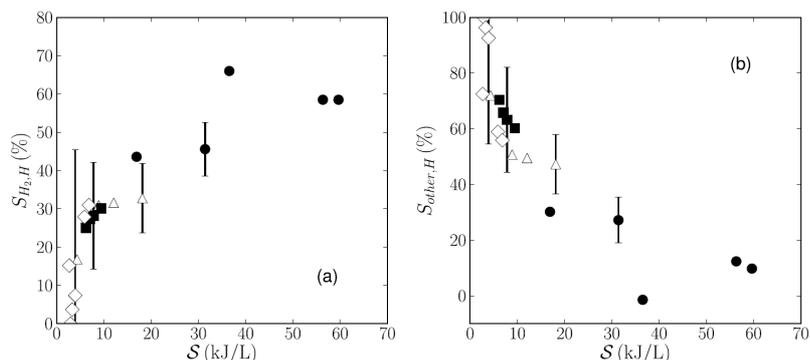


<sup>1</sup>Technical Univ. of Lisbon/IST, IN and Centre for Molecular Physical Chemistry.

**Conversion of Methane by Non-Thermal Plasma**

N. R. Pinhão, A. Janeco, J. B. Branco

The conversion of methane by a non-thermal plasma produced by DBD (dielectric barrier discharge) was studied using mixtures of CH<sub>4</sub>/O<sub>2</sub> and CH<sub>4</sub>/CO<sub>2</sub> with a rare gas (helium or argon). The main products obtained were H<sub>2</sub>, CO, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> but traces of other hydrocarbons, carbon deposition and the formation of condensable products (e.g. ethanol) were also detected. The dependence of the conversion, selectivities and abilities on the rare gas nature and concentration, specific input energy (S), type of electric plasma excitation (sinusoidal or pulsed power supplies) and synergies with both commercial and home-made catalysts was studied. It was found that helium has a significant influence on the discharge, decreasing the breakdown voltage and increasing the rate of conversion of CH<sub>4</sub> and CO<sub>2</sub>.



**Molecular Energetics of Organic, Inorganic and Organometallic Compounds**

*J. P. Leal, T. Almeida Gasche, P. G. Rosado, J. M. Vitorino<sup>1</sup>, M. E. Minas da Piedade<sup>1</sup>, J. A. Martinho Simões<sup>1</sup>, R. Borges Santos<sup>1</sup>, R. Melo, L. Botelho, A. Teixeira<sup>2</sup>, A. Falcão<sup>2</sup>*

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

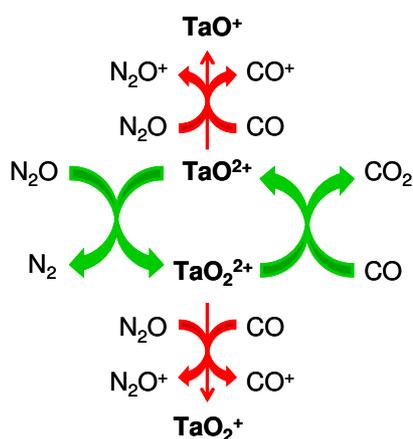
During 2011, an extended revision of ThermoInfo database ([www.therminfo.com](http://www.therminfo.com)) was undertaken. The main goal is to make the database structure more flexible and also enlarge its size (from the previous 3000 compounds to around 25000). The nature of ionic liquids in the gas phase continued to be studied by using FTICR/MS. The study of metallic polyalkoxides continued and in addition to alkaline and alkaline-earth metals, lanthanide and mixed (lanthanide and silicon) polyalkoxides were synthesised, characterized and studied. The degradation/decomposition mechanism of acetovanillone and sculetine were studied by using pulse-radiolysis and mass spectrometry (ESI-QIT/MS).



<sup>1</sup> Centro de Química e Bioquímica, FCUL. <sup>2</sup> Large-Scale Informatics Systems Lab., FCUL.

**Gas-Phase Studies of d-Transition Metal Species**

*M. C. Oliveira<sup>1</sup>, J. Marçalo, C. Lourenço<sup>1</sup>, M. Santos, J. K. Gibson<sup>2</sup>, M. C. Michelin<sup>3</sup>*



We have been examining the gas-phase chemistry and thermochemistry of transition metal oxide ions by FTICR/MS, to provide fundamental chemical models to complex multi-charged systems and obtain new thermodynamic data for ionic and neutral species containing these elements.

The study of gas-phase oxidation reactions of  $Ta^{2+}$  was completed and the properties of  $TaO^{2+}$  and  $TaO_2^{2+}$  were inspected by experiment and theory. Formally “hypervalent”  $TaO_2^{2+}$  was shown to be a dioxide,  $\{O-Ta-O\}^{2+}$ , based on density functional theory (DFT) results. It was found that  $TaO_2^{2+}$  oxidizes CO to  $CO_2$  and that it acts as a catalyst in the oxidation of CO by  $N_2O$ ;  $TaO_2^{2+}$  also activates  $H_2$  to form  $TaO_2H^{2+}$ . The study of gas-phase oxidation reactions of  $Hf^{2+}$  was initiated and the formation of  $HfO^{2+}$  and  $HfO_2^{2+}$  were observed. DFT computations showed that “hypervalent”  $HfO_2^{2+}$ , unlike  $TaO_2^{2+}$ , is a peroxide.

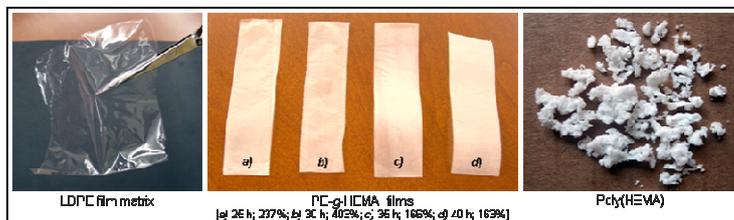
<sup>1</sup> Centro de Química Estrutural, IST. <sup>2</sup> Lawrence Berkeley National Lab. (Berkeley, CA, USA). <sup>3</sup> U. Calabria (Arcavacata di Rende, Italy).

**Gamma Irradiated Membrane Systems for Bioapplications**

*L. M. Ferreira, M. H. Casimiro<sup>1</sup>, J. P. Leal*

Membranes using polyethylene as backbone polymer and HEMA as grafting molecule, produced through irradiation on a  $^{60}Co$  source, were synthesized and the corresponding properties extensively studied. The prepared films were characterized through nuclear microprobe techniques. Qualitative analysis showed a random and non homogeneous distribution of contaminant elements, independent of the grafting degree, suggesting the existence of several sources of contamination at different stages of their preparation.

Results also suggest that this “phased” contamination occurs simultaneously with mechanisms of agglomeration/entrapment of impurities during the gamma induced copolymerization reaction. Moreover, quantitative data showed that all contaminants found in the copolymeric films are natural contaminants of their reagents of preparation, although at concentrations without toxicological hazard, which points to a low cytotoxic potential of the films.



<sup>1</sup> REQUIMTE, CQFB, FCT-UNL.

**Glass Science with Applications in Art Studies**

*A. Pires de Matos<sup>1</sup>, C. Queiroz<sup>2</sup>, A. Ruivo<sup>2,3</sup>, F. Lopes, R. C. Silva*

In 2011 A. Pires de Matos continued as Senior Researcher in the Research Unit VICARTE - “Glass and Ceramics for the Arts”, and work was developed by members of ITN, VICARTE - FCT/UNL and REQUIMTE - FCT/UNL in the development of new materials for artistic applications and in archaeology of Marinha Grande glasses.

Studies on thin layer deposition on glass continued using the spray pyrolysis technique. The first experiments with copper acetate in methanol and water gave origin to a thin layer deposition of copper oxide which after heating at about 600°C gave origin to nanoparticles of copper. They were analysed by X-ray fluorescence and by Rutherford Backscattering. The deposition on the tin side of the float glass and on the other side were studied.

The studies of Marinha Grande glasses continued and a special attention was given to the 18th century arcana of Guilherme Stephens. The study of the four arcana available was completed. The recipes used for coloured glass were discussed while interpreting the chemical nomenclature used.



<sup>1</sup> IOC Group/UCQR-ITN & VICARTE, FCT-UNL. <sup>2</sup> VICARTE, FCT-UNL. <sup>3</sup> REQUIMTE, FCT/UNL.